Bulk Hydrides and Delayed Hydride Cracking in Zirconium Alloys

by

Eric F. Tulk

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Abstract

Zirconium alloys are susceptible to engineering problems associated with the uptake of hydrogen throughout their design lifetime in nuclear reactors. Understanding of hydrogen embrittlement associated with the precipitation of brittle hydride phases and a sub-critical crack growth mechanism known as Delayed Hydride Cracking (DHC) are required to provide the engineering justifications for safe reactor operation.

The nature of bulk zirconium hydrides at low concentrations (< 100 wt. ppm) is subject to several contradictory descriptions in the literature associated with the stability and metastability of γ phase zirconium hydride. Due to the differing volume expansions (12-17%) and crystallography between γ and the stable δ hydride phases, it is suggested that the matrix yield strength may have an effect on the phase stability. The present work indicated that although yield strength can shift the phase stability, other factors such as microstructure and phase distribution can be as or more important. This suggests that small material differences are the reason for the literature discrepancies.

DHC is characterised by the repeated precipitation, growth, fracture of brittle hydride phases and subsequent crack arrest in the ductile metal. DHC growth is associated primarily the ability of hydrogen to diffuse under a stress induced chemical potential towards a stress raiser. Knowledge of the factors controlling DHC are
paramount in being able to appropriately describe DHC for engineering purposes. Most studies characterise DHC upon cooling to the test temperature. DHC upon heating has not been extensively studied and the mechanism by which it occurs is somewhat controversial in the literature. This work shows that previous thermo-mechanical processing of hydrided zirconium can have a significant effect on the dissolution behaviour of the bulk hydride upon heating. DHC tests with $\gamma$ quenched, furnace cooled $\delta$ and reoriented bulk hydrides upon heating and DHC upon cooling suggest that the amount of hydrogen in solution is the primary factor controlling the occurrence of DHC and consistent with the postulation that the stress induced chemical potential is the driving force for DHC.
Acknowledgments

I would like to acknowledge the support of many who helped me out along the past couple years. There have been far too many to name everyone individually so I will be brief:

I cannot thank Dr. Matthew Kerr, who supervised me on my undergraduate work while he was a graduate student, half-supervised me during my Master’s project remotely, co-authored my first publication, invited me to join in on some fun conferences I would not have otherwise attended, zirconium goodwill ambassador and my professional and science mentor, enough for showing me the ropes of graduate engineering and science. My supervisor, Professor Mark Daymond, who managed to convince a confused fourth year engineering student to stick around for additional higher education, being the first to edit my thesis (no easy task), co-authoring my paper, and being an overall extraordinary mentor that provided me with basically every opportunity I asked for.

The other professors in Nicol Hall: Prof. Diak, Rick, Zhongwen, Dr. Krstic, Dr. Boyd and Dr. Pilkey. Charlie, Zoran and Kate. My undergraduate students (minions) Justin, Kevin and Simon. My fellow grad students and postdocs, many of who have helped me out over the past few years: from Abdul to Yasir (didn’t miss anyone). My closest friends: Sloan (Metal), Jen (girlfriend), Dunner (Rock), Leon,
Evan Magnum (fire type), Link and majority of 237 Earl St: you helped preserve my mental health. My immediate family back in Calgary has been very supportive. Also, I have left out nearly all my supportive friends.

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Statement of Contributions

Professor M.R. Daymond (Queen’s University) co-authored on the paper submitted from the first two chapters of this work.

Graduate Students
M. Kerr helped design much of the present experimental work, modified much of the DHC ovens designs from a version used by Kinectrics Inc. during his time as a graduate student, co-authored on the paper submitted from the first two chapters of this work and was an ongoing source of advice throughout the project.

F. Long provided the TEM image of Zr 2.5wt% Nb pressure tube CC 097-89.

M. Swain assisted with the NSLS diffraction runs.

Industry
Kinectrics Inc. was responsible for reorienting the hydrides in the pressure tube section and machining all radial samples.

D. Khatamian and P. Wilson at AECL completed the DSC measurements for the DHC section.

E. Cochran, from RMC provided the use of the DSC apparatus.

H. Chatput at AECL orchestrated the VHEMS measurements.

G. Shek suggested the study described in Chap. 5.

E. DiMasi was the beamline scientist from the NSLS experiments.
J.D. Almer provided guidance with some of the peak fitting in Chap. 3.

**Undergraduates**

J. Huneault designed the control loop for monitoring constant K in the DHC tests.
S. Langeille assisted in running some of the initial DHC tests.
K. Middleton and S. Grondin are responsible for much of the optical and SEM metallography of hydrides that appears in this thesis.

At the present date, much of the content in chapters 2 and 3 in this thesis are in press for the Journal of Nuclear Materials: doi:10.1016/j.jnucmat.2011.10.051.

Unless stated above, the following was completed by the author and is original work.
Abbreviations and Symbols

0.1 Nomenclature

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>CANDU</td>
<td>CANada Deuterium Uranium (reactor)</td>
</tr>
<tr>
<td>BWR</td>
<td>Boiling Water Reactor</td>
</tr>
<tr>
<td>PWR</td>
<td>Pressurized Water Reactor</td>
</tr>
<tr>
<td>RBMK</td>
<td>Russian high power channel-type reactor</td>
</tr>
<tr>
<td>DHC</td>
<td>Delayed Hydride Cracking</td>
</tr>
<tr>
<td>DSC</td>
<td>Differential Scanning Calorimetry</td>
</tr>
<tr>
<td>VHEMS</td>
<td>Vacuum Hot Extraction Mass Spectroscopy</td>
</tr>
<tr>
<td>hcp</td>
<td>hexagonal close-packed crystal structure</td>
</tr>
<tr>
<td>bcc</td>
<td>body centred cubic crystal structure</td>
</tr>
<tr>
<td>fct</td>
<td>face centred tetragonal crystal structure</td>
</tr>
<tr>
<td>fcc</td>
<td>face centred cubic crystal structure</td>
</tr>
<tr>
<td>α</td>
<td>low temperature hcp phase of zirconium</td>
</tr>
<tr>
<td>β</td>
<td>high temperature bcc phase of zirconium</td>
</tr>
<tr>
<td>δ</td>
<td>stable fcc hydride phase in zirconium</td>
</tr>
<tr>
<td>γ</td>
<td>metastable fct hydride phase in zirconium</td>
</tr>
<tr>
<td>ε</td>
<td>stable fct hydride phase in zirconium</td>
</tr>
<tr>
<td>PT</td>
<td>Pressure Tube</td>
</tr>
<tr>
<td>AR</td>
<td>As Received</td>
</tr>
<tr>
<td>PF</td>
<td>Pole Figure</td>
</tr>
<tr>
<td>T</td>
<td>Temperature (Kelvin)</td>
</tr>
</tbody>
</table>
\( C_{\text{nucl}} \) Concentration of hydrogen in solution until nucleation
\( C_s \) Stress free hydrogen solvus
\( C_{\text{diss}} \) Concentration of hydrogen in solution upon heating
\( \overline{w_e} \) Hydride elastic accommodation energy
\( \overline{w_p} \) Hydride plastic accommodation energy
\( \overline{w_{e-p}} \) Hydride elastic-plastic accommodation energy
\( Q_{\text{cool}} \) Total hydride accommodation energy upon precipitation
\( Q_{\text{heat}} \) Total hydride accommodation energy upon dissolution
\( \overline{w_{\text{inc}}} \) Hydride accommodation energy
\( \overline{w_a} \) Hydride interaction energy
TSSD Terminal Solid Solubility of Dissolution
TSSP Terminal Solid Solubility of Precipitation
AE Acoustic Emission
DCPD Direct Current Potential Drop
pd Potential Drop
LBB Leak Before Break
CCT Curved Compact Toughness sample geometry
CT Compact Toughness sample geometry
SEM Scanning Electron Microscopy
SEI Secondary Electron Imaging, an imaging technique on SEM
BEI Backscatter Electron Imaging, an imaging technique on SEM
\( K_I \) Stress intensity factor for a mode I crack
\( K_{IH} \) Critical stress intensity factor below which DHC will not occur
\( DHC_v \) Crack growth rate of a DHC crack
\( DHC_{vt} \) Terminal crack growth rate of a DHC crack (stage II)

Labelling of some equation terms are instead located in Appendix A
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Chapter 1

Introduction

"Right now I feel like I could take on the whole Empire myself"

— Dak

This is a thesis describing work on bulk hydride phase stability in zirconium alloys as well as the effects of bulk hydrides on a sub-critical crack growth mechanism known as Delayed Hydride Cracking (DHC).

1.1 Zirconium in the Nuclear Industry

Nuclear reactor cores present a unique environment for application of structural materials. Reactor core materials are required to provide reliable mechanical strength in operating conditions consisting of elevated temperatures (\(\sim 300 \, ^\circ\text{C}\)) for the current generation III+ reactors, higher for future generations), a corrosive environment produced by the high temperature pressurised coolant as well as a neutron flux, without affecting the reactor kinetics in a detrimental manner. The unique combination of
high temperature strength, corrosion resistance and low neutron capture cross section
has resulted in the use of zirconium for all core applications where neutron absorbtion
is undesirable and long term environmental integrity is required. The initial application
of zirconium alloys were as a replacement of stainless steel fuel cladding in
water cooled reactors. Later, zirconium alloys were developed for use as the pressure
boundaries in types of reactors that require neutron transmission for reactor operation
such as a CANDU-PHWR (CANadian Deuterium Uranium Pressurised Heavy
Water Reactor) pressure and calandria tubes.

A summary of common zirconium alloys, their compositions, and applications is
given in Table 1.1.

<table>
<thead>
<tr>
<th>Nb wt%</th>
<th>Mo wt%</th>
<th>Sn wt%</th>
<th>Fe wt%</th>
<th>Cr wt%</th>
<th>Ni wt%</th>
<th>O wt-ppm</th>
<th>Zr</th>
<th>Typical Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zircaloy-2</td>
<td>–</td>
<td>–</td>
<td>1.2-1.7</td>
<td>0.07-0.24</td>
<td>0.05-0.15</td>
<td>0.03-0.13</td>
<td>1000-1400</td>
<td>Balance</td>
</tr>
<tr>
<td>Zircaloy-4</td>
<td>–</td>
<td>–</td>
<td>1.2-1.7</td>
<td>0.18-0.24</td>
<td>0.07-0.13</td>
<td>–</td>
<td>1000-1400</td>
<td>Balance</td>
</tr>
<tr>
<td>Zr-2.5Nb</td>
<td>2.5</td>
<td>–</td>
<td>–</td>
<td>&lt;1300 ppm</td>
<td>–</td>
<td>–</td>
<td>950-1500</td>
<td>Balance</td>
</tr>
<tr>
<td>Zr-1Nb</td>
<td>1</td>
<td>–</td>
<td>–</td>
<td>300-500 wt-ppm</td>
<td>–</td>
<td>–</td>
<td>1000-1400</td>
<td>Balance</td>
</tr>
<tr>
<td>Zirlo</td>
<td>1</td>
<td>–</td>
<td>1</td>
<td>300-500</td>
<td>–</td>
<td>–</td>
<td>1000-1400</td>
<td>Balance</td>
</tr>
<tr>
<td>M5</td>
<td>1</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>1000-1400</td>
<td>Balance</td>
</tr>
<tr>
<td>Excel</td>
<td>0.8</td>
<td>0.8</td>
<td>3.5</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>Balance</td>
</tr>
</tbody>
</table>

There are two distinct types of zirconium alloys that are used in reactor cores:
largely single Zr-phase \( \alpha \)-zirconium alloys and dual phase \( \alpha/\beta \) alloys. Although other
phases do exist as precipitates in single phase zirconium alloys, these alloys are still
described as being single phase. The single phase (\( \alpha \)) Zircalloys are generally Zr-Sn
alloys that contain minor amounts of O, Fe, Cr, and Ni and were first developed by
the U.S Navy Nuclear Propulsion Program for their water cooled reactors. These alloys generally have improved mechanical strength and corrosion resistance relative to unalloyed zirconium. Initial CANDU pressure tubes were made from Zircaloy-2, but have since been replaced with two-phase Zr-2.5 wt% Nb. Zircaloy-2 and Zircaloy-4, which are the only Zircaloy's that are still used, are primarily used in both fuel cladding and the calandria tube in CANDU nuclear facilities. Two phase zirconium alloys (often with Nb acting as a bcc $\beta$-phase stabiliser) were developed in an attempt to improve the commercial alloy mechanical properties and corrosion resistance [2]. Of particular importance is two-phase Zr-2.5 wt% Nb which has been successfully used in the current generation of CANDU pressure tubes. These pressure tubes, which are extruded at high temperature, cold drawn and autoclaved contain elongated fine $\alpha$ grains surrounded by filament like $\beta$-grains at the grain boundaries. The increase in strength in this alloy is a result of the high dislocation density produced from the cold working, small grain size and the filament strengthening of the $\beta$ grains. One consequence of using cold work to increase the strength of the alloy is that it leads to increased levels of in-reactor creep and irradiation growth [3]. In order to mitigate this reactor operational problem, alternative material strengthening routes must be taken. This has been the driver for the development of Excel alloy, which is an experimental alloy that attempts to acquire additional increases in strength from solution strengthening as opposed to cold work and is a candidate for future generation reactor pressure tubes.
1.2 Hydrogen Embrittlement of Zirconium Alloys

During their in-service lifetimes, zirconium alloy reactor core components experience several types of material degradation associated with the aggressive reactor core operating environment including creep, irradiation damage and hydrogen embrittlement. Engineers must be able to understand and monitor these degradation mechanisms in order to safely and accurately operate nuclear reactors. In particular, hydrogen embrittlement and a sub-critical crack growth mechanism known as Delayed Hydride Cracking or DHC have caused several failures in both pressure tube and fuel cladding. A corrosion reaction occurs between the zirconium metal and the reactor coolant (either water or heavy water)

$$Zr + 2H_2O^- \rightarrow ZrO_2 + 4H$$

or as deuterium and hydrogen are isotopes and chemically indistinguishable

$$Zr + 2D_2O^- \rightarrow ZrO_2 + 4D$$

and some of the deuterium or hydrogen is absorbed into the zirconium. Over the lifetime of the component the total hydrogen content will increase (in the case of a CANDU fuel channel, Fig. 1.1) resulting in a reduction in mechanical properties due to hydride embrittlement or DHC. When the Terminal Solid Solubility of Precipitation (TSSP) of hydrogen in zirconium is reached, brittle zirconium hydride platelets precipitate. This is a significant problem in zirconium reactor components because the solubility of hydrogen in zirconium is relatively low (few ppm at room temperature, tens of ppm at CANDU pressure tube operating temperatures. The level of embrittlement is generally affected by the quantity, distribution, orientation and size of the precipitates. Sub-critical crack growth via DHC can occur under conditions where hydrogen exists both in the metal hydrides and in solution, such as in a nuclear
reactor in temperature or load transients. This can cause the preferential diffusion of hydrogen towards a tensile stress riser where a brittle hydride can precipitate, grow and fracture until the crack is arrested in the otherwise ductile matrix. This process can repeat itself until the component fails. In the nuclear industry, hydrogen embrit-

![Figure 1.1: Deuterium ingress into CANDU pressure tube [4]](image_url)

...ment and DHC have resulted in real in-reactor component failures. Since zirconium components can serve both as a pressure boundary, such as in CANDU pressure tubes, as well as a nuclear-fuel boundary, such as fuel cladding in nearly all reactors, a failure can result in significant safety and economic issues. The first instance of DHC during CANDU operation occurred when primary coolant was observed in the annulus gas in Pickering 3 in August 1974 as a result of a leaking cold worked Zr-2.5 wt% Nb pressure tube (Fig. 1.2). Eventually sixteen total pressure tubes in the reactor developed leaks and fifty-two tubes were replaced in Pickering reactors 3 and 4. These leaks were rather unexpected as no significant failures were observed in the longer...
running Pickering 1 and 2 reactors, which were made from Zircaloy-2. The blame for the failures was subsequently placed on improperly installed rolled joints that had unexpectedly high tensile residual stresses [5] which was later proven to lead to DHC. Later, in August 1983, a Zircaloy-2 pressure tube ruptured without warning near the centre of the tube. Analysis concluded that this was a result of the pressure tube sagging into contact with the cooler calandria tube as a result of a garter spring that had moved out of place. The localised cooling of the pressure tube resulted in a large concentration of hydrides forming at the contact interface as a row of hydride blisters, which then cracked. The cracks then propagated by DHC [5]. Subsequently, there has been significant and continued work by both Canadian and international nuclear generation bodies into the prevention and monitoring of DHC.

Figure 1.2: DHC crack in Pickering A near rolled joint

1.3 Organisation

This thesis describes two separate experiments with some overlapping elements on the hydrogen embrittlement of zirconium alloys, with each experiment described in two chapters; one containing the relevant literature required to understand the experiment and one containing the experimental work. The first section concerns the conditions
for the precipitation of bulk hydride phases in zirconium at low hydrogen concentrations. Chap. 2 describes the formation of bulk zirconium hydride phases in zirconium. Chap. 3 describes a study that tests some of the conditions that affect zirconium hydride precipitation including microstructure and matrix yield strength and serves to explain some long term discrepancies in the literature. This chapter is mostly content from a paper currently in-press for the Journal of Nuclear Materials [6]. However, additional details have been added in order to facilitate continuation of work by others in the research group. The second experiment concerns a sub-critical crack growth mechanism known as Delayed Hydride Cracking or DHC. Chap. 4 describes the relevant literature concerning DHC. Chap. 5 describes experimental work that correlates differences in bulk hydrides to DHC behaviour in an effort to provide experimental evidence for suggested DHC models. These sections are finally discussed in a general sense and suggestions for further experimentation are described in Chap. 6.
Chapter 2

Literature Review I: Bulk Zirconium Hydrides

“There will be a substantial reward for the one who finds the crew of Millennium Falcon. You are free to use any methods necessary, but I want them alive. No disintegrations.”

— D. Vader

The following chapter provides a review of the literature relevant to bulk hydride precipitates in zirconium alloys.

2.1 Zirconium Hydrogen Alloy System

Hydrogen is known to have low solubility in zirconium and its alloys, only a few parts per million at room temperature. If the solubility limit is exceeded, brittle hydride phases precipitate. Three phases are known to precipitate: $\delta$, $\gamma$ and $\epsilon$ hydride, each
with different crystallography and hydrogen enrichment. Zirconium hydrides have face centered crystal structures with zirconium atoms at the face centered sites and hydrogen atoms occupying tetrahedral sites. Three hydride phases in the zirconium-hydrogen system have been observed including ZrH(γ) tetragonal, ZrH_{1.6–1.7}(δ) cubic and ZrH_{1.74–2}(ε) tetragonal, which forms at higher hydrogen concentrations. There is some discrepancy regarding the composition of the hydride phases and phase boundaries reported in the literature, but the preceding compositions are typical of the ranges cited [7,8]. For hydrides precipitating in an α-zirconium matrix, the literature contains contradictory results for which conditions favour the formation of a given hydride phase, especially between δ and γ-hydride phases. In particular, at hydrogen concentrations below the δ-hydride phase boundary (ZrH\_x where x < 1.55 to 1.7) three phases are reported (α + δ + γ) indicating the presence of a metastable phase.

The conventional view as outlined by two review papers on the subject [7,9] is that the γ-hydride phase is metastable. In these instances the equilibrium δ-hydride phase is favoured by slower cooling rates, such as furnace cooling or a reactor shut down. The metastable γ-hydride phase is favoured as cooling rate is increased towards quenching, transforming to the δ-phase at temperatures in excess of 150 °C [8, 10]. Fig. 2.1 presents the phase diagram for the conventional view that the δ-hydride phase is the equilibrium phase at low temperature [7,11–16]. At low hydrogen concentrations (x << 1.5) this view seems to be supported by recent X-ray diffraction studies [9,17–20] where δ-hydrides appear to be the equilibrium phase, stable even after long term aging at room temperature and 150 °C. However there are several studies that report a stable population of hydrides under these conditions, but with some fraction of γ-hydrides retained [10,21]. The retention of a small and apparently stable quantity of
γ-hydrides is also reported at higher hydrogen concentrations (x < 1.5) [13,18,19]. It is possible that this retained γ-hydride phase is still metastable, where the δ-hydride phase (x ≈ 1.3) that initially forms at elevated temperature increases in hydrogen enrichment on cooling to room temperature (x ≈ 1.5). Under these conditions, some of the δ-hydride formed at high temperature transforms to zirconium in order to increase the hydrogen enrichment of the remaining δ-hydrides. It has been suggested that this transition may only partially occur, leaving behind metastable γ-hydrides near the stoichiometric ZrH composition [13]. There are also several studies reporting the γ-hydride phase as the equilibrium phase below ~250°C [22–28]. In these studies aging of hydrides at room temperature leads to the conversion of γ → δ-hydrides. These studies therefore suggest that the γ-hydride phase is in equilibrium at room temperature, but that the formation of the equilibrium γ-hydride phase is sluggish or diffusion limited (Fig. 2.1, dotted line). Some properties of δ, γ, ϵ zirconium hydride as well as α and β zirconium are shown in Table 2.1 and further discussion on the phase stability is included as the introduction to Chap. 3.

<table>
<thead>
<tr>
<th>Phase</th>
<th>PDF Nos.</th>
<th>crst. str.</th>
<th>vol. ex.-α Zr</th>
<th>comp.</th>
<th>a (nm)</th>
<th>c (nm)</th>
</tr>
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<tbody>
<tr>
<td>δ-ZrH</td>
<td>00-034-0649</td>
<td>fcc</td>
<td>17.2%</td>
<td>$ZrH_{1.6-1.7}$</td>
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<tr>
<td>γ-ZrH</td>
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<td>-</td>
<td>$Zr$</td>
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Table 2.1: Some properties of zirconium hydrides [29,30]
Figure 2.1: Zirconium hydrogen phase diagram showing conventional view that $\gamma$-hydride is metastable [7, 8, 11, 13–15], and the alternative view with the $\delta$-hydride as metastable below a transition temperature (180-240 °C) [16, 23–27]. [ ] indicates a metastable state.


2.2 Terminal Solid Solubility

The Terminal Solid Solubility (TSS) of hydrogen in zirconium has been extensively studied by numerous researchers using various techniques [31–42]. The precipitation of hydrides upon cooling and dissolution of hydrides upon heating occur at different temperatures, with hydrides precipitating at a higher temperature than they dissolve. This means hydrides in zirconium have distinct and separate Terminal Solid Solubility of Precipitation (TSSP) and Terminal Solid Solubility of Dissolution (TSSD). This hysteresis is a result of the work done on the zirconium matrix by the volume expansion associated with the precipitation of hydrides [41, 43]. The difference in the solvus are governed by elastic accommodation for the nucleation of hydrides and by elastic-plastic hydride-matrix accommodation for growth and dissolution. The nucleation of a hydride upon cooling can be described as

\[
C_{\text{nucl}} = C_s \exp \left[ \frac{\bar{w}_e}{RT} \right]
\]

(2.1)

where \(C_{\text{nucl}}\) is the concentration of hydrogen that can be maintained in solution until the first precipitation of hydrides, \(C_s\) is a stress free solvus (which is most often described as being the 'Kearns' line measured in Ref. [39]) and \(\bar{w}_e\) is the pure-elastic accommodation energy per mole of hydrogen. If the hydride grows past a certain size, the accommodation is no longer purely elastic and plasticity must be accounted for such that:

\[
C_{\text{nucl}} = C_s \exp \left[ \frac{\bar{w}_{e,p} + \bar{w}_p}{RT} \right] = C_s \exp \left[ \frac{Q_{\text{cool}}}{RT} \right]
\]

(2.2)

where \(\bar{w}_{e,p}\) is the elastic accommodation energy in the presence of the plasticity, and \(\bar{w}_p\) is the plastic accommodation energy and \(Q_{\text{cool}}\) represents the total hydride

accommodation energy. The dissolution solvus is described in the same manner as the expression in Eq. 2.2, but the plastic and elastic interaction energies are physically different

\[
C_{\text{diss}} = C_s e^{\exp \frac{w_{e,p} + w_p}{RT}} = C_s e^{\exp \frac{Q_{\text{heat}}}{RT}}.
\]

where \( Q_{\text{heat}} \) represents the total interaction energy required for complete hydride dissolution. Although Eq. 2.2, which is the effective solvus for most real life hydride precipitates, and Eq. 2.3 appear to be the same, the contribution of the plastic work term \( w_p \) is significantly different whether the hydride is precipitating or dissolving. In the case of a dissolving hydride, the plastic work is non-reversible, and therefore the plastic work \( w_p \) contributing to the hydride stability is near zero, shifting the dissolution solvus lower than the precipitation solvus. It is commonly accepted that the TSSP can be shifted based the sample’s thermal history, with prior maximum temperature, maximum temperature holding time and cooling rate shown to be the most important factors [33,41,43,44]. In general, the thermal history affects both the amount of dissolved hydrogen and degree of hydrogen supersaturation, which directly affect the subsequent precipitation behaviour of hydrides and DHC [45]. The thermal history has been shown to affect the TSSP by over 50°C, which is significant over the practical range of nuclear plant operation temperatures and has actually lead to common descriptions of TSSP1 and TSSP2 which are the upper and lower bound TSSP curves [46]. The TSSP will be different depending on whether or not existing hydrides are growing or if completely new hydrides must precipitate, either as a new hydride or at the locations of previously dissolved hydrides. This is due to the memory effect in hydrides [47], where hydrides re-precipitate at dislocations produced by the previous precipitates, increasing the effective TSSP. In addition, TSSP decreases with
increasing cooling rate [33]. There is significantly less of a literature consensus on variances in the TSSD, particularly at lower temperatures. Heating rate and prior 'peak' temperature were shown not to affect TSSD in Ref. [33]. Different hydride distributions such as the fine distributions occurring in quenched hydride populations have been shown to experience dissolution at lower temperatures as opposed to slow cooled coarse hydrides (present work, Sec. 3.4.5) either from variations in the hydride constraint affecting the plastic and elastic work terms due to alternate phase (volume expansion), hydride size or the different interfacial energy due to coherency or surface area phase boundary effects. Actual measurements of the hydride constraints or work terms are difficult and large assumptions and uncertainties exist. The most recent and general discussion was completed by Puls in several review commentary papers [48,49] and takes into account crystallographic coherency between the hydride and matrix and external stresses. The internal stress and strain state of the hydride is representative of the work terms and thus provide the possibility of a shift in the dissolution or precipitation behaviour. The elastic-plastic and plastic work terms in Eq. 2.3 can also be described in terms of the accommodation energy \( w_{\text{inc}} \), which is the sum of the two or equal to \( Q_{\text{heat}} \) or \( Q_{\text{cool}} \) dependant upon whether the hydride is precipitating or dissolving. A different bulk hydride (due to phase, orientation or morphology) is likely to have different strain energy around it, and consequently, different dissolution behaviour. Puls [50] derived different accommodation energies for spherical \( \delta \) and \( \gamma \) hydrides and suggested that \( \gamma \) hydrides would have a lower solvus than \( \delta \) hydrides upon heating. However, no experimental measurements of this have been made (and spherical particles are not realistic for real hydrides). The discussion of bulk hydrides and their effect on dissolution is further elaborated upon in Chap. 5.
2.2.1 Hydrogen Supersaturation

In order to account for the effect of the direction of temperature approach to the TSS hysteresis, the amount of hydrogen in solution can be expressed as the hydrogen supersaturation. The hydrogen supersaturation is defined as the hydrogen in solution in excess of the TSSD concentration at that same temperature. The schematic in Fig. 2.2 illustrates this concept. A sample of zirconium with the TSSD and TSSP curves characterised by the red and blue lines respectively in the figure is subject to several conditions. First the sample is heated from low temperature to 250°C. Provided the sample contains sufficient hydrogen, the amount of hydrogen in solution will correspond to the point A on the TSSD curve and the amount of supersaturation will be zero. Subsequent heating from point A to a peak temperature at point B and then cooling back to 250°C results in the amount of hydrogen in solution to be representative of point C, with the supersaturation to be representative of the solubility at point C minus the solubility at point A. Alternatively, if the sample was heated up to a peak temperature at point D, the solubility curve would once again follow the TSSD curve to point D. Cooling from this point back to 250°C would have the solubility follow the arrows from D → E → F and the amount of hydrogen in solution would correspond to the TSSP at F and the supersaturation would be the solubility at F minus solubility at A. This is very relevant to work on DHC as cracking behaviour is very sensitive to both the amount of hydrogen in solution and the hydrogen supersaturation. Ultimately, it indicates that temperature alone is not the only factor required to determine the amount of hydrogen in solution for a given zirconium-hydrogen component, as different amounts of hydrogen in solution can exist at the same temperatures depending on the heat treatment.
Figure 2.2: Schematic demonstrating the possible thermal routes to change the amount of hydrogen in solution and hydrogen supersaturation at 250°C. red → TSSD, blue → TSSP
2.3 Hydride Microstructure

Microscopically, hydrides have a fine structure composed of hydride laths or platelets (few $\mu m$), that typically agglomerate into larger 'macroscopic' hydrides (visible in the optical microscope, 10s to 100s of $\mu m$, depending on treatment). The microscopic platelets do not necessarily have the same physical orientation to the zirconium material as do the larger macroscopic hydrides that they agglomerate into [18, 51] (see below). It should be noted, that the microstructure of the parent material appears to have an effect in morphology of the hydride phase formed. Larger grain sized ($\sim 20 \mu m$) single phase alloys, such as the Zircaloys, tend to form macroscopic hydrides composed of a small number of hydride platelets as shown in Fig. 2.3, while alloys with a highly refined microstructures and small grain sizes ($\sim 0.2 \mu m$), such as Zr-2.5 wt % Nb pressure tube material, tend to form macroscopic hydrides composed of many hydride platelets as shown in Fig. 2.4. The proposed origin of the hydride platelets is a shear nucleation and growth of the hydride phase, where the strain field produced by existing hydrides serves to nucleate smaller daughter hydrides [52]. During precipitation, the hexagonal structure of the zirconium transforms to the face centered cubic structure of the $\delta$-hydride by shear along the zirconium $\{0002\}$ planes [52–54]. Shear along the zirconium basal planes is idealized and experimentally this process is observed to occur on near ($<15^\circ$) basal orientations, with $\{1017\}$ reported as a common variant. This yields an approximate $\{0002\}Zr(\alpha)//\{111\}ZrH(\delta)$ orientation relation between the hydride and the zirconium matrix, which has been confirmed by both SEM, TEM and synchrotron diffraction techniques [8, 18, 31, 52]. This orientation relationship for hydride precipitation is general, as it describes the behaviour of inter and intra-grain boundary hydrides [31, 52]. In addition to near basal orientations, $\delta$-hydrides can also
form by a shearing on prism planes. This produces a \{10\overline{1}0\} hydride habit planes with an approximate \{0002\}Zr(\alpha)\/{001\overline{1}}ZrH(\delta) orientation relationship. Similar orientation relationships are reported for the face centered tetragonal \gamma\hydrides [54].

There is also some question as to hydrogen distribution prior to the precipitation of a \delta or \gamma\hydride. The presence of a coherent transitory hydride phase that precipitates prior to the growth of larger hydrides has also been suggested [53] with the existence of a small (< 500 nm) coherent metastable \xi\hydride phase apparently confirmed by high resolution TEM [55]. As hydrides are formed by a shear process, precipitation preferentially occurs at features that reduce the shear energy for formation such as dislocations and grain/phase boundaries [52, 56]. Therefore in a given material both inter- and intra-grain boundary hydrides will form, with relatively more grain boundary hydrides expected with slower cooling rates [31]. In the absence of a stress field (either applied or residual) the orientation relationship indicates that the basal texture of the parent zirconium will determine the orientation of the macroscopic hydrides, with several macroscopic hydrides and microscopic hydride platelet orientations expected. In the presence of stress fields microscopic hydride platelets will precipitate in locations that minimize the stress, such as grain boundaries or near basal orientations perpendicular to the stress field and registry of the macroscopic hydrides with microscopic hydride platelets orientation is not required [31, 52]. Applied stresses can cause the reorientation of the ‘macro’ hydride itself. This has been studied extensively [57–63] as hydrides of unfavourable orientations resulting from stress reorientation are primarily the cause of hydride fracture toughness problems experienced in both pressure tubes and fuel cladding. Stress reorientation can be a diffusion controlled process such as in DHC, but is usually observed upon cooling.
under an applied load from a temperature where a significant amount of hydrogen is precipitating as hydride. The degree of reorientation is subject to several factors including the previous strains in the material (i.e. how stable the natural orientation is), texture, microstructure and applied stress. In situ experiments by Colas et al [62] estimated a threshold applied stress for hydride reorientation upon cooling of approximately 80MPa in Zircaloy-4 at several hydrogen contents, where the amount of reoriented hydride increased to approximately 40%. In Zr-2.5 wt% Nb micro pressure tube, the threshold for complete reorientation was observed to be around 300 MPa [30,64]. An example of the differences between naturally oriented and reoriented hydrides in Zr-2.5 wt% Nb is shown in Fig. 5.6 and Fig. 5.9.

2.4 Diffusion of Hydrogen in Zirconium

The diffusion of hydrogen in zirconium is very fast, with diffusion coefficients several orders of magnitude faster than that of carbon in steel, even at low temperatures. A study by Kearns [65] measured the diffusion coefficient of hydrogen in zirconium to be independent of alloy (pure Zr, Zircaloy-2 and Zircaloy-4), cold work and grain size, but affected by texture, with diffusion along the c-axis of the crystal measured to be up to twice as high as that across the c-axis. The diffusion coefficient of hydrogen in $\beta$-zirconium was also measured by Gelezunas et al to be several times faster than in $\alpha$ zirconium [66]. The extent that the anisotropic diffusion due to texture and $\beta$ phase affects hydride precipitation and growth and diffusion controlled delayed hydride cracking is still not fully understood. Both the present work and a study reported in Ref. [67] suggest that changes in the microstructure of $\beta$ phase might affect how hydrides precipitate due to a proposed hydrogen sink effect (Sec. 3.4.3).
Figure 2.3: Hydrides in large grained Zircaloy-4 showing coarse hydrides intersecting several grains in (a) SEM micrograph and (b) EBSD grain map and (c) larger macro-hydrides made up of smaller hydride platelets shown in (a) [31]
Figure 2.4: Hydrides in coarse grained Zr-2.5 wt% Nb pressure tube optically in (a) and with TEM in (b). It is noted that the macro-platelets in (a) are made from agglomerations of considerably more micro-platelets on the grain level [52].
Also, DHC studies have indicated that decreased $\beta$ phase continuity can decrease crack velocities by up to a factor of 5 \cite{68,69}.

\subsection{2.5 Synchrotron Diffraction}

Unfortunately, it is difficult to make reliable measurements about the \textit{general} nature of hydrides in zirconium. One issue is that at low concentrations, it is difficult to experimentally measure the hydride phase(s) present and produce a suitable average measurement. TEM measurements present numerous challenges from small sampling areas to potential artifacts arising during specimen preparation. Lab X-ray and neutron measurements require relatively high hydride volume fractions to achieve good counting statistics, since zirconium containing 100 wt-ppm hydrogen represents $\sim$1\% hydride volume fraction. The high-spatial resolution and photon flux provided by synchrotron diffraction has made it an increasingly popular means to study minority zirconium hydride phases. The ability to differentiate and quantify both minority hydride phases with synchrotron diffraction was originally shown by Daum et. al \cite{19} on Zircaloy-4 and later used in studies by Santisteban et. al \cite{70} and Vicente-Alvarez et. al \cite{71} to quantify the hydrogen content of bulk hydrides in Zircaloy-4 and hydride blisters in Zr-2.5 wt\% Nb respectively. Other authors have used synchrotron diffraction to study not only bulk hydrides and their mechanical response \cite{19,72,73} but the mechanical response of hydrides at crack tips \cite{74–76} hydride precipitation dissolution and hydride reorientation \cite{62,71}, and phase transformations \cite{72}. Experiments by Kerr et. al \cite{73} and Steuwer et. al \cite{72} have examined the evolution of hydride strains embedded in a zirconium matrix under an applied load with the former analyzing the load transfer between hydride and matrix and the latter observing
an apparent stress induced $\delta \rightarrow \gamma$ phase transformation that to date has not been observed in other studies. Recently, Santisteban et. al [70] and Vicente-Alvarez et. al [71] have observed the matrix-hydride textures and stress states of hydride precipitates. The Vicente-Alvarez et. al study of hydride blisters in Ref. [71] confirmed the commonly reported $\{0002\}Zr(\alpha)//\{111\}ZrH(\delta)$ orientation relationship to be independent of the volume fraction of hydride phase. Their study did confirm that some selective precipitation occurs at $\alpha$-Zr grains when their c-axis is under a tensile stress and at grain boundaries that are favourably oriented for hydride nucleation as a result of grain shape or anisotropic phase growth behaviour. These findings are in support of the hypothesis that stress state can influence the hydride phase formation energy. The study by Santisteban et. al [70] describes a similar experimental technique applied to the measurement of stresses in bulk hydrides in Zircaloy-4. The same $\{0002\}Zr(\alpha)//\{111\}ZrH(\delta)$ orientation relationship texture analysis is, for the most part, confirmed as in Ref. [71]. Additionally, large compressive stresses in hydride precipitates (360 ± 20 MPa) are observed and explained to be due to the constraint imposed by grain boundaries as no significant lattice strains were observed in materials that had hydrides that were smaller than the grain size. Santisteban et al. also observe correlations between the hydride strain in the constrained direction and hydride volume fraction during in situ thermal cycling past the point of near-complete hydride dissolution.
Chapter 3

Effect of Yield Strength on ZrH Phase Stability

"That’s impossible, even for a computer"

— Anonymous Rebel Pilot

3.1 Introduction

Hydrogen uptake in zirconium components is a life limiting mechanism for both pressure tubes and fuel cladding in nuclear reactor applications. During reactor operation, corrosion slowly occurs at the zirconium/coolant (either water or heavy water) interface $\text{Zr} + 2\text{D}_2\text{O} \rightarrow \text{ZrO}_2 + 4\text{D}$ or as deuterium and hydrogen are isotopes and chemically indistinguishable $\text{Zr} + 2\text{H}_2\text{O} \rightarrow \text{ZrO}_2 + 4\text{H}$ and some of the deuterium/hydrogen released is absorbed into the zirconium; with both isotopes here termed as hydrogen. The presence of hydrogen degrades the mechanical properties of these components as the solubility of hydrogen in zirconium is low and brittle hydride phases form [7,9].
This has been the driver for numerous studies on zirconium hydrides over the past few decades. One area of the zirconium hydride literature that has been studied extensively and, to the current date still debated is the stability of hydride phases at low hydrogen concentration. It is most commonly reported that fcc $\delta - ZrH_{1.6-1.7}$ is the stable phase below the hydrogen Terminal Solid Solubility of Dissolution (TSSD) and fct $\gamma$-ZrH is a metastable phase formed only upon fast quenches [9]. However, there have been studies that have shown evidence that $\gamma$-hydride is the stable phase below $\sim 180^\circ$C [22] and even a $\delta \rightarrow \gamma$ phase transformation [22,72]. In order to explain these discrepancies in the literature, studies are required with a goal of understanding the conditions required for the apparent stability or metastability of $\gamma$-hydride. The fact that the theoretical formation energies for $\delta$ and $\gamma$-hydride are relatively similar, that the two hydrides have different volume expansions when they precipitate, and that the matrix deforms plastically around the hydride as it precipitates are all well documented [51, 59, 77]; this suggests that alterations to the yield strength of the matrix material could have a significant effect on the hydride phase stability. If this was true, it could contribute to the varied behaviour of $\delta$ and $\gamma$-hydrides that has been observed.

In an attempt to unite the literature, Lanzani and Ruch suggest that the $\delta$-hydride is the equilibrium phase in low purity zirconium alloys (<99.8 wt% Zr, including the Zircaloys), while the $\gamma$-hydride phase is stable for high purity zirconium and perhaps Zr-2.5 wt% Nb [9]. Cann et al. also identified alloy purity, as affecting the hydride phase formed in zirconium and proposed a mechanism for the observed behaviour [78]. Specifically they note that as the oxygen concentration increases, the yield strength of the zirconium increases and $\delta$-hydrides tend to form. If the formation energies of
the $\delta$ and $\gamma$-hydrides are similar, then changing the zirconium yield strength could produce 'small strain energy differences' that favour one phase over the other [78,79] as there is a different volume increase associated with the precipitation of $\delta$ (17.2%) and $\gamma$ (12.3%) hydrides relative to the $\alpha$-Zr matrix unit cell [22,78,79]. Properties of both hydride phases and the zirconium matrix were listed previously in Table 2.1.

The review of the literature above indicates that there is a strong relationship between hydride phase formed and the stress/strain state of the hydride/matrix. The current study alters the yield strength of two commonly used nuclear reactor grade materials: single phase Zircaloys-2 and ($\alpha/\beta$) dual phase Zr-2.5 wt% Nb pressure tube with various thermo-mechanical treatments and then measures the hydride populations arising from various quenching rates above the hydrogen TSS. The decision to study several different alloys is based on the authors’ belief that many of the previous studies on the subject study too narrow a range of material and therefore the often unique results reported may not be representative of the bulk behaviour of hydrides in zirconium. This paper serves to comment upon several of the seemingly contradictory results that have been reported in the literature to date.

3.2 Experimental

3.2.1 Material

Samples were prepared from both warm-rolled Zircaloys-2 slab and Zr-2.5 wt% Nb pressure tube (CC097-89). A section of the Zircaloys-2 slab was subsequently cold rolled to increase its yield strength of the material as a result of increases in the dislocation density and modification to the grain structure and texture. In addition, a
section of the otherwise high yield strength Zr-2.5 wt% Nb pressure tube was annealed in order to decrease its yield strength. Overall a ‘soft’ and ‘hard’ version of both single phase and dual phase zirconium alloy was produced in an attempt to isolate some of the potential \( \beta \)-phase and microstructural effects. These materials were examined by a combination of SEM, TEM and optical microscopy techniques in order to confirm their respective thermo-mechanical treatments. Additionally a basal-pole figure measurement was made for each material at Chalk River National Laboratory (AR Zircaloy-2) or Los Alamos National Laboratory (rolled Zircaloy-2, Zr-2.5 wt% Nb, annealed Zr-2.5 wt% Nb) and these are presented in Fig. 3.1.

The 0.2% offset engineering yield strength of each material was measured from a constant displacement uniaxial compression (0.127 mm/min) test of samples measuring approximately \( 4 \times 4 \times 4 \) mm. Because of the inherent crystallographic anisotropy of hcp metals, the strength was determined in three Cartesian directions. An uncertainty of \( \pm 20 \) MPa estimated from the scatter in the yield stress measurements is within the range required for the present study.

### 3.2.1.1 AR Zircaloy-2

The ‘as received’ or AR Zircaloy-2 was prepared from a warm rolled slab which has been well characterised in a previous experiment [80]. The composition of this alloy is described earlier in Table 1.1 but is in general a single phase alloy containing a small amount of tin precipitates. The microstructure was examined with optical microscopy (Fig. 3.2) and was shown to consist of relatively equiaxed \( \alpha \)-Zr grains measuring approximately 20 \( \mu m \). The basal \{0002\} pole figure shown in Fig. 3.1 for this material shows that the majority of the basal plane normals are oriented
Figure 3.1: Basal pole figures of experimental zirconium alloys (a) AR warm rolled Zircaloy-2, (b) cold rolled Zircaloy-2, (c) AR CW Zr-2.5wt% Nb pressure tube and in (d) annealed 700 °C, 1 week Zr-2.5wt% Nb pressure tube.
CHAPTER 3. EFFECT OF YIELD STRENGTH ON ZrH PHASE STABILITY

Table 3.1: Engineering yield strength of experimental zirconium alloys under uni-axial compression. **Bold** indicates direction of highest basal texture

<table>
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<td>AR Pressure Tube</td>
<td>Radial</td>
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<td></td>
<td>Transverse</td>
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<tr>
<td></td>
<td></td>
<td>Axial</td>
<td>396</td>
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</tbody>
</table>

along the normal direction (ND) of the plate; there is a spread around the ND, with more basal plane normals approaching the rolling direction (RD) than the transverse direction (TD).

3.2.1.2 Cold Rolled Zircaloy-2

Cold rolling of some of the AR Zircaloy-2 was completed in order to create a single phase material with greater matrix yield strength. A piece of the AR Zircaloy-2 measuring $15 \times 70 \times 40 mm$ was cross cold-rolled 66% to a thickness of approximately $5 mm$ with each rolling pass reducing the thickness of the slab by $\sim 0.1 mm$. A 700 °C hour-long stress relief treatment was completed before and after the rolling process. This resulted in a material that had significantly higher yield strength than the AR Zircaloy-2, which is a result of the significant dislocation density, confirmed by TEM in
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Figure 3.2: Metallography of normal surface of warm rolled AR Zircaloy-2 showing grain size on the order of 20 µm

Fig. 3.3(a), generated from the rolling process. Optically, the grains were observed to be similar sized to those in the AR material (Fig. 3.3(b)). The texture of this material showed most basal normals aligned in the ND with significant concentrations located about 15° away from that axis towards the direction of deformation (Fig. 3.1).

3.2.1.3 AR Zr-2.5 wt% Nb Pressure Tube

The AR Zr-2.5 wt% Nb material was cut from pressure tube CC 097 - 89. Pressure tubes undergo a hot-extrusion and cold drawing process followed by an autoclave anneal [81–83]. This results in a material with a fine, two-phase microstructure, consisting of elongated hcp α-Zr grains surrounded at the grain boundaries by bcc β-phase. Zr 2.5-wt% Nb alloy is characterised by a high temperature (≥ 700°C) β-Zr, intermediate temperature (620°C - 850°C) α-Zr + β-Zr and low temperature (≤ 620°C) α-Zr + β-Nb. Therefore, as pressure tube is cooled from high temperature to low temperature, α-zirconium precipitates at the phase transformation temperature
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Figure 3.3: Metallography of 66% cold worked Zircaloy-2

increasing the niobium content of the $\beta$-Zr. Below the eutectic temperature, the remaining $\beta$-Zr transforms into $\alpha$-Zr and $\beta$-Nb. However, this transformation is very slow and limited by the diffusion of Nb, often resulting in alloys with a significant amount of retained metastable $\beta$-Zr [84]. Since pressure tube is autoclaved at 400°C for 24 hours as it’s final manufacturing step, the beta-Zr is partially decomposed into $\beta$-Nb and Zr rich $\omega$-phase, which is an intermediate step in the $\beta$ decomposition [84,85]. The $\alpha$ grain size is tens of $\mu$m in the Axial Direction (AD, extrusion direction) by a few hundred nm in the Transverse or Hoop Direction (TD; Fig. 3.4. The texture of Zr-2.5 wt% Nb is also generally well defined [81]. This specific section of pressure tube has the strongest texture of basal normals in the TD, with a decreasing number of basal normals in the Radial Direction (RaD) and nearly no basal texture in the AD, which is consistent with the literature; Fig. 3.1. The yield strength of this material is known to be very high as a result of the significant dislocation density that exists
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from the cold drawing, fine grain size and $\beta$ distribution. The niobium rich $\beta$-phase is known to possess significantly higher hydrogen diffusion rates and H solubility levels than the $\alpha$ phase [66].

![TEM micrograph of Zr-2.5 wt% Nb pressure tube showing elongated $\alpha$ grains (light) with $\beta$ (dark) located at the grain boundaries. Image compliments of F. Long.]

**Figure 3.4:** TEM micrograph of Zr-2.5 wt% Nb pressure tube showing elongated $\alpha$ grains (light) with $\beta$ (dark) located at the grain boundaries. Image compliments of F. Long.

### 3.2.1.4 Annealed Zr 2.5 wt% Nb Pressure Tube

Since the AR Zr-2.5wt% Nb pressure tube is characterised by a high yield strength and significant dislocation density, an annealing treatment was required to produce a soft version of this alloy. Some AR pressure tube was annealed at 700°C for 1 week in an inert argon atmosphere. This particular heat treatment was that used by Root and co-workers prior to neutron diffraction experiments that suggested the stability of $\gamma$-hydride below 180°C [22]. The annealing treatment brought on significant changes to the microstructure (Fig. 3.5 relative to Fig. 3.4), texture (Fig. 3.1) and yield strength
Within the microstructure, there was a significant increase in the size of both $\alpha$ and $\beta$ grains as well as a trend towards a more equiaxed grain shape, with $\alpha$-Zr grains approximately 5-10 $\mu m$ in diameter. Additionally, the distribution of $\beta$-phase changed from the fine continuous distribution along the grain boundary shown in Fig. 3.4 to the more agglomerated distribution of $\beta$-grains at $\alpha$-Zr triple points shown in Fig. 3.5. The observed change in texture due to the annealing treatment was the elimination of any radial basal texture that had previously existed in the AR pressure tube. Due to the annealing temperature being in the $\alpha$-Zr + $\beta$-Zr region, for an extended length of time, and then slow cooled from there, there will be a greater amount of retained metastable $\beta$-Zr in comparison to the AR pressure tube. Lastly, the yield strength measurement confirmed that the annealing treatment resulted in a significant reduction in the yield strength.

**Figure 3.5:** SEM micrograph of annealed Zr-2.5 wt% Nb pressure tube showing large $\alpha$ grains with significant $\beta$ grains located at the triple points.
3.2.2 Hydrogen Charging

Each zirconium sample was hydrogen charged to approximately 100 ppm by an electroplate-anneal method. Samples measuring approximately $70 \times 5 \times 15 \text{ mm}$ were electroplated with a layer of hydride approximately $20 \text{ µm}$ thick in a 0.2 molar solution of distilled water and sulphuric acid at $65 \pm 5 ^\circ \text{C}$ for 48 hours. The hydriding rig is shown in Fig. 3.6. The sample of zirconium to be hydrided (cathode) was secured to a zirconium wire with a spot weld and suspended in the solution surrounded by a platinum coated niobium cage (anode). A current density approximately $1 - 2 kA/m^2$ was applied between the platinum cage and the sample and care was taken that the sample showed bubbles characteristic of the cathodic charging reaction. This was followed by a homogenization treatment at $334 ^\circ \text{C}$ for 24 hours including a 6 hour slow heat and cool from room temperature in an attempt to reach $\sim 100$ ppm hydrogen under pseudo equilibrium conditions. The entire electroplate-anneal procedure was completed twice to ensure that sufficient hydrogen was added to the sample. Any remaining hydride layer was mechanically removed after the homogenisation treatment. The temperature $334 ^\circ \text{C}$ was selected due to the fact that that is approximately the TSSD of hydrogen at 100 ppm and is based from a recommendation in Ref. [86]. This treatment is based upon the principal that the hydride layer acts as a hydrogen source for the bulk of the sample to reach whatever concentration is soluble (and no more) than the peak annealing temperature. A similar method is described in greater detail in a report by Lepage et al. [86].
3.2.3 Quenching Procedures

Samples of each material were solutionised at a temperature of 350°C for three hours in order to completely dissolve all hydrides in the material and were then subject to one of five different quench rates. Each piece of material measured approximately $4 \times 4 \times 15$ mm. As noted previously, the formation of $\gamma$-hydride tends to be favoured when the material is subject to faster quenches while $\delta$-hydride tends to precipitate with slower cools. One sample from each material was quenched from the hydrogen solutionisation temperature in chilled brine, water, oil, air or subjected to a slow furnace cool ($1 ^\circ$C/minute). This range of quenches provided a broad range of hydride populations for study.
3.2.4 Synchrotron Diffraction

Synchrotron diffraction experiments were carried out on the X-6B bending magnet beamline at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratories in Upton, New York, USA several weeks after the quenching treatments. X-ray scattering measurements were made on metallographic samples encased in epoxy resin and polished to a mirror finish with a 17.75 keV beam measuring $250 \times 450 \, \mu m^2$ in size which penetrated a depth of $\sim 20 \, \mu m$ (see appendix in Ref. [29] for calculation in a similar experiment). The detector was a linear Charge Coupled Detector (CCD) with a sample to detector distance of 532.25 mm. The diffraction experimental setup is shown in Fig. 3.7.

Because of the strong orientation relationship between the $\{0002\}$ $\alpha$-Zr basal planes and the $\{111\}$ ZrH planes [52, 70, 71], the incident beam was directed to the surface with the strongest basal texture. In the Zircaloy-2 samples this was in the direction normal to the rolling/transverse plane and in the Zr-2.5% Nb pressure tube this was in the direction normal to the radial/axial plane as shown in Fig. 3.8(a) and Fig. 3.8(b) respectively. Each sample was measured in $\theta/2\theta$ reflection geometry similar to the schematic shown in Fig. 3.8(c). Diffraction patterns were collected for each of the four materials for all five quench rates. Exposures were carried out for 10 seconds over a range of $\Delta \theta = 4$ degrees. A $2\theta$ correction was completed in order to account for the differences in the shape of the linear detector and the curvature of the diffraction pattern. This is because the diffraction pattern is curved in opposition to the linear detector resulting in the measured detector image having $2\theta$ values that increase with distance from the central pixel. Based upon the measured $2\theta$, the sample to detector distance and pixel position, the true $2\theta$ was calculated. On the
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diffraction pattern produced, peaks associated with \{10\bar{1}0\} \(\alpha\)-Zr, \{111\}\(\delta\)-ZrH, \{11\} \(\gamma\)-ZrH and \{0002\} \(\alpha\)-Zr diffraction peaks were identified. These peak locations were referenced from known diffraction patterns in the powder diffraction files (Table 2.1). A background fit was first applied to each set of diffraction data followed by a least squares error refined pseudo-Voigt shape to each peak using MATLAB. This refinement created a 'guess' peak based upon estimated peak locations, height, full width half maximum and fraction gaussian (as a pseudo-Voight shape is a combination of Gaussian and Lorentzian distributions). The 'guess' shape was allowed to change those parameters until the error measured by the differences between the measured and fit data were minimised. This 'fit' curve was used to extract the material data from. From each diffraction fit, measurement of the integrated intensity of each individual was possible. Daum et. al in [19] adapts a procedure described in Cullity [87] to relate the integrated intensity of the \{0002\} Zr peak to the integrated intensity of the \{111\} hydride peaks in order to estimate the volume fraction hydride such that:

\[
\frac{I_{\delta111}}{I_{\alpha0002}} = \frac{R_{\delta111}V_{\delta}}{R_{\alpha0002}V_{\alpha}} \tag{3.1}
\]

or

\[
\frac{I_{\gamma111}}{I_{\alpha0002}} = \frac{R_{\gamma111}V_{\gamma}}{R_{\alpha0002}V_{\alpha}} \tag{3.2}
\]

where \(I_{\alpha0002}\), \(I_{\delta111}\) and \(I_{\gamma111}\) represent the integrated intensities the hkl peaks, \(V_{\alpha}\), \(V_{\delta}\) and \(V_{\gamma}\) represent the volume fraction of the respective zirconium and zirconium hydride phases respectively and

\[
R_{(hkl)} = \frac{1}{v^2} \left[ |F_{hkl}|^2 p_{hkl} \frac{1}{\sin^2 \theta_{hkl} \cos \theta_{hkl}} \right] (e^{-2M})_{hkl} \tag{3.3}
\]
where $R_{hkl}$ is a factor that relates the volume fraction of the phase to its diffraction intensity and is a function of the unit cell volume $v$, structure factor $F$, multiplicity factor $p$, temperature factor $e^{-2M}$ and the Bragg angle $\theta$ for the specific peak. The value of the temperature factor $M$ can be calculated as

$$M = 8\pi^2 u^2 \left( \frac{\sin\theta}{\lambda} \right)^2$$  \hspace{1cm} (3.4)

where $u$ is the mean square atomic displacement taken from the literature in Ref. [88] and $\lambda$ is the wavelength of the x-ray beam [87] described as:

$$\lambda = \frac{hc}{E}$$  \hspace{1cm} (3.5)

where $h$ is Planck’s constant, $c$ is the speed of light and $E$ is the beam energy. Most of the constants used in the preceding descriptions were directly taken from the work by Daum et. al in [19, 29] due to the fact that he performed a similar experiment, and are therefore not reproduced in the present work. However, all values used in these calculations that contained either the Bragg angle $\theta$ or energy had to be recalculated to account for the differences between the work by Daum and this work. An example of how to calculate all values is also included in Ref. [29]. Of other interest is the temperature factor, which accounts for the decrease in scattering intensity with increased temperature due to atomic vibrations which needed to be calculated for the various temperatures of the heating experiments, described later, which was not performed in Ref. [19, 29].

This procedure for determining hydride volume fraction was shown to have excellent agreement with hydride volume fractions determined from vacuum extraction
Figure 3.7: Experimental setup used in synchrotron diffraction setup showing locations of incident beam, sample inside heating vacuum chamber and detector
methods for hydrogen content up to 1250 wt ppm H by Daum in measurements on hydrided Zircaloy-4 fuel cladding [19]. This procedure was applied to the integrated intensities determined from our measurements in order to determine the volume fraction of each hydride phase and is referred to in this chapter as the ‘direct comparison method’. These measurements are based upon the assumption that although other hydride/matrix orientation relationships than the \{0002\}/\{111\} may exist, they are in significantly lower quantity and do not need to be included to draw conclusions as to volume fractions, and is supported by the hydride-matrix texture analysis in Ref. [70, 71].
3.2.5 \textit{In situ} heating experiment

\textit{In situ} heating experiments were carried out in the synchrotron beam in order to monitor the change in hydrogen populations upon heating. A sample was secured to a copper block containing resistance heaters in a vacuum chamber. This setup allowed diffraction measurements to be made on samples while heated up to temperatures over 300 °C without significant interference to the diffraction signal. The purpose of these measurements was to (1) examine evidence for any $\gamma \rightarrow \delta$ phase transformations, (2) observe how such $\gamma \rightarrow \delta$ hydride phase transformations were affected by matrix material, and (3) seek indications of a $\delta \rightarrow \gamma$ phase transformation, with the intention of providing additional data for the ongoing $\gamma$-hydride stability/metastability discussion. Three alloy-quench combinations were tested in this way: brine $\gamma$-quenched AR Zircaloy-2 and AR Zr-2.5 wt% Nb pressure tube as well as furnace cooled Zr-2.5 wt% Nb. In a given test, measurements of the hydride phase populations were made at intervals of 50 °C up to 300 °C with several measurements made at each temperature to document any changes in hydride populations at that temperature as a function of time. Samples were held at each test temperature for a total of 1 hour. The heating stage is shown in the synchrotron setup in Fig. 3.7 and in more detail in Fig. 3.9.

3.3 Results

The volume fraction of both $\delta$ and $\gamma$-hydride was determined using the direct comparison method described in Sec. 3.2.4. Fig. 3.10 shows the fitted region of interest of the zirconium diffraction pattern. Visible are the $\{10\overline{1}0\}$ $\alpha$-Zr, $\{111\}$ $\delta$-ZrH, $\{111\}$ $\gamma$-ZrH and $\{0002\}$ $\alpha$-Zr peaks, providing perspective on the difference in intensity between
Figure 3.9: Detail of interior of *in situ* heating stage used in ZrH synchrotron dissolution measurements
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the zirconium matrix and hydride phases diffraction peaks. The \{10\overline{1}0\} \(\alpha\)-Zr, \{111\} \(\delta\)-ZrH and \{111\} \(\gamma\)-ZrH peaks were fitted simultaneously because of close overlap between the peaks and the fit for the \{0002\} \(\alpha\)-Zr peak was completed separately. It is considered that while other hydride peaks exist, the \{111\} peaks were readily visible and minimally obstructed by the overlapping zirconium diffraction pattern. Fig. 3.10(b) shows a typical fit of the area with both minority hydride peaks present. The volume fractions of each hydride phase relative to the volume fraction of \(\alpha\)-Zr which were calculated from the diffraction data are presented in Table 3.2. Theoretical calculations from unit cell dimensions, atomic masses and crystallographic structures in Table 2.1 reveal an expected total volume fraction hydride of \(\sim\)0.01, which is in reasonable agreement with the diffraction measurements.
Table 3.2: Hydride phase volume contents from the direct comparison method

<table>
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<th>Material</th>
<th>Treatment</th>
<th>vol%delta</th>
<th>vol% gamma</th>
<th>vol% hydride</th>
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<td>Zircaloy-2</td>
<td>AR</td>
<td>Brine</td>
<td>0.44</td>
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<td>Water</td>
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<td>0.81</td>
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</tr>
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</tr>
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<td>0</td>
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<td>Air</td>
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<td>Annealed PT</td>
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<td>1.4</td>
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<td>Oil</td>
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<td>Air</td>
<td>0.82</td>
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<tr>
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<td>Furnace</td>
<td>0.93</td>
<td>0.12</td>
</tr>
</tbody>
</table>
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(a) Entire region of interest

(b) Close up of hydride peaks.

Figure 3.10: Diffraction pattern of hydrided Zr 2.5 wt% Nb showing a typical fit of \{10\overline{1}0\} α-Zr, \{11\overline{1}\} γ-hydride, \{111\} δ-hydride and \{0002\}
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The hydrogen content of some samples were verified with Differential Scanning Calorimetry (DSC) at the Royal Military College of Canada and Vacuum Hot Extraction Mass Spectroscopy (VHEMS) at AECL Chalk River Laboratories and Lu-vak Inc. The DSC tests heated samples from room temperature to 400 °C and the Terminal Solid Solubility of Dissolution (TSSD) of the hydrides is recognized by a measurable change in the heat absorbed by the sample. The 'peak temperature' DSC curve technique used by Khatamian [37] was used to determine the TSSD for select samples. These temperatures were converted into a measurement of the hydrogen content with the Canadian Standards Association N285.8 method for the technical requirements for in-service evaluation of 2.5 wt% Nb zirconium alloy pressure tubes in CANDU reactors [89],

\[
[H] = 81900 \exp\left(\frac{-34500}{RT}\right)\text{ppm} (4) \tag{3.6}
\]

and from a study by Une and Ishimoto [52] for Zircaloy-2,

\[
[H] = 128000 \exp\left(\frac{-36500}{RT}\right)\text{ppm} (5) \tag{3.7}
\]

where \(T\) is the TSSD in degrees Kelvin and \(R\) is 8.314 J/(K-mol). In addition, the volume fractions measured with synchrotron diffraction were converted into weight fractions of hydrogen based upon known unit cell and hydrogen enrichment properties (Table 2.1) with the intention of comparison between the DSC and VHEMS data. These values are listed in Table 3.3. The DSC measurement uncertainty is a conservative estimate and is based upon the spread in the data relative to the direct comparison and VHEMS results. In addition, only one thermal cycle was completed
on the samples used in the DSC tests and consequently, the differences in the hydride morphology as well as matrix behaviour may have shifted the TSSD and consequently the estimated H content away from the correct measure, which may also contribute to the large error range. VHEMS is often thought of as the most reliable means of measuring the hydrogen content of materials with low concentrations of hydrogen. The measurements from VHEMS are also presented in Table 3.3 and agree reasonably with the other H-content measures. The hydrogen content in the direct comparison method is calculated as in Sec. B.2. The differences and scatter within the direct comparison data sets between samples are attributed to grain sampling; the small volume of material measured (Sec. 3.2.4) is of a similar length scale to the spacing of macroscopic hydrides, hence may lead to uncertainty in statistics at a given point. In future experiments a larger sample volume and stage motion (not available on said beamline) or transmission geometry should be used to provide better statistics. Ultimately, the intention of these hydrogen content measurements was to verify that the H-content was similar in all samples, and the three content measurement techniques agree reasonably well that the content in all samples is ~100 ppm H. The DSC and VHEMS measurements do confirm that the hydrogen contents in all samples to be quite similar (on the order of how accurately hydride contents can be assigned) and the content variability is not expected to shift the relative hydride phase populations.

Fig. 3.11 shows the gradual dissolution and transformation of the synchrotron diffraction hydride peaks in quenched Zr-2.5 wt% Nb pressure tube. Fig. 3.12 shows the amounts of $\delta$, $\gamma$ and total hydride phase contents in brine quenched AR Zircaloy-2 and AR Zr-2.5wt% Nb pressure tube during in situ heating within the synchrotron
Table 3.3: Hydrogen content in zirconium samples determined by Direct Comparison, Differential Scanning Calorimetry and Vacuum Hot Extraction Mass Spectroscopy. All values in wt. ppm hydrogen/zirconium.

<table>
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<th>Dir. Comp.±40</th>
<th>DSC ±20</th>
<th>VHEMS</th>
</tr>
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<td>114</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Brine</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Water</td>
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<td>-</td>
<td>-</td>
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<tr>
<td></td>
<td>Oil</td>
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<td>-</td>
<td>-</td>
</tr>
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<td>Air</td>
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<td>Furnace</td>
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<td>Brine</td>
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<tr>
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<td>AR PT</td>
<td>75</td>
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<td>Brine</td>
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<tr>
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<td></td>
<td>Air</td>
<td>65</td>
<td>-</td>
<td>99±5</td>
</tr>
<tr>
<td>Zr 2.5wt% Nb</td>
<td>Annealed PT</td>
<td>63</td>
<td>97</td>
<td>100±5</td>
</tr>
<tr>
<td></td>
<td>Brine</td>
<td>176</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Water</td>
<td>175</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Oil</td>
<td>129</td>
<td>-</td>
<td>149±8</td>
</tr>
<tr>
<td></td>
<td>Air</td>
<td>161</td>
<td>90</td>
<td>124±6</td>
</tr>
<tr>
<td>Zr 2.5wt% Nb</td>
<td>Annealed</td>
<td>158</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
beam. As expected, the total hydride content of every sample decreased upon heating to the point where only trace amounts, eventually indistinguishable with respect to phase, were present as the low intensity hydride peak had a width that nearly crossed the whole range of $\delta$ and $\gamma$-hydride (near 300 $^\circ$C). It is clear from the presented figures that there were no instances of a $\delta \rightarrow \gamma$-hydride phase transformation in any of the materials at any temperatures. There is evidence of a shift from $\gamma \rightarrow \delta$ intensity. This could be due either to a direct phase transformation $\gamma \rightarrow \delta$ or a dynamic equilibrium where dissolution of $\gamma$-hydride at one location is followed by precipitation of $\delta$-hydride nearby. The furnace cooled Zr-2.5 wt% Nb pressure tube sample (not shown) which started with a 100% $\delta$ hydride population did not show any increase in $\gamma$-hydride intensity, simply the reduction in $\delta$ hydride intensity. Unfortunately the local grain sampling resulted in a measurement that significantly underestimated the hydrogen content, and no reliable inference on the dissolution curve could be established for the furnace cooled sample.

3.4 Discussion

3.4.1 Direct Comparison Method

The results described in the previous section appear to have produced hydride volume fractions expected from the hydriding treatment. At room temperature hydrogen has a very low solubility in the Zr-H system, hence nearly all of the hydrogen is expected to be in hydride form. Based upon theoretical calculations involving 100 ppm hydrogen and the crystallographic properties, it is expected that ~1% of the material volume should be hydride. This agrees reasonably well with the volume fractions measured
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Figure 3.11: Diffraction images of dissolving $\gamma$ hydride in zirconium
Figure 3.12: Dissolution curves for brine quenched hydrides in AR Zircaloy-2 and AR Zr-2.5wt% Nb from in situ synchrotron heating study showing $\delta$, $\gamma$ and total hydride content.
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with the direct comparison method. Due to the high synchrotron flux there is only a small error associated within the actual diffraction measurements and least squares fits, meaning that it can be expected that the volume fractions given are a good measure of the compositions within the sampled volume. The differences in the total volume hydride fraction within the same samples are attributed to spatial variation of the hydride distribution in the sample. This assumption is supported by the fact that in the current work samples with faster quench rates, which have a finer hydride microstructure and shorter distribution length scale, have better counting statistics.

3.4.2 Yield Strength Effects

It was not initially clear how an increased matrix yield strength would affect hydride phase stability. One hypothesis is that since the volume expansion of a single δ-hydride unit cell relative to the surrounding matrix is greater than the volume expansion of a single γ-hydride unit cell, the higher yield strength in the matrix would suppress the formation of δ-hydride locally. A perhaps more likely alternative is that because of the lower hydrogen enrichment of γ-hydride, more unit cells will precipitate for any given amount of hydrogen, resulting in more net strain for γ-hydride [9] than for δ-hydride on average in the material\(^1\), suggesting that a harder material may actually suppress γ-hydride. Atomistic studies may have the ability to provide some further insight into these assumptions. Examination of Table 3.2 and Fig. 3.13 shows that γ-hydride was indeed observed in significantly higher quantities in the softer AR

\(^1\)Since the composition and volume expansion for δ hydride is Zr\(H_{1.66}\) and 17.2% and for γ hydride is ZrH and 12.3%. Normalisation of the δ hydride relative to the hydrogen enrichment of γ hydride gives an expansion of 10.36% for the same hydrogen content, which is less than the equivalent expansion from γ hydride of 12.3% ie. more γ unit cells exist for the same hydrogen content. See Sec. B.1
Zircaloy-2 than in the cold rolled Zircaloy-2. The high yield strength cold-rolled material succeeded in suppressing the occurrence of $\gamma$-hydride in the samples with faster quench rates, which were the only quenches expected to produce significant $\gamma$-hydride populations; this suggests that the total net strain in the sample as a result of hydrogen enrichments is more important than individual unit cell expansion strain. This observation is consistent with the hypothesis that alterations to the yield strength of the material can shift the hydride phase stability and the behaviour apparently observed by Cann et. al in TEM [78], who observed a suppression of $\gamma$ hydrides in materials with low oxygen content (postulated to be associated with lower yield strength).

One other possibility is that the increased dislocation density of the rolled material relative to the AR Zircaloy-2 enhanced local hydrogen diffusion enough to produce higher quantities of hydrogen enriched $\delta$-hydride either by transformation or precipitation. That is, if there was a significantly increased ability of hydrogen to diffuse towards a precipitated or precipitating $\gamma$ hydride, there could be an increased ability to form the hydrogen enriched $\delta$ hydride. There are sharp differences in the hydride phase fractions between the brine/water quenches and the completely $\delta$-hydride population present in the oil quenched samples of the Zircaloy-2. This suggests that the quench rate likely affects the hydride population significantly more than the effect from cold work on increased hydrogen diffusion, which is confirmed by other studies indicating hydrogen diffusion on a larger length scale is not significantly affected by cold work [65,90]. It should also be considered that dislocations may act as hydride nucleation sites. If this was significant, it would mean that more nucleation sites for
Figure 3.13: Hydride populations in experimental zirconium alloy material under various quench rates increasing from right to left
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hydrides would exist in the cold worked material and therefore, shift phase stabil-
ity towards the decreased hydrogen enriched $\gamma$-hydride, which was the case for the
Zircaloy-2 in the present experiments.

The two-phase Zr 2.5 wt% Nb pressure tube hydride population data shown in
Table 3.2 and Fig. 3.13 contains results that are not conclusively consistent with the
yield strength hypothesis. The fact that softer annealed pressure tube retained some
$\gamma$-hydride under slow quenches, a condition known to favour $\delta$-hydride, as well as form
$\delta$-hydride in the faster quenches (which would otherwise favour $\gamma$-hydride) suggests
that other factors significantly affect the precipitation and stability of the hydride
phases, especially in these complex microstructural conditions.

3.4.3 $\beta$-phase Effects

Although the single-phase Zircaloy-2 hydride populations appear to demonstrate a
yield strength effect on hydride phase stability, this trend is not observed in the
Zr-2.5wt% Nb. One possibility is that the effect of quench rate on the hydride popu-
lation produced can be altered if there are differences in the (local) supersaturation
of hydrogen within the material. For example, if the hydrogen supersaturation as a
result of either phase segregation or localised diffusion differences in the zirconium
matrix at the length scale of the hydrides was affected, it could possibly suppress
the formation of hydrogen enriched $\delta$-hydride. Conversely, if local supersaturation
on the length scale of the hydrides is easily accommodated in a certain material, it
may provide conditions that could shift the phase stability towards the precipitation
of more $\delta$-hydride.

The niobium rich bcc $\beta$-Zr distribution within the pressure tube material is thus
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of particular interest because it is known to have a diffusion rate of hydrogen several times faster than that in hcp $\alpha$-Zr \[66]\ and a very high solubility of hydrogen, again relative to the hcp $\alpha$-Zr (estimated to be $\approx$83\% of H in $\beta$-phase in a sample of annealed Zr 2.5wt\%Nb containing 300ppm H \[67]\). Also, studies by Cann et al. and Khatamian have shown that hydrogen solubilities in $\beta$ phase is a dependent on the niobium content of the alloy, with increasing solubilities observed with increasing niobium content \[36,91\]. Consequently, the annealed pressure tube material is expected to have a higher hydrogen solubility in both the material (due to the annealing temperature of the hydriding treatment) and in the $\beta$-phase, which would be $\beta_{Zr}(20\%\text{Nb})$. This is probably the reason why the hydrogen contents in the annealed material were measured to be somewhat higher (less than 2 times the contents measured in AR pressure tube) in both VHEMS and the direct comparison method.

Since the hydride populations in the single phase Zircaloy-2 material showed the expected trend of $\gamma$-hydride suppression in the harder material and the two-phase material produced no obvious trend, it again suggests that the $\beta$-phase distribution affects the precipitation of hydride phases in zirconium. Fig. 3.4 and Fig. 3.5 shows both the continuous $\beta$-phase distribution in the grain boundaries of the $\alpha$-Zr grains in the AR pressure tube and $\beta$-phase agglomerations at triple points and grain boundaries in the annealed pressure tube material.

Hydrides, which are known to precipitate at the $\alpha/\beta$ interfaces \[56\] in the quenched AR Zr-2.5wt\% Nb PT were all $\gamma$-hydride, followed by increasing amounts of $\delta$-hydride as the cooling rate decreased. This suggests that diffusion is reasonably uniform within the material at the length scale of the hydrides. Also, it appears to support the interpretation that $\gamma$-hydride is a metastable phase, since it is found only in the
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quenched samples and is not present at all in the furnace cooled sample; i.e. no $\gamma \rightarrow \delta$ phase transformation occurred over the weeks between the quenching treatments and the synchrotron measurements. Comparisons between the AR Zr-2.5wt% Nb PT and the cold-rolled Zircaloy-2, materials which have similar yield strengths, shows that $\gamma$-hydride is produced in greater amounts in the Zr-2.5wt% Nb than in the Zircaloy-2 at all quench rates (when it is produced). This suggests that either a $\gamma \rightarrow \delta$ phase transformation is relatively suppressed in the Zr-2.5 wt% Nb microstructure or perhaps that the precipitation of $\gamma$-hydrides is more easily accommodated possibly due to the increased number of favourable nucleation sites in the AR Zr-2.5 wt% Nb pressure tube relative to the cold rolled Zircaloy-2.

The hydride populations produced in the annealed Zr 2.5wt% Nb PT, which according to a recent study by Mani Krishna [67] also precipitate primarily at $\alpha/\beta$ phase boundaries, suggest that $\beta$-phase distribution affects the precipitation and stability of hydride phases. The fact that $\delta$-hydrides were present in the fast cooled samples and $\gamma$-hydrides were present in the slow cooled samples is of particular interest. The presence of $\delta$-hydrides in the soft material is the opposite trend as to what would be expected from the argument that yield strength controls the hydride phases. The fact that some $\delta$-hydride was formed upon these fast quenches could be explained by the possibility that differences in the local hydrogen supersaturation are possible within this material due to variances in hydrogen solubility [36,67] and diffusion rates [65,66] between the $\alpha$ and $\beta$ phases. This could shift the hydride phase stability upon its formation to what is essentially precipitation of second phase containing different hydrogen quantities next to a hydrogen sink. For example, a hydride precipitating at a $\alpha/\beta$ phase boundary is precipitating right next to a hydrogen sink, and hence may
have a greater availability of hydrogen to precipitate the more H enriched δ hydride even upon quenches that would otherwise favour γ-hydride, which is diffusion limited. This suggestion is increasingly likely due to the increased solubility of hydrogen in the metastable β-Zr in the annealed pressure tube relative to the decomposed β-phase in the pressure tube.

The other consideration is why γ-hydride is still present in the slow cooled annealed Zr-2.5wt% Nb material, a condition which is expected to allow the hydrogen enough time to diffuse to form hydrogen enriched δ-hydride. This could be explained by the possibility that the lower yield strength of the material shifted the stability of the hydride phases to the point where γ-hydride is a energetically favoured even under the slow cool conditions. Alternatively the δ-hydride produced upon the slow cool could have transformed in the weeks between the quenches and the subsequent synchrotron measurements into γ-hydride; remembering that the δ → γ phase transformation apparently observed with neutron diffraction and TEM by Root [22] was in material of this same condition (annealed pressure tube). Root et al., however, do not report any preferred precipitation of hydrides within the β-phase agglomerates in his material. Observations by Dey and Banerjee [92] show that γ-hydride is known to form in β-phase in preference to δ-hydride, although no comment is made as to whether this is preferential to the precipitation of hydrides in the α-Zr. Additionally, the β-phase in the annealed Zr-2.5 wt% Nb material is expected to have increased amounts of hydrogen in it relative to the α phase when the hydrogen is in solution [36,67,91] above TSSD, which supports the fact that the seemingly anomalous hydride populations in this material are a result of the microstructural features. It is possible that the different constraints in the β-phase could also accommodate
the precipitation more easily, and thus shift stability towards $\gamma$-phase as was also suggested by Lanzani et. al [9].

3.4.4 Other Microstructural Considerations

Although the present study has isolated some of the effects of matrix yield strength and $\beta$-phase distribution, grain size and grain shape may also influence the hydride phases. This is because yield strength does appear to shift hydride phase stability and grain size has been postulated to influence the stress state of hydrides in the bulk (largely influenced by hydride grain morphology, where the stress state is considerably higher when the hydride length is similar to the grain size) [70]. Cann et. al [78] did attempt to study the effect of altering grain size on the precipitation of hydrides; their results were inconclusive. Their study showed that in one particular material with two different grain sizes and one heat treatment, *intragranular* $\gamma$-hydrides were predominantly observed during furnace cools. However, the size of the observed hydrides were equal to or less than the grain size, and therefore, no phase shift would likely be expected as a result of the lower amount constraint on hydrides smaller than the grain size was apparently observed by Santisteban [93]. Because of the suggestion that the hydride can affect hydride phase stability, it is possible that the phase behaviour of intragranular hydrides would be different from *intergranular* hydrides - due to the stress state imposed by the grain boundaries [70], which may have been the case in the Cann et. al study [78].

Grain shape is another factor that could influence hydride phase stability. Not only could the grain shape affect the hydride phase stress state in a similar manner to grain size described previously, it could also change the number of favourable hydride
nucleation sites at grain boundaries. If the number of nucleation sites was increased, it would shift the phase populations towards the precipitation of more $\gamma$-hydride as a result of more hydride nuclei decreasing the availability of hydrogen for $\delta$-formation.

Although much of the observed behaviour is not fully understood, results from this study suggest that the hydride phase stability can be shifted significantly by the thermo-mechanical processing of the material. This is consistent with the varied descriptions seen in the literature as well as consistent with much of the discussion from Lanzani et. al [9]. Further studies need to be undertaken to understand the role of $\beta$-phase, microstructure and hydrogen diffusion in the precipitation and stability of zirconium hydrides.

Much of the speculation, particularly in the previous section on $\beta$-phase effects can be further studied by undertaking a TEM study of the material and hydride populations in the yield strength test in order to image hydride morphology (size, shape, platelet), precipitation locations ($\beta$-grains, $\alpha/\beta$-phase boundaries, grain boundaries), nature (inter/intra granular). The addition of bulk measures of hydride populations can show whether or not the individual hydrides viewed in TEM are representative of the typical formations.

### 3.4.5 In situ Heating Experiment

The in situ heating experiment was an opportunity to observe the differences in hydride dissolution and transformation behaviour of AR Zircaloy-2 and AR Zr-2.5 wt% Nb. In both alloys under both furnace and brine quench conditions, no evidence of any $\delta \rightarrow \gamma$ phase transformation was observed, which is in support of the argument that $\gamma$-hydride is a metastable phase in those alloys. Additionally, in the
samples that began the heating process with \( \gamma \)-hydride present, either significant \( \gamma \rightarrow \delta \)-hydride phase transformations (or preferential \( \gamma \)-hydride dissolution followed by re-precipitation of \( \delta \)-hydride) occurred, which also supports the argument that \( \gamma \)-hydride is a metastable phase in these alloys. Comparisons between Fig. 3.12(a) and Fig. 3.12(b) (AR Zircaloy-2 brine quench and AR Zr-2.5wt%Nb brine quench) shows that hydride dissolution and \( \gamma \rightarrow \delta \) phase transformations or preferential \( \gamma \)-dissolution/\( \delta \)-re-precipitation occurred in both materials upon heating, which was expected. The change from \( \gamma \rightarrow \delta \) phase was observed to occur at temperatures lower than typically reported in the literature, with some changes happening at temperatures as low as 100\(^\circ\)C and more significant transformations at 150\(^\circ\)C. The most noted difference between the two materials is described by the fact that \( \gamma \)-hydride was still present in Zr-2.5 wt% Nb at 250\(^\circ\)C while none was apparent in the Zircaloy-2. Although this is consistent with the argument that matrix yield strength can shift the hydride phase stability due to greater hydride constraint, it is not the only explanation as the physical morphologies of the two alloys hydride populations are different. Any of the other local effects on particular hydrides described previously could also cause this apparent shift in the transition temperature.

Fig. 3.14 shows the hydrogen contents measured by the direct comparison method in the heating experiment converted into hydrogen wt ppm compared to TSSD curves from the literature [34,89]. The hydrogen content in solution was calculated by subtracting the measured amount of hydride at a given temperature from the measured content at room temperature. This shows that quenched hydrides have significantly different dissolution behaviour than the established curves based upon equilibrium hydrides, with significant amounts of hydrogen in solution at temperatures as low as
100 °C. The reasoning for this is likely from the different hydride morphology, different hydride/matrix interfaces and possibly an effect from the hydride stress state arising from the matrix constraint (accommodation energy term $\overline{w}_{inc}$, Sec. 2.2, [4,48,49]).

Figure 3.14: Hydrogen measured to be in solution in comparison to established TSSD Arrhenius curves for Zircaloy-2 [34] and Zr-2.5 wt% Nb PT [89]

3.5 Conclusions

The following conclusions can be drawn regarding the formation of low hydrogen content $\delta$ and $\gamma$ hydride phases in zirconium alloys:

- Changing the yield strength of the matrix alloy does appear to have significant
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effect on the hydride populations formed for a given heat treatment with close to 100 ppm H in zirconium alloys.

- In single phase Zircaloy-2, a stronger matrix appears to have hindered the formation of \( \gamma \)-hydride, i.e., that \( \gamma \)-hydride is suppressed in harder materials.

- The significantly varied hydride populations between the AR Zr-2.5 wt% Nb pressure tube containing continuous and distributed \( \beta \)-phase and the annealed Zr-2.5 wt% Nb pressure tube with large agglomerated metastable \( \beta \)-phase zones indicates that \( \beta \)-phase distribution or composition plays a significant role in the conditions for the stability and metastability of \( \gamma \)-hydride.

- Upon heating to the hydrogen dissolution temperature, \( \delta \rightarrow \gamma \) hydride phase transformations were never observed, supporting the argument that \( \gamma \)-hydride is a metastable phase in the alloys and conditions studied.

- \( \gamma \rightarrow \delta \) phase changes were observed at similar temperatures in single phase Zircaloy-2 and AR Zr-2.5 wt% Nb pressure tube, but \( \gamma \)-phase remained up to higher temperatures in the Zr-2.5 wt% Nb possibly due to the greater constraint from the matrix.

- \( \gamma \)-quenched hydrides dissolve into solution at significantly lower temperatures than the slower cooled equilibrium \( \delta \) hydrides.
Chapter 4

Literature Review II: DHC in Zirconium Alloys

"Hokey Religions and Ancient Weapons ain’t nothing compared to having a good blaster at your side"

— H.Solo

The present chapter is a review of the literature related to Delayed Hydride Cracking in zirconium alloys. Sec. 4.2 discusses some of the fitness for service operational considerations by industry with regards to preventing or controlling DHC. Sec. 4.3 describes the driving force for hydrogen accumulation at the crack tip, which is the theoretical basis for understanding how DHC occurs and is essential to describing experimental DHC behaviour. Sec. 4.4 describes experimental observations of crack initiation and Sec. 4.5 discusses the experimental observations of crack growth rates. Sec. 4.6 discusses some considerations regarding the present understanding and modelling capabilities of DHC.
4.1 Introduction to Delayed Hydride Cracking

Delayed Hydride Cracking, or DHC is a sub-critical crack growth mechanism that has caused failures in hydride forming metals including zirconium, which is commonly used in nuclear reactor core components. In zirconium alloys, it is characterised by the repeated formation, growth and subsequent fracture of brittle zirconium hydride at a stress raiser. Knowledge and mitigation of the conditions resulting in both DHC and other hydrogen embrittlement mechanisms enable nuclear reactor operators to safely operate their reactors. CANDU pressure tube DHC failures such as those in the Pickering reactors in the 1970’s (described in more detail in Sec. 1.2) are significant safety and economic problems that must be prevented in order to ensure the long term viability of CANDU reactors. DHC in zirconium alloys itself can occur under varied conditions, but in general, a material must possess a significant stress raiser or area of high residual/applied stress, contain sufficient hydrogen and be subject to temperature conditions where the solubility of hydrogen in the material is low enough that some hydrides can precipitate (at the crack tip) but high enough that sufficient hydrogen is in solution. At the present, DHC in CANDU reactors is mitigated primarily by:

- Monitoring the concentration of hydrogen isotopes dissolved within the pressure tube and ensuring that concentrations necessary for DHC are not reached or minimised and monitored (see Sec. 3.3 or Sec. 5.2.4)
- Ensuring that the thermo-mechanical manoeuvres required for operation are selected to avoid making the core component vulnerable to DHC (see Sec. 4.2).
- Ensuring that no significant flaws or high stresses exist or are at a significant risk of initiating cracks (see Sec. 4.2).
• Monitoring and controlling the migration of fuel channel garter springs in order to prevent pressure tube to calandria tube contact, which can result in hydride blistering due to a pronounced thermal gradient, and subsequently DHC may occur.

Close and conservative consideration of the above has eliminated occurrences of DHC cracking in modern CANDU reactors. However, constant and continued vigilance is still required in order to prevent further possibilities of DHC related failure. Additionally, the continued development of the knowledge base surrounding DHC and hydrogen embrittlement can improve reactor component lifetimes and their engineering justification due to better models and assessment techniques. These better models and levels understanding could result in the implementation of less conservative engineering constraints and therefore better economical forecasts through component life extensions. Attempts to either describe or model DHC generally focus on characterising nature of hydrogen migration towards the flaw tip [48,94–97] (Sec. 4.3) or the conditions required for the fracture of a hydride at a crack tip [74, 75, 97–106] (discussed in Sec. 4.4).

4.2 Pressure Tube Fitness for Service

Canadian Standards Association (CSA) Standard N285.8-10 [89] (hereon referred to as CSA N285.8) contains the technical requirements for in-service evaluation of zirconium alloy pressure tubes in CANDU reactors. There are a number of considerations that are made when determining fitness for service. In general the requirements for service consist of an assessment of the flaws detected or conservatively assumed within the pressure tube, evaluation of possible pressure tube-calandria tube contact
in addition to justification of the material surveillance methods [89]. The following is intended to provide a general summary of pressure tube fitness for service and detail is only provided for DHC assessments

4.2.1 Flaw Evaluation

Detailed flaw analysis is required by CSA285.8 [89] in order to demonstrate pressure tube fitness for service. A flaw must be proven to not risk pressure tube failure due to DHC, fatigue crack propagation, fracture initiation or plastic collapse. The degradation mechanism and/or source of the flaw, the flaws geometry and location must be determined in order to make the appropriate assessment. The flaw is first determined to be of planar or volumetric geometry. A planar flaw such as a crack or manufacturing flaw is projected into components relative to the loading axes of the pressure tube. Volumetric flaws such as scratches or debris fretting flaws are resolved into their largest projections in the loading axes of the pressure tube. If multiple flaws are found in close proximity to each other, it may be concluded that flaw interaction may occur and they are conservatively assumed to be one large flaw. Once the geometry of the flaw can be conservatively estimated, it is subjected to several considerations for a given evaluation period such as a pre-determined number of operating hours or temperature transients. Expected flaw evolution is determined for the duration of a given evaluation period such that pressure tube failure will not occur. Following a given evaluation period, the tube is re-assessed and the process repeated.
4.2.2 Pressure Tube Overload Failure

Once flaw geometry is determined and the expected loading conditions during the present evaluation period are used to determine if critical flaw propagation will occur. This requires following the criterion for critical fracture to be satisfied:

\[ K_I \leq \frac{K_i}{SF_F} \]  

(4.1)

where \( K_I \) is the applied stress intensity factor for the flaw geometry corresponding to several service loading conditions, \( K_i \) is the lower bound fracture toughness of the material taking into account temperature, irradiation, hydrogen equivalent concentration (\( Heq \)) and material variability and \( SF_F \) is an appropriate safety factor. A similar methodology is applied to the onset of plastic collapse [89].

4.2.3 Fatigue Crack Initiation and Growth

The flaw may also be subject to fatigue crack initiation and propagation. This is of exceptional importance as a sharp crack formed by even the slowest fatigue crack propagation can become a possible site for DHC. A given flaw is either measured or conservatively estimated to not form a fatigue crack for the duration of a given evaluation period. This is done by analysing the flaw geometry in relation to a material fatigue crack initiation curve for blunt flaws. The curve describes the relation between the allowable alternating effective peak stress or effective peak strain and the number of cycles until initiation. Also considering surface roughness, material variability, temperature, fluence and the mean stress from the fatigue curve data [89]. The combined effects of different loading cycles throughout an evaluation period is
accounted for in a conservative damage accumulation based method similar to Miner’s rule. Fatigue crack growth is evaluated for all load transients and is treated by Paris’ law fatigue growth \[107\] in Eq. 4.2

\[
\frac{da}{dN} = C_0(\Delta K_I - \Delta K_{th})^{n_o}
\]  

(4.2)

Where \(da\) is the amount of crack growth given for \(dN\) cycles, \(C_0\) is the fatigue crack growth coefficient, \(\Delta K_I\) is the range of applied stress intensity factor \(K_I\), \(\Delta K_{th}\) is the threshold range of stress intensity factor for the onset of fatigue crack growth and \(n_o\) is the fatigue crack growth exponent. \(C_0\), \(\Delta K_{th}\) and \(n_o\) are values that take into account environmental factors (such as contact with coolant), temperature, loading frequency, material variability and the ratio between the minimum and maximum effective stress intensities.

### 4.2.4 Delayed Hydride Cracking

In order to initiate and propagate a DHC crack, a loaded flaw must exist in a material with limited hydrogen solubility and a certain amount of hydrogen in solid solution. The engineering practice associated with the mitigation of DHC includes close monitoring of flaw geometries, bulk hydrogen equivalent concentration \(Heq\) as well as temperature and load transients.

#### 4.2.4.1 Hydrogen Equivalent Concentration

Over the course of a reactor component’s lifetime, it is subject to the pickup of hydrogen and deuterium in a mechanism described previously in Sec. 1.2. Due to the damaging effects of hydrogen embrittlement mechanisms, the amount of hydrogen
in new pressure tubes is highly controlled and the hydrogen or deuterium ingress is closely monitored throughout the pressure tube’s lifetime by measuring the hydrogen content in scrapes removed from the inside of in-service pressure tubes. The amount is determined either by Differential Scanning Calorimetry (DSC) or Vacuum Hot Extraction Mass Spectroscopy (VHEMS) techniques described elsewhere (Sec. 5.2.4 and Sec. 3.3). Hydrogen equivalent concentration (hereupon referred to as $H_{eq}$) is a measure of the concentration of hydrogen or deuterium in the material. Since hydrogen and deuterium are chemically equivalent and act in combination for hydrogen embrittlement mechanisms their amounts are combined when factored into DHC engineering assessments as $H_{eq}$. $H_{eq}$ is the weight concentration of hydrogen if all deuterium was replaced by hydrogen such that:

$$H_{eq} = [H] + [D]/2 \quad (4.3)$$

and in the present application is referred to in weight of hydrogen equivalent atoms relative to the weight zirconium atoms in the mixture, or wt ppm.

### 4.2.4.2 Temperature and Load Transients

Although $H_{eq}$ concentration remains as the measurable quantity used to justify DHC mitigation in pressure tubes, simply having hydrogen in the material is not sufficient to cause DHC. Since the solubility of hydrogen in zirconium varies significantly with temperature from ambient temperatures (few ppm H) to CANDU pressure tube outlet temperatures (300 °C, ~60 ppm upon heating from ambient or 115 ppm upon cooling from higher temperature; Annex D.2 in Ref. [89]). Thermal history significantly affects the amount of hydrogen in solution. In the extremes, a pressure tube with all
of the hydrogen in precipitates will not cause DHC because there will be no ability for significant hydrogen to diffuse to a crack tip and conversely, if the hydrogen solubility is well above the amount of hydrogen in the material, hydrides may not be able to precipitate at the crack tip due to an insufficient chemical potential gradient, which is limited by the yield stress (Sec. 4.4.4.4).

4.2.4.3 Leak Before Break

Pressure tubes in CANDU power stations are required to be qualified to Leak Before Break, or LBB. This means that if a crack appears in a pressure tube it will leak coolant into the annulus gas where it can be detected before the crack grows to a critical size. In short, this means that the amount of time available to detect a significant crack is much greater than that required to detect the crack [108]. This is a means to mitigate catastrophic pressure tube failure and a driver to understand DHC in different cracking directions. For further information on LBB, refer to Ref. [109–111]

4.2.4.4 Pressure Tube-Calandria Tube Contact Assessment

The final incidence that must be monitored to avoid major pressure tube failure is the possibility of pressure tube - calandria tube contact. Since the pressure tube is held nominally at a 300°C and the calandria tube operates at closer to 80°C, in the event that the pressure tube were to physically contact the calandria tube, a strong thermal gradient would occur, resulting in a hydride blister on the pressure tube [71,112] if the blister formation threshold is exceeded. This can and has caused failures in CANDU pressure tubes. The main strategies in eliminating this is proper maintenance of
the locations of pressure tube garter springs, which maintain the space between the calandria and pressure tubes, and awareness of in reactor pressure tube deformation.

## 4.3 Driving Force for Hydrogen Accumulation at Crack Tips

### 4.3.1 Chemical Potential

Hydrogen in zirconium alloys primarily migrates towards a stress riser as a result of the chemical potential gradient between the crack tip and the bulk of the material as a result of a pronounced stress gradient. This is commonly described in terms of the following schematic of region immediately surrounding a loaded stress riser, shown in Fig. 4.1. The chemical potential \( \mu^D_H (r, p) \) driving the diffusion of hydrogen in the \( \alpha \) phase of zirconium under an arbitrary hydrostatic tensile stress, \( p(r) \), can be approximated as in Eq. 4.4, adapted from various sources [45,113], originally [94,95], but primarily from [48], which is a recent review publication of the constantly updated steady state DHC model by a member of the original modelling group.

\[
\mu^D_H (r, p) = \mu^0_H + RT \ell n C^D_H (r, p) - p(r) \nabla_H
\]  

(4.4)

Here \( \mu^0_H \) is the chemical potential at zero stress, \( p \) is the average hydrostatic stress (positive if tensile) and \( \nabla_H \) is the partial molar volume of the mobile species (here hydrogen) in the stressed solid [45,114] and is equal to \( 1.67 \times 10^{-6} \text{ m}^3/\text{mol} \) in zirconium. The partial molar volume represents the amount of additional volume one mole of a minority species produces in addition to the other medium, or in the present case, the
amount of extra volume occupied by the addition of 1 mole of hydrogen in zirconium.

At zero-stress Eq. 4.4 reduces to:

\[
\mu^D_H(r, p) = \mu^o_H + RT \ln C^D_H(r, p)
\]  
(4.5)

When the stressed and zero-stress parts of the material are at equilibrium, their chemical potentials for hydrogen diffusion (Eq. 4.4, Eq. 4.5) are equal, which requires the hydrogen concentration in the stressed crystal to be higher than in the zero-stress crystal. The hydrogen concentration in the stressed region \(C^D_H(r, p)\) is greater than the concentration in the zero-stress region \(C^D_H(r, 0)\) in accordance with:

\[
C^p_H(r, p) = C^p_H(r, 0) \exp \left[ \frac{p(r) \nabla_H}{RT} \right]
\]  
(4.6)

or if hydrides are present in the zero-stress region:

\[
C^p_H(r, p) = C^s_H(r, 0) \exp \left[ \frac{p(r) \nabla_H}{RT} \right]
\]  
(4.7)

where \(C^s_H(r, 0)\) is the equilibrium hydrogen solvus concentration under zero stress at the distance \(r\) from the stressed region and \(C^p_H(r, p)\) is the concentration at the stress raiser. The end relationship between equilibrium concentrations of hydrogen in zirconium is more generally put in Ref. [45] as:

\[
C^p_H(r, p) = C^o_H \exp \left[ \frac{\Delta p \nabla_H}{RT} \right]
\]  
(4.8)

where the \(\Delta p\) term is the difference in hydrostatic stress between the stressed and unstressed regions of the material. Thus, hydrogen will diffuse from an area of lower
stress to one of higher (more tensile) stress until equilibrium is reached. This is the
main driving force for hydrogen accumulation at the crack tip.

The flux of hydrogen towards the crack tip per unit depth $J_H$ is thus defined based
on the boundary conditions $\ell$, which are usually taken as the size of the plastic zone
at the crack tip and $L$, which Puls suggests [49] represents the average bulk hydride spacing (Fig. 4.1), although this is debated. Although $L$ was initially designed in the
Puls publications to represent the boundary condition of hydrogen diffusion from a
dissolving hydride far from the crack tip, the presence of bulk hydrides is no longer
considered to be required for DHC to occur [49, 113] due to the fact that diffusing
hydrogen will hardly reduce the effective source of hydrogen in solution, and therefore,
more accurately represents an area where the hydrogen concentration far from the
crack tip is constant [49,113]. The flux then results in the following expression:

$$J_H = \frac{C^\ell_H(r, p)D_H}{\Omega_{Zr}r\phi(\ell, L)} \nabla \mu^D_H(r, p)$$  (4.9)

where $J_H$ is the flux of hydrogen into the crack tip cylindrical region defined by $r=\ell$,
$D_H$ is the diffusivity of hydrogen in zirconium, $\Omega_{Zr}$ is the atomic volume of zirconium,
$\phi(\ell, L)$ is the hydrogen concentration gradient and $\nabla \mu^D_H(r, p)$ is the chemical potential
gradient. In summary, the presence of a tensile stress results in a gradient of chemical
potential resulting, on average, in the diffusion of hydrogen towards the stress riser.
The lowered chemical potential exists because the tensile stress strains the crystal
lattice, making it a lower energy state for hydrogen atoms to exist there, and therefore,
if diffusion is active, hydrogen accumulation at the crack tip can occur.
Figure 4.1: Schematic of crack-tip process zone used to explain chemical potential diffusion of hydrogen [48].
4.3.2 Effect of Stress on TSS

Another suggestion [115] with regards to the driving force of hydrogen to stress concentrations was the possibility that stress could shift the Terminal Solid Solubility of the hydride phase in zirconium, resulting in the precipitation of hydride at the crack tip. For example, if hydrogen was uniformly dispersed in the material slightly below the TSSP, the addition of stress could cause precipitation. This process was driven from understandings of other hydride forming metals such as vanadium. Studies by Takano, Koike and Suzuki [116, 117] demonstrated in TEM that applied stress would precipitate $\beta$ hydride in bcc vanadium as a result of stress shifting the effective terminal solid solubility of precipitation. Discussions of the effects of stress on hydrogen solvus were published by Eadie and Coleman [115]. With reference to [118], they approximate the change in solvus with the following form:

$$C_p^H = C_o^H \exp \left( -\frac{pV_H}{RT} \right) \exp \left( \frac{pV_{H_H}^h}{RT} \right)$$  \hspace{1cm} (4.10)

where $C_p^H$ is the solvus under applied stress relative to the stress free solvus $C_o^H$, $V_{H_H}^h$ is the partial molar volume of hydrogen in the hydride and the remaining variables are as defined previously (Sec. 4.3.1). Rearranged in terms of hydrogen concentration and effective change in the temperature of the solvus, this equation becomes:

$$\Delta T = \frac{p \left( V_{H_H}^h - V_H \right)}{R \ln \left( C_H^{S_S}/9.9\times10^4 \right)}$$  \hspace{1cm} (4.11)

where $\Delta T$ is the change in the temperature of the solvus as a result of the applied stress. Initially, work by Ells and Simpson [119] defined $V_{H_H}^h = 14 \times 10^{-7} m^3$ per mole.
and $V_H = 7 \times 10^{-7} \text{ m}^3$, with the value of $V_H$ taken from general formulations by Wriedt and Oriani [120]. The use of these two values results in an appreciable change in the solvus (~10 degrees at typical DHC temperatures, which is significant). A direct measurement of $V_H$ was made by MacEwen et al. [121] with neutron diffraction and it was determined that the actual value was closer to $1.67 \times 10^{-6} \text{ m}^3/\text{mol}$. Additionally, $V_H^{\text{th}}$ was corrected to be closer to $1.45 \times 10^{-6} \text{ m}^3/\text{mol}$, which results in a change in solvus of only a few degrees at typical DHC temperatures. Ultimately, this is because the stress has about the same chemical effect on the dissolved hydrogen as it does on a hydride.

### 4.3.3 Concentration Gradient

Korean researchers headed by Y.S. Kim have suggested yet another possibility for hydrogen migration to the crack tip [97, 99, 122–129] which relies upon a localised decrease in hydrogen saturation at the crack tip as a result of a stress induced precipitation of a hydride. This model was first discussed in Ref. [122] where Kim pointed out several perceived shortcomings in the Dutton-Puls DHC models, the basis of which was described in Sec. 4.3.1 [49]. Ultimately, Kim’s model suggests that an applied tensile stress acts to trigger the nucleation of hydrides only at the crack-tip. This correspondingly results in an overall reduction in the hydrogen saturation locally at the crack tip, thus setting up a concentration gradient between the far-field hydrogen in solution and the crack tip. Although Kim’s model was developed in an attempt to address some of the potential shortcomings of the Dutton-Puls models [48, 49], a model based upon experimentally determined solvus measurements with very limited theoretical grounding is described. Challenges by other authors to produce a more
complete theoretical description appear to have been mis-interpreted by Kim. Although Kim’s model does appear to have the ability to predict some experimental DHC data, his thermodynamic justification for this mechanism has been shown by other authors to be a mis-interpretation of the Dutton-Puls thermodynamic basis [49]. In later publications, Kim also makes the suggestion that crack tip hydrides are of $\gamma$ phase at lower temperatures based upon the postulation that it is the stable phase at lower temperatures, as reported in several studies. This was observed with neutron diffraction in Ref. [22] and observed in thin film TEM DHC experiments by Cann et al [130]. This might make DHC occur at elevated rates and conditions otherwise not predictable by the Puls model [126]. However, with the debated stability/metastability arguments aside, this is not a reasonable approach until experimental verification of bulk crack tip $\gamma$ hydrides is provided.

4.4 Crack Initiation and Growth

4.4.1 Experimental Observations

Delayed Hydride Cracking is a sub-critical crack growth mechanism that is characterised by the repeated precipitation, growth and fracture of a brittle hydride phase at a stress raiser and is shown schematically in Fig. 4.2. First, hydrogen in solution diffuses towards the loaded crack tip or flaw as a result of the change in hydrogen chemical potential because of the stress gradient around the crack tip (see Sec. 4.3.1 for explanation). Once conditions for hydride precipitation occur (TSSP concentration is exceeded), a brittle zirconium hydride will precipitate. Continued loading of the hydrided flaw promotes either the growth or precipitation of additional hydride
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Figure 4.2: Pictorial representation of DHC showing the loading of a crack or flaw, subsequent precipitation and growth of a hydride at the stress raiser and subsequent crack extension through the brittle hydride into the ductile matrix [131].

Figure 4.3: Fractured hydride clusters along crack path \((K_I > K_{IH}, K_I > K_{IC})\) and un-cracked crack tip hydride formed upon loading below \(K_{IH}\) at 275°C [45].
platelets ahead of the crack tip hydride oriented in the crack plane. Once the hydride cluster at the crack tip has reached a certain condition, the matrix material is no longer able to provide the appropriate crack closure constraint and the brittle hydride fractures, and the crack extends into the ductile matrix beyond the hydride cluster, Fig. 4.3, where the process repeats itself until component failure.

Both the initiation and propagation of a DHC crack relies heavily upon characteristics of the brittle hydrides that must precipitate, grow and fracture at the crack tip. Consequently, numerous studies have sought to experimentally characterise the conditions that result in the formation of crack tip hydrides in addition to the conditions that result in the fracture of a crack tip hydride. Additionally, since material behaviour at the crack tip is the general basis for most DHC models (Sec. 4.5.3), comprehensive experimental studies of crack tip hydrides, their material properties and their formation behaviour can provide evidence to back up the theoretical descriptions required to reliably predict DHC in an engineering application.

Crack tip hydrides were first investigated with Transmission Electron Microscopy (TEM) shortly after the Pickering DHC failures in the 1970’s by Cann and Sexton [130]. Their study was able to physically observe the repeated formation, growth and fracture crack growth mechanism that was predicted from the initial observations of DHC (Fig. 4.4). Although the suspected mechanism of operation for DHC was characterised, the thin TEM foil offered little information about the conditions required for hydride fracture in real reactor components.

More recently, studies of crack tip hydrides observed by synchrotron diffraction by Kerr et al. [74,75] have given more insight into the nature of load-sharing between the crack tip hydride phases and surrounding matrix in the process zone (shown in
Figure 4.4: Dark field images of crack tips formed and fractured in a zirconium specimen with 100ppm H. (a) 3 hours after initial strain, (b) hydride precipitation at new crack tip 1 hour after additional strain, (c) fracture of initial hydride and new hydride precipitate, (d) crack growth after 2 days, (e) same as (d) but showing crack tip hydride and (f) coarsening of crack tip hydride after 1 additional day [130].
Fig. 4.1). In Ref. [75], observations of the overload behaviour of a zirconium sample with a large crack tip hydride showed that the load at the crack tip is transferred to the hydride upon loading and transferred back to the matrix following hydride fracture. Ref. [74] observed crack tip stress relaxation during crack tip hydride growth confirming expected changes in the stress gradient and differences in hydride overload behaviour, or the mechanics when the hydride is fractured, at various temperatures.

4.4.2 $K_{IH}$

The measured parameter $K_{IH}$ is loosely defined in the literature as the stress intensity factor below which DHC will not occur. In most tests measuring $K_{IH}$, this means the highest stress intensity that no measurable crack growth was observed, and depends upon a large number of variables such as the resolution of the crack growth monitoring system, time held at a given stress intensity/experimenter patience, sample thickness, crack tip geometry, hydride geometry, direction of applied load (increasing or decreasing) and the environment itself. In order for a DHC crack to occur the applied stress intensity must have:

- Sufficient stress to provide the driving force for hydride diffusion towards the crack tip (see Sec. 4.3.1).
- Sufficient stress to precipitate and grow a hydrided region oriented in the crack plane
- Sufficient stress to fracture the crack tip hydride.
- Stress must be applied for sufficient time to allow the hydride at the crack tip to build up to some critical size at which point it can fracture due to the combined properties of the hydride and the surrounding matrix.
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If the conditions above are not met, DHC will not occur. The factors that are known to affect $K_{IH}$ are described below.

4.4.2.1 Incubation Time

The American Society for the Testing of Materials (ASTM) Standard E 1681 describing the Standard Test Method for Determining Threshold Stress Intensity Factor for Environment-Assisted Cracking of Metallic Materials [132] does not provide a specific time at which to hold at a given stress intensity due to the general basis of the test standard and various mechanisms causing environmentally assisted cracking. The standard describes the test duration to be one of the most difficult test parameters to select due to its strong dependence on the cracking mechanism and environment. DHC $K_{IH}$ measurement literature generally reports $K_{IH}$ measurements at holds of 24 hours or longer [45,99,133,134] for initiation at sharp crack tips, and greater holds for more blunt flaws. Unfortunately, a 24 hour hold at a given test temperature and load may not be enough time to initiate cracking, particularly under conditions where the hydride is growth limited (as opposed to fracture limited, see Sec. 4.4.4). However, other issues can arise from running slower tests, particularly test management considerations, and 24 hours is a very reasonable length of time to get a sufficient test for DHC under most conditions.

4.4.2.2 Specimen Thickness

Sample thickness may significantly affect the measurements of $K_{IH}$. ASTM Standard E 1681 describes the measurement of two different stress intensities for environmentally assisted cracking: $K_{IEAC}$, or the linear-elastic threshold stress intensity factor for
environmentally assisted cracking intensity, which is a material property and $K_{EAC}$, which is the threshold stress intensity for environmentally assisted cracking and is dependent on thickness due to plane stress effects. Evaluation of the criterion for plane strain conditions requires the following condition to be satisfied

$$B \geq 2.5 \left( \frac{K_{IC}}{\sigma_{ys}} \right)^2 \quad (4.12)$$

Where $B$ is the sample thickness, $K_{IC}$ is the plane strain fracture toughness for Zr-2.5 wt%Nb pressure tube in the axial direction (taken as 20 MPa$\sqrt{m}$ at room temperature and 40 MPa$\sqrt{m}$ at 200°C [135]) and $\sigma_{ys}$ is the yield stress (taken to be 1149.6-1.02T(K) MPa, which corresponds to 850 MPa at room temperature or 667 MPa [69] at 200°C). Thus, the thickness required for plane strain is approximately $\geq 1.38 \text{ mm}$ at room temperature or $\geq 9 \text{ mm}$ at 200°C. Consequently, the measurement of $K_{IEAC}$, which would be a material property would require a sample thickness greater than $9 \text{ mm}$ thick for testing at $200^\circ \text{C}$, which is unfortunately not the situation in the case of Zr-2.5 wt% Nb pressure tube material, which has a nominal thickness of $4.2 \text{ mm}$ and a very specific microstructure that would be arduous to achieve at a greater thickness. For this reason, most tests which seek to characterise axial direction cracking in PT without modifying the microstructure or defect structure are forced to compromise by running tests with either Curved Compact Toughness (CCT) samples machined from a pressure tube as in Fig. 4.5, mechanically flattened and stress relieved CCTs or flat machined CT samples at a compromise with even lower sample thickness. However, since the maximum applied stress used in DHC testing is less than $K_{IC}$, a thickness requirement is thus based upon the highest stress intensity factor that is used in the test. Calculations with the full thickness
pressure tube indicate that plane strain can actually be satisfactorily maintained up to $27 \, MPa \sqrt{m}$ at 200°C. Most industry based research tends to make use of CCT sample geometries and thicknesses because they seek to characterise in reactor behaviour as closely as possible and CCT samples have full pressure tube thickness. One disadvantage of CCT sample geometries is the fact that the stress intensity at the crack tip may be non-uniform as a result of the bending moments induced on the inner diameter from the curves. For measurements of crack growth rates this is not a problem as the crack growth rate is not sensitive to stress intensity at higher loads (see Sec. 4.5.2.1). Conversations with Gordon Shek [45] indicated that tapered loading pins can be used to even out the loading at the crack tip, but the precision of this technique has not been confirmed by this author. Flattened and stress relieved samples capture the full thickness of the PT without compromising load differences at the crack tip and allowing measurements of pure axial DHC parameters, and were empirically developed at Chalk River Laboratories [136]. However, the deformation during flattening may change the texture and stress relief treatment is known to affect the $\beta$ phase distribution and/or microstructural features (Sec. 3.2.1), both of which can affect DHC parameters. Samples machined from PT itself have the advantages of both maintaining unique microstructural features as well as even stress distributions at the crack tip removing the possibility of differences in the loading at the notch tip. The compromise is that the samples must have a lower thickness, which means that the measured quantities are even farther away from the plane strain condition and difficulties may then arise comparing measured quantities to other literature. A diagram showing a sample machined from a pressure tube is shown in Fig. 4.6. It must however be stated that even though the threshold stress intensity
for the initiation of DHC in PT alloy is delegated $K_{IH}$ in virtually every situation, it is in all cases not representative of the plane strain condition, and must be treated as a quantity that depends on thickness.

**Figure 4.5:** A Curved Compact Toughness (CCT) sample commonly used in industry DHC tests [45]

4.4.3 Striation Formation

The stepwise nature of DHC results in characteristic fracture surface features referred to as striations or 'beach marks' shown in Fig. 4.7. Every time a hydride grows and fractures, a mark is made in the ductile matrix where the crack arrests Fig. 4.7.
Studies [45,102–104,137] have successfully been able to correlate the piecewise crack growth measured with acoustic emission or potential drop methods (see Sec. 5.3.1.3) with the striations examined on DHC fracture surfaces. Consequently, the length of a given striation is representative of the critical hydride length and ductile stretch zone for the given cracking conditions, and consequently it is a feature that is often measured in order to justify cracking model assumptions regarding the criterion for hydride fracture.

Many publications refer to the fracture of one critical hydride resulting in the formation of a striation, but this is not a complete description. Crack tip hydrides are often more accurately described as a hydride cluster consisting of many hydrides at or near the crack tip with zirconium ligaments between them. It should also be noted that each hydride platelet within the cluster also does not grow across the entire width of the sample. Therefore, when a fracture event occurs it does not necessarily mean that one giant crack tip hydride is fracturing, but that the crack
extends through many favourably oriented hydrides, in three dimensions, plastically rupturing the zirconium ligaments in between them. This cracking event also may not crack the entire width of the sample, but often just a portion of the width (see wavy striation shape in Fig. 4.7 and Fig. 4.9) and thus, the expected piecewise crack growth may appear somewhat continuous, depending on the cracking conditions. SEM images of DHC fracture surfaces shows several characteristic features confirming the presence of brittle fracture facets followed by ductile dimples at striation marks, Fig. 4.8. Fig. 4.9 is a schematic describing the formation of the complex fracture surface between striations (Fig. 4.8) as a result of the brittle fracture of several hydride platelets oriented in the crack plane, but not necessarily in it, accompanied by the ductile overload tearing of the surrounding matrix material. This is what causes the characteristic crystal facets (brittle hydrides fracturing) and cliffs/ridges (ductile matrix behaviour) and further confirms the description of a critical hydride cluster cracking mechanism. The length of the striations is often correlated with the criterion for hydride fracture as the striation length is representative of the length of a specific hydride fracture step.

4.4.4 Experimental Observations of $K_{IH}$

4.4.4.1 Texture Effects

Crystallographic texture has a distinct effect on $K_{IH}$ as determined in Refs. [45, 140]. Increase in the basal pole component normal to the crack plane was correlated with a decreasing $K_{IH}$ in rolled Zr-2.5 wt% Nb plate as shown in Fig. 4.10. The explanation for this lies in the fact that in a grain with a basal component in the crack plane normal, the preferred orientation of the hydrides would be directly oriented with the
Figure 4.8: SEM image of the DHC fracture surface between two striations showing characteristic features. 'S' is a striation, 'CF' is a crystallographic facet characteristic of brittle hydride fracture, 'NCF' is non-descript cleavage facet possibly resulting from decohesion in the hydride matrix interface of hydride β-phase interface, 'D' are plastic dimples formed by plasticity at the striation [138].
Figure 4.9: Schematic description of the formation of characteristic DHC fracture surface. (a) and (b) represent the fracture before and after the formation of one striation or crack step [139].
tensile stress at the crack tip as opposed to crack tip hydride clusters forming with the hydride platelets at angles offset to the cracking plane as shown in Fig. 4.11. Therefore, either a smaller crack tip hydride would be required for DHC propagation or the ease with which a crack tip hydride reorients would be increased, resulting in a lower required stress gradient. Similar conclusions were reached by Shek [45] from his experiments on crack plane orientation effects and Kim [141] from similar experiments.

4.4.4.2 Thermal Manoeuvres

Temperature and the thermal manoeuvres affect both the concentration and supersaturation of hydrogen in solution as described in Sec. 2.2.1. Two different effects are described, the first being measurements of $K_{IH}$ purely as a function of test temperature independent of different hydrogen supersaturation levels. This was completed by Shek [45] where he measured $K_{IH}$ upon cooling from a temperature well above that corresponding to the TSSP of the test temperature (tests were run with the maximum possible hydrogen supersaturation at the test temperature) and limiting the highest test temperature to one below the TSSP of the hydrogen content in the sample. The results are shown in Fig. 4.12 and it is demonstrated that $K_{IH}$ increases with increasing temperature. Shek suggest that this trend is likely due to a combination of factors. First, due to the lowered yield stress ($\sigma_{ys}$) at elevated temperatures, the normal stress at the crack tip will be lowered as it is a function of $\sigma_{ys}$. Secondly, creep relaxation at the crack tip could also relax the normal crack tip stresses and require a higher stress intensity to provide the conditions for hydride formation. The
Figure 4.10: Dependency of $K_{IH}$ on crystallographic texture. Lower $K_{IH}$ values are correlated with a high component of basal plane normals in the crack plane [140].
Figure 4.11: A cluster of fractured crack tip hydrides with the crystallographic texture oriented diagonal to the crack plane. Notice the hydrides still form oriented to the texture. [45]
other consideration is total hydrogen in solution and the TSSP at different test temperatures will be different under similar supersaturation conditions. Consequently, unless these shift proportionately at different temperatures, there is likely a further contribution. However, this was not confirmed.

![Dependency of $K_{IH}$ on temperature, from [45]. Square and star represent ascending temperature test, triangles are decending temperature test.](image)

**Figure 4.12:** Dependency of $K_{IH}$ on temperature, from [45]. Square and star represent ascending temperature test, triangles are decending temperature test.

The effect of hydrogen supersaturation on $K_{IH}$ was also studied by Shek in Ref. [45] by measuring the critical stress intensity to initiate cracking under thermal cycles from different 'peak' temperatures to the same test temperature. Shek was able to conclude that $K_{IH}$ increases with decreasing amounts of supersaturation, as shown in Fig. 4.13. Shek cites two different extremes for $K_{IH}$. In the case of high
supersaturation, where the bulk hydrogen content is close to the TSSP at the testing temperature (characteristic of DHC upon cooling from a high test temperature), only a slight increase in load is required to precipitate a hydride at the crack tip, and although the local stress field around the crack tip will relax, it won’t be enough to prevent further migration of hydrogen to the crack tip. Consequently, $K_{IH}$ represents the condition where the applied stress is just not enough to fracture the hydride at the crack tip, i.e. that hydride growth is not the crack growth limiting factor. Alternatively, under low hydrogen supersaturation, such as DHC upon heating (heating from A to B, where B is the test temperature, in Fig. 2.2), a significant stress will be required to shift the solvus from the hydrogen concentration near TSSD all the way to TSSP and hence precipitate a hydride at the crack tip. Under these conditions, the hydride may only be able to form in a localised area, and subsequent stress relaxation around the crack tip may be enough to prevent further hydride precipitation at the crack tip. Therefore, $K_{IH}$ at low hydrogen supersaturation is more a function of having a high enough stress to promote significant hydride growth. These inferences were made by Shek [45] and are supported by his experimental observations of the critical crack tip hydrides. Crack tip hydrides under high supersaturation are generally large hydride clusters and consequently, $K_{IH}$ is not growth dependent (see Fig. 4.14(a) while crack tip hydrides under low supersaturation tend to be very narrow, resulting in a growth dependant hydride; shown in Fig. 4.14(b).

### 4.4.4.3 Loading Manoeuvres

Since the driving force for hydrogen diffusion is the change in the chemical potential of hydrogen as a result of the stress gradient between a stress concentration and the
**Figure 4.13:** Dependency $K_{IH}$ on hydrogen supersaturation, from [45]
Figure 4.14: Crack tip hydrides observed by Shek [45] under high and low hydrogen supersaturation
unstressed bulk, any unusual stresses at the crack tip can shift the chemical potential gradient. Consequently, if a sample is loaded to a high stress intensity, then unloaded and subject to an increasing load $K_{IH}$ test, the measurement would have a tendency to overpredict $K_{IH}$ due to the significant residual compressive stresses at the crack tip. Therefore, there are two different $K_{IH}$ measurements: one where $K_{IH}$ is measured by increasing the load from a low load until cracking initiates and another where load is subsequently decreased from a load where cracking is well established until it ceases. The load increasing mode generally requires a fatigue crack that had the last section grown at or below the expected $K_{IH}$ measurement, and hence would be representative of the applied stress field only. Load decreasing mode is likely of more interest to reactor operators due to the fact that it is more realistic to have some crack blunting going from reactor operating conditions to a condition that would be susceptible to DHC, and produces a lower bound measure due to the fact that DHC is initiating from an already hydrided crack tip. Load decreasing mode does have two experimental difficulties. First, there is a possibility of cracking all the way through the sample due to the fact that crack growth will occur at all test loads before arrest. Secondly, subsequent attempts at understanding the crack tip stress state and relating it to the critical condition for crack growth leaves experimenters with an additional factor (residual stress) to consider.

Work by Kim [99] has characterised the physical differences between $K_{IH}$ measured with both increasing and decreasing loading modes and with different fatigue crack stresses. He observed that increased fatigue crack stresses before testing resulted in slightly higher $K_{IH}$ values, especially in load increasing mode and that $K_{IH}$
measured in load decreasing mode produced consistently lower $K_{IH}$ values. This inference is supported by calculations by Shek and Graham [142] on the effect of loading a crack to a high load, unloading and subsequent intermediate loading, possessing lower crack tip stress. Kim attributes the lower $K_{IH}$ values in load decreasing mode to the presence of a ‘sharper’ crack in load decreasing mode and the suggestion that creep relaxation only occurs in load increasing mode. Although Kim’s measurements are likely correct, one can argue with his interpretation. It is more probable that the decreased $K_{IH}$ from load decreasing mode is due to the fact that the energy barrier to initiate DHC when a crack tip hydride does not exist is higher than that to stop an already growing hydride (see Sec. 2.2). A growing crack’s measure of sharpness is characteristic of the highest applied stress intensity factor it experiences, not necessarily the mechanism by which it was formed. A DHC crack at $K_I=9MPa\sqrt{m}$ will have a higher amount of crack blunting than a fatigue crack grown at a highest $K_I=6MPa\sqrt{m}$, which is contrary to what Kim suggests. In addition, creep relaxation at the crack tip is no less likely to occur in load decreasing mode than in load increasing mode (Shek describes a length scale of minutes for this to occur [45]). This means creep relaxation is not expected to affect load increasing mode differently from load decreasing mode because of the fact that similar amounts will occur in both.

4.4.4.4 Irradiation and Yield Stress

The effect of irradiation on $K_{IH}$ has only been studied by Sagat et. al [143] by comparing measurements from irradiated pressure tubes and their offcuts. $K_{IH}$ was shown to slightly decrease with irradiation. The reason for this is likely due to the material hardening from irradiation damage, hence affecting the crack tip stress field.
A similar effect is expected from increased yield stress due to cold work. These conclusions come from experimental measurements of a critical hydride lengths, with longer critical hydrides observed at higher temperatures (lower $\sigma_{ys}$) and lower stress intensities due to plastic crack tip hydride mechanics in Ref. [69,98,144].

4.5 DHC Velocity

4.5.1 $DHC_v$

The measurement of the velocity of a DHC crack, or $DHC_v$, can offer inferences into the mechanism of DHC and is one of the most commonly studied DHC parameters. Measurements in the literature have been done with several methods, each with different interpretations. Perhaps the most commonly used and most robust method is to grow a DHC crack at a certain load, and monitor when cracking occurs with either potential drop or acoustic emission methods. Following the test the sample is removed, may be heated to oxidise the surface, and broken open with a fatigue crack, and the DHC crack is measured by examining the oxidised surface. The crack velocity is then measured by dividing the amount of crack growth during the cracking time. This is the method that was recommended for use in an International Atomic Energy Association round robin report on DHC velocity [131,145]. While this method is very robust and indicates definitive cracking velocities, it unfortunately is still an average crack velocity over the range of stress intensities developed by the constant load condition (increasing $K_I$). Additionally, crack velocity measurements are often limited to one or two per sample due to the requirement of differentiating every single crack segment. Other methods attempt to evaluate the crack velocity directly from
the potential drop signal or acoustic emission output. Where these methods are likely less accurate due to uncertainties in the crack length measurements, they allow the measurement of crack velocity several times on the same sample.

4.5.2 Experimental Observations of $DHC_v$

4.5.2.1 Stress Intensity Effects

There is a distinct effect of applied stress intensity at the notch tip on the propagation rate of a DHC crack in zirconium alloys. In general, only mode I cracks appear susceptible to DHC because of the tensile stress at the stress raiser resulting in the precipitation of hydrides oriented within the crack plane. Cracking will not occur below a certain applied stress intensity known as $K_{IH}$ (see Sec. 4.4.2). Increasing the applied stress intensity past this point shows three distinct stages of DHC cracking velocity. Stress intensities larger than $K_{IH}$ are associated with an increase in $DHC_v$ (stage I crack growth) followed by a region where the $DHC_v$ is independent of applied stress intensity (stage II crack growth, hereon referred to as terminal cracking velocity $DHC_{vt}$) followed by a point where the critical stress intensity factor $K_{IC}$ of the zirconium matrix is approached and the material critically fractures (stage III crack growth). This behaviour is shown graphically in Fig. 4.15. Measurements of how abruptly the $DHC_v$ approaches the terminal $DHC_{vt}$ as a function of stress intensity are unclear at best in the literature, likely due to the variability in cracking variables such as $Heq$, yield strength and hydrogen supersaturation. The 'knee' appears to happen over 1-4 MPa$\sqrt{m}$ past $K_{IH}$ in the literature [133] and in the current work Sec. 5.4. Explanation of this behaviour requires (i) a description of why increasing $K_I$ results in an increase in $DHC_v$ for stress intensities immediately above $K_{IH}$ and
Figure 4.15: Dependency of DHC velocity on applied stress intensity factor $K$ [133]
(ii) why $DHC_v$ is independent of $K_I$ past a certain stress intensity. An interpretation of why increasing stress intensity leads to increased crack velocity can be made in terms of an increase in the rate of formation of crack tip hydride. This understanding was developed in attempt to describe the criterion for hydride formation and fracture at crack tips. This dependency was originally considered by Gerberich in Ref. [146], noting that in steels, stage I crack growth was primarily influenced by the elastic stress field around the crack tip, and that stage II crack growth was more influenced by the plastic stress (yield stress). Later when Dutton et. al were developing the first DHC models in Ref. [95], they further developed some of these ideas by suggesting that in stage II crack growth, all hydride growth was occurring in the plastic zone at the crack tip, and consequently, the driving force for hydrogen accumulation is due to the stress in the yielded material, which \textit{does not} change with increasing $K$, or functionally, the yield stress. Therefore, stage II crack growth rates can be referred to the terminal cracking velocity, or $DHC_{vt}$, which is dependant on the material and hydrogen diffusion properties. Within the stage I crack growth, the stress was considered not to be high enough to fracture the hydride without hydride extension through the plastic zone, and consequently, the elastic stress past the plastic zone would change with change in $K_I$ and consequently, the hydrogen diffusion driving force would be different. This inference is further developed by measurements of the critical hydride sizes for DHC growth and was completed in papers by Shek [104] and Yan et al. [147]. Shek correlated each cracking step with a striation formation on the crack surface and that each striation was similar to the size of a critical hydride. He was able to conclude that increasing $K_I$ resulted in decreasing striation lengths. Yan did a more complete study on the stress dependency of hydride lengths above and
below $K_{IH}$ showing that hydride lengths increased up to $K_{IH}$ (growth controlled) and then decreased past that point and eventually leveled out (fracture controlled), which is consistent with the hypothesis in work by Dutton et. al [95]. They later developed their model [148] to account for a range of temperatures and to relate crack velocity measurements and striation lengths in experimental work with the stage II growth accounted for by indicating a critical hydride size dependant on material properties. Later, this was studied by Kim and Park [133], who produced similar results, but came to a slightly different conclusion.

4.5.2.2 Thermal Manoeuvres

Crack velocity is heavily influenced by temperature as well as the thermal history of the sample. Primarily, four factors are of interest and controlled by the immediate thermal history of the sample: the concentration of hydrogen in solution, the amount of hydrogen supersaturation, diffusion coefficient of hydrogen in zirconium (increasing with temperature) and yield stress (decreasing with temperature) of the zirconium matrix. Unfortunately many of these parameters overlap and direct differentiation is often difficult. Although initially hydrogen supersaturation, or the concentration of hydrogen in solution in excess of the TSSD, was studied almost unknowingly with several studies, the first concise study was completed by Shek [45]. Supersaturation, which was previously discussed in Sec. 2.2.1, is changed by modifying the ‘peak’ temperature that a sample is cooled from in a thermal cycle. Higher supersaturation was shown to produce crack velocities 3-5 times higher than in conditions with lower hydrogen supersaturation up to approximately 50% of the maximum supersaturation.
The obvious conclusion is that increased amounts of hydrogen in solution is associated with increased crack velocities because of the improved ability of hydrogen to diffuse to the crack tip. However this effect must be differentiated from purely the amount of hydrogen in solution. In order for crack growth to occur, the applied stress must shift the solubility at the crack tip to something past the TSSP (Sec. 4.3). If chemical potential between the bulk and the crack tip is only enough to just lower the crack tip solubility to the TSSP, then hydrogen diffusion towards the crack tip will only occur at a very slow rate. However, if chemical potential difference is significant, the hydrogen flux will be high. First, any situation with a greater driving force for hydrogen accumulation to the crack tip will have a greater cracking velocity due to the requirement of continued fracture of crack tip hydrides for crack growth. However, the rate of accumulation has actually been shown to change the critical crack tip hydride size and shape. At conditions where the crack tip solubility is shifted well past the TSSP and the chemical potential is high, precipitation of hydrides in a large area around the crack tip is possible (Fig. 4.14(a)) and each hydride fracture results in a larger jump in crack length. Under conditions where crack tip hydrides are formed under low supersaturation where the hydride growth is otherwise restricted to a very local high stress region Fig. 4.14(b) [45,104]. However the effect of this depends on criteria for hydride fracture which is presently debatable due to the fact that varied striation lengths are observed at otherwise identical cracking conditions [104]. Consequently, the thermal history of the sample has a significant effect on cracking behaviour and even though certain conditions could have the same amount of hydrogen in solution, they may not have the same cracking behaviour due to the effective
solubility differences between the bulk and crack tip. Regardless, both increased hydrogen in solution and increased hydrogen supersaturation are associated with higher crack growth rates.

4.5.2.3 Texture Effects

Crack velocity has been measured to increase with increased proportion of basal planes parallel to the crack plane [140]. This is because the hydride habit plane is the basal plane of $\alpha$-zirconium grains (see Fig. 4.11). Consequently, in samples with increasing deviance between the crack plane and the basal plane of the matrix, the hydrided region needs more hydride precipitated to produce a crack the same step length, and consequently, the crack velocity decreases. The texture can also directly affect the diffusivity of hydrogen towards the stress raiser due to anisotropy of the diffusion coefficients, the effect of which is not exactly clear due to the fact that it is not implicitly clear where hydrogen is predominantly diffusing from. The other consideration concerning textural effects on the crack velocity is that the stress gradient under terminal velocity conditions is a function of the yield stress. The yield stress in sample orientation with the crack plane parallel to a direction of high basal texture is higher than that of one with low basal texture Table 3.1. Therefore, under conditions where the main stress is oriented more towards a plane with a high basal texture, a greater crack velocity due to the elevated stress gradient will be observed [140].
4.5.2.4 Microstructural and Yield Stress Effects

Microstructure can affect the crack velocity based upon both changes in the diffusion of hydrogen in the material, and to microstructural differences in the crack tip hydrided region affecting the hydride morphology and yielding behaviour. Although the latter effect is difficult to describe, progress has been made in identifying some of the potential effects of microstructure on the diffusion of hydrogen. Both the diffusivity and solubility of hydrogen in $\beta$-zirconium is greater than that in $\alpha$-zirconium and consequently, $\alpha/\beta$ morphology has an effect on the ability of hydrogen to get to the crack tip. The first observations of this were made by Kim et al [140], where it was shown that samples with a decomposed $\beta$ phase experienced lower crack growth rates than samples with more continuous $\beta$ distributions. This effect is however also linked to decreased yield stress. Yield strength affects crack velocity primarily due to the fact that the magnitude of the chemical potential under terminal velocity conditions is a function of the yield strength. These effects were separated in a study by Mieza et al. [69] where they determined that hydrogen diffusion affected crack velocity more than the yield stress.

4.5.3 DHC Susceptibility

4.5.3.1 Modelling efforts

There has been considerable effort to properly model DHC over the past few decades including attempts to understand the thermodynamic basis, prediction of crack velocities, predict crack initiation, model conditions for hydride fracture and more [48,49,69,96,101,103,113,123,124,126,128,129,137,144,147,149–151]. Ultimately, the
main intent is understanding the contribution of every metallurgical and test condition to the initiation and growth rates of cracks. Probably the most useful theoretical models are those based upon the thermodynamic basis for DHC, due to the fact that they can explain and predict the main DHC behaviour characteristics including susceptibility to crack growth, crack tip hydride morphology and crack velocities.

4.5.4 Dutton-Puls Model

The original thermodynamic based model of DHC was initially developed by a group [94,95] at Atomic Energy of Canada Limited Whiteshell Laboratories in the late 1970’s in response to some of the DHC pressure tube failures that had occurred earlier in the Pickering reactors. This model has been subsequently developed and improved over the past few decades and has culminated in a recent (2009) review paper by one of the original DHC paper contributes, M.P Puls [48]. This review corrects sign convention considerations from previous publications and accounts for updates to the present stage of development and is at present the most complete description of this model. At present it is the most commonly accepted and cited model and is the theoretical basis for many of the DHC assessments described in Sec. 4.2. However, although the model does successfully describe the essential elements of experimental DHC behaviour, the model is still, as admitted by the authors, not fully developed and further development is required. In particular, much of the model relies upon conservative analysis and/or idealized conditions. This original model, herein referred to as the Puls Model due to Puls continued development of it over the past few decades, describes the driving force for hydrogen diffusion and precipitation at a stress riser to be based upon the chemical potential described in Sec. 4.3.1. It relates this
chemical potential to a hydrogen flux towards the stress raiser, and based upon the amount of hydrogen in a ‘critical’ hydride, evaluates a crack velocity. Consequently, this is described as a steady state model, and is primarily useful to evaluate if DHC will occur under certain conditions, and the magnitude of the velocity. In addition, it can aid attempts to understand the factors that affect DHC. The Puls model is used to simulate some aspects of the experimental work in the next chapter, and consequently, Sec. B.3 contains a fully worked interpretation of the Puls model using values commonly used in the literature.

4.5.5 Kim Model

A more recent DHC model has been proposed by Korean researchers Kim et al., who note several shortcomings in the Dutton-Puls model [96, 125, 126, 129, 133, 137, 152]. They claim that the Dutton-Puls model cannot predict the following:

- Why DHC velocity becomes constant regardless of the applied stress intensity factor even though the stress gradient is affected by the stress at the notch tip.
- Why the DHC velocity has a strong dependency on the way the test temperature is approached (by cooling or heating)
- It cannot predict any far field hydride size effect on the DHC velocity

In summary, Kim suggests that the loading of the crack results in the precipitation of a crack tip hydride, resulting in a concentration gradient of hydrogen which then drives diffusion towards the crack tip. However, according to both Puls [48, 49] and McRae [113] et al., this model is physically flawed and therefore not considered in any further analysis in this thesis. The shortcomings suggested by Kim were satisfactorily covered in publications by both Puls in Ref. [48] and [49] in addition to an alternate
approach by McRae et al. in Ref. [113].

### 4.5.6 McRae Approach

A recent publication by McRae et al. [113] takes a similar approach to modelling DHC steady state crack growth to that of Puls in Ref. [48, 49]. There are however several distinctions between the McRae et al. and Puls approaches. First, McRae makes no attempt to model the solubility of hydrogen beyond the established TSSD/TSSP curves; the concentration of hydrogen in solution and TSSP at a given temperature are the two inputs for the model. Secondly, since the McRae et al approach is based upon the concentration of hydrogen in solution, the dissolution behaviour of bulk hydrides accounted for in Puls approach is not required. Finally, McRae et al. formulate the chemical potential in a different manner than Puls. They do not attempt to model the chemical potential based upon the interaction energies (which requires a stress free formation strain) formulated by Puls, but instead rely purely upon the effect of the hydrostatic stress gradient on the equilibrium hydrogen concentration. In short, the McRae et al. approach appears to be an attempt to eliminate many of the complicating terms in Puls model, which in contrast can be considered an attempt to account for absolutely everything, without physical evidence of how important a given term actually is. By accounting for only hydrogen solubilities and the hydrostatic stress gradient description, similar DHC prediction capabilities have been demonstrated with McRae’s approach as by Puls. Consequently, although the Puls model does contain terms that are physically correct, some terms seem to have little effect within the current experimental range.
4.6 General Discussion and Experimental/Model Shortcomings

4.6.1 Critical Temperatures for DHC

A critical temperature for DHC is a temperature in which DHC behaviour changes significantly, such as crack arrest upon heating or that which it starts at upon cooling. Understanding of the critical temperatures is of significant interest for both reactor operations considerations as well as validations of inferences regarding the DHC mechanism because it provides a distinct and measurable test condition. The following inferences are made with reference to the TSSD/TSSP curves plotted in Fig. 2.2.

- Significant DHC will not occur at an extremely low temperature, such as room temperature due to the low concentration of hydrogen in solution and lowered diffusivity of hydrogen. DHC under these conditions would be very slow and require a very large stress gradient in order to be possible.

- DHC will not occur at a temperature well above the TSSD solvus of the test sample due to the fact that the TSSP solvus at the crack tip is not low enough for a precipitation event, even with the effective lowering of TSSP by the applied stress.

Consequently, there are essentially two conditions that need to be satisfied: There must be enough hydrogen in solution and it must be possible to reach TSSP at the crack tip due to the chemical potential variation resulting from the stress gradient.
Studies by Ambler and Coleman [153] first showed that cracking behaviour was different depending upon the direction of approach to the test temperature. Test temperatures approached by heating had incubation times that decreased up to 150°C and then increased past that point in contrast to cracking upon cooling, which always decreased past 150°C. In addition, cracking above 250°C upon heating was arrested and only returnable by a thermal cycle consisting of heating to a higher temperature followed by cooling back down. Nuttall [154] also investigated the effect of thermal cycling on DHC behaviour and showed that crack growth rates during cooling were higher than the equivalent isothermal (heated to the test temperature) rates. Ultimately it was proven that the concentration of hydrogen in solution was significantly affected due to the fact that the solubilities of dissolving and precipitating hydrides are significantly different [118], as later developed by Puls [41, 43, 48].

Of major interest is the existence of a 'crack arrest temperature’, which is a temperature above which DHC can not occur. For DHC upon cooling from a high enough temperature, since the bulk solubility will always be the same as the crack tip TSSP, crack arrest will only occur when the hydrogen content in the sample is near the TSSP and crack arrest occurs because of the elevated solubility of hydrogen at that temperature (ie. no precipitates form regardless of how strong the chemical potential gradient is). In contrast, for DHC upon heating, where the concentration of hydrogen in solution is much lower than at the crack tip, arrest occurs when the gap between the concentration of hydrogen in solution and the precipitation solvus is larger than the chemical potential difference from the stress gradient (chemical potential, dependent on yield stress). Some authors have suggested that based upon the present theoretical approach (including present postulations of solubility curves
and stress gradient), DHC is not even possible upon heating [45]. Consequently, it is suggested that there may actually be several insufficiently modeled aspects of DHC, in particular the real life representation of hydrogen diffusion in the stress gradient, effect of bulk hydride phase, and hydride phase and morphology at the crack tip.

4.6.2 Model Shortcomings

Although numerous papers have successfully modeled crack velocities and crack arrest behaviour using the Puls model, there remain several considerations that need to be made. First, due to the fact that there are a large number of terms in the Puls approach, and that several of these values are ambiguously or inadequately measured or assumed means that the model predictions are somewhat ‘tunable’ to match experimental results. Basically, although the physical logic behind the model is completely sound, the estimates and measurements of the several internal parameters are varied to fit a particular data set. In particular, the ‘stress free solvus’, the accommodation energy, the interaction energy (uncertainties of which are compounded by estimates of the stresses and stress-free transformation strains) and the criteria for hydride fracture are all subject to interpretation which can drastically shift the output of the DHC models prediction of crack velocity and description of when cracking will and will not occur (see Sec. B.3 and Sec. 5.5.4). Consequently, since the McRae approach utilizes far fewer variables, it may suggest that several of the considerations that the Puls approach uses may be unnecessary for reliable prediction of DHC. It also suggests that a reliable quantitative determination of the stress induced chemical potential is not available.
Ultimately, although these models can predict DHC behaviour, the correct accounting for every term is subject to interpretation, and consequently, there are considerable uncertainties on the conditions for DHC and crack velocities based upon a purely theoretical approach. This is discussed further in Chap. 6.
Chapter 5

Effect of Bulk Hydrides on DHC

"Sir, the possibility of successfully navigating an asteroid field is approximately 3,720 to 1."

— C-3PO

5.1 Introduction

It was pointed out by Shek [45] that DHC can occur at low temperatures ( \(< 200 \, ^{\circ}\mathrm{C}\) when the test temperature is approached by heating, even though the current hydride solubility equations indicate that this is not possible. This suggests that either the DHC mechanism is different at low temperatures or the extrapolation of TSS equations at lower temperatures is not correct. The suggestion that DHC at low temperatures may be different is based upon some conflicting evidence that some authors have reported showing that \(\gamma\)-hydride may be the stable hydride phase at lower temperatures [22, 129] (see Chap. 3), and consequently hydride dissolution in the bulk or precipitation at the crack tip may be different. This could allow DHC
to occur under conditions where it is otherwise not theoretically possible based upon current formulations.

The purpose of this study is primarily to observe and verify suggested mechanisms for low temperature DHC upon heating, as this is an area of the literature that has seen limited experimental work. The majority of studies characterise DHC upon cooling from elevated temperatures (where additional hydrogen is in solution due to the pronounced TSSD/TSSP hysteresis, described previously in Sec. 2.2), as that is usually the situation that occurs during reactor operation. DHC is primarily controlled by the ability of hydrogen to diffuse towards a stress raiser. Consequently, both the concentration of hydrogen in solution, the precipitation solvus, and the chemical potential of hydrogen due to the stress gradient between the bulk and the crack tip directly affect cracking behaviour. During DHC upon cooling the concentration of hydrogen in solution is given by the TSSP curve, provided the material was heated to a high enough temperature in the preceding thermal cycle. Precipitation of a crack tip hydride therefore only requires a very small stress induced chemical potential to drive hydrogen diffusion. In DHC upon heating, the concentration of hydrogen in solution is given by the dissolution solvus TSSD, which is much lower than the TSSP. Therefore, the hydrogen stress gradient governing hydrogen diffusion to the crack tip should only cause DHC to the extent that it shifts the effective solubility at the crack tip past the TSSP. The preceding describes the general differences between DHC upon heating and cooling. However, there remains several aspects of DHC upon heating that are currently not fully developed.

Further explanation of DHC upon heating requires understanding of the physical nature of zirconium hydrides. It is well understood that zirconium hydrides are
heavily constrained inclusions due to the misfit strains required for their precipitation [51,77]; stresses can be hundreds of MPa [70] and the plastic deformation required for their accommodation is considered the main reason for the TSSD/TSSP hysteresis (Sec. 2.2). Of most importance to DHC upon heating is the nature of the dissolution behaviour of the zirconium hydrides. Two main considerations are made. First, it is not well understood which factors control the natural unstressed dissolution behaviour of zirconium hydride. Secondly, it is not directly understood if there is an added effect concerning the ability of additional hydrogen to dissolve from a bulk hydride to replace that precipitating elsewhere in the material in a chemical potential. Since the physical and chemical constraints on a dissolving hydride should affect the amount of hydrogen dissolving from it, different bulk hydrides (either morphology, phase, or stress state) would be expected to have different dissolution behaviour, while precipitation behaviour for the new crack tip hydride for the same material should be similar. Thus, DHC upon heating tests with different bulk hydrides should result in different DHC behaviours that can be correlated with their dissolution behaviours. Thus a more fundamental understanding of both the DHC mechanism, and expected cracking behaviour during heat-up may therefore be possible. Such a test could also provide an addition data set to evaluate presently contested DHC models.

The steady state DHC thermodynamical models that have been developed over the past few decades rely upon the quantification of hydrogen diffusion from the bulk or dissolving hydrides towards a precipitating crack tip hydride. Eq. 5.1 (or Eq. B.8 for more detail) shows a general model of DHC used by numerous authors but initially developed by AECL researchers between the 1970’s and 1990’s [95] and subsequently in references [32, 41, 43, 118, 154–156] to account for experimental observations and
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completely reviewed in Ref. [48, 49] (see Sec. 4.5.4 and Sec. B.3).

\[ DHC_v(T) = C(T)\{E_L - E_\ell\} \]  \hspace{1cm} (5.1)

where \( C(T) \) is representative of some properties of hydrogen and hydrides in zirconium at temperature \( T \), and \( E_L \) and \( E_\ell \) are a representations of the equilibrium solubilities at the dissolving far-field and precipitating crack tip hydride respectively affected by the stress induced chemical potential such that

\[ E_x = C_s \times \exp^{-\overline{w}_a/RT} \times \exp^{-\overline{w}_{inc}/RT} \]  \hspace{1cm} (5.2)

where \( C_s \) is the stress free solvus shifted by \( \overline{w}_{inc} \), the accommodation energy characteristic of either the precipitation or dissolution of a hydride, and \( \overline{w}_a \), the interaction energy of hydrogen evaluated either away from the crack tip at location \( x=L \) or near the precipitating hydride at \( x=\ell \). A more detailed description of these terms is located in Sec. B.3. Alternatively:

\[ E = TSS \times \exp^{-\overline{w}_{inc}/RT} \]  \hspace{1cm} (5.3)

here the exponential term incorporating the accommodation energy \( \overline{w}_{inc} \) and the stress free solvus is replaced by either the TSSP for the \( E_\ell \) term or the concentration of dissolved hydrogen for the bulk \( E_L \) term. For DHC upon heating, this is the TSSD for a given hydride population and for DHC upon cooling, this will be the TSSP. Thus, if \( E_L > E_\ell \), then the the bracketed term in Eq. 5.1 will be positive, and be scaled from the effective equilibrium solubility difference into a crack velocity while if negative,
then the crack velocity is zero since there will be no hydrogen accumulation at the
-crack tip. Each solubility term is not a direct scaling of the real hydrogen solvus,
but the *effective* solubility as a result of the nature of the hydride (precipitating or
dissolving) and the effects of the applied stress on the chemical potential of hydrogen.

A hydride in the bulk is dissolving during DHC, and is therefore subject to a solubility
characteristic of the dissolving bulk hydride. Consequently, at a stress riser such as
a sharp crack, the solubility will be that of a *precipitating* hydride, which will be
higher than the bulk dissolving hydride due to irrecoverable plastic work that exists
in precipitation and not dissolution. For example, for DHC reached upon heating to
the test temperature, the solubility in the bulk at the dissolving hydrides is lower
than that required to precipitate hydrides at the crack tip (the equivalent TSSP).

When a sufficient stress gradient is applied the chemical potential of hydrogen is
lowered at the crack tip, and consequently, the equilibrium solubility at the crack tip
is decreased, possibly below the TSSP, resulting in hydride precipitation and a net flux
of hydrogen towards the stress raiser. Models attempt to describe DHC behaviour
as best as possible, but some of the terms in their descriptions can be subject to
interpretation. Determination of the relative contributions of both the dissolution
solvus (as a function of the prior thermomechanical processing of the material, ie.
alterations to $w_{inc}$) and the ability of hydrogen to diffuse from the hydride source
due to the chemical potential (bulk hydrides, ie. interaction energy $w_a$) is required to
further understand the DHC mechanism. This is possible through the study of DHC
at low temperatures as it provides the conditions for a significant amount of hydride
to exist in the bulk precipitates. In addition, approaching the test temperature by
heating also provides a wide scope to investigate this behaviour as it allows DHC to
be observed with different bulk hydrides, which is not possible after high temperature dwells or a thermal cycle.

A study by Ambler [157] used modifications to the commonly used Dutton-Puls DHC model in an attempt to study the effects of hydride morphology, hydrogen content and the direction of approach to temperature effects in Zr-2.5 Nb pressure tube. In Ambler’s study, samples with hydride populations containing slow cooled or ice-quenched hydride populations were tested upon heating and cooling, with the ice-quenched hydrides expected to be of the $\gamma$ phase and in a very fine distribution in contrast to the coarse furnace cooled $\delta$ phase hydrides. Ambler was able to show that samples heated to the test temperature showed the same increase in crack velocity as those cooled to the test temperature, but only up to a certain temperature that was subject to the hydride heat treatment. More importantly, Ambler was able to apply the suggested effects of bulk and crack tip hydride constraint on the TSSD/TSSP hysteresis suggested by Puls [32] to predict the differences in DHC behaviour. $\bar{w}_{inc}$ terms for both naturally oriented $\delta$ platelets, $\gamma$ needles as well as reoriented (radial axial) hydride plates are discussed as causing different DHC behaviour as a result of shifts in the effective solvus upon heating, but this is not directly measured. Although significantly different isothermal crack velocities are not observed in the Ambler study between the varied hydride populations upon heating, limited data was present in the temperature range where $\gamma$ hydride is expected to be present. Much of the analysis is instead centered around a temperature known as the crack arrest temperature, $T_{arr}$, above which DHC is not possible. Theoretically determined $\bar{w}_{inc}$ terms are suggested for both the ice quenched and furnace cooled samples based upon these measurements in order to match the experimental data. The arrest temperature upon heating is

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representative of the temperature where the applied stress is not great enough to set up a sufficient difference in the crack tip and bulk solubilities. However, through much speculation regarding the observed behaviour including conformation that the prior thermal history of the material can significantly affect DHC, the reasoning is not fully developed and more work can be done to better illustrate the observed mechanisms. Shi et. al demonstrated that the TSSP could be significantly varied depending on the thermal history, with TSSP values decreasing with higher annealing temperatures in the most recent thermal cycle [33]. Shek and Graham [142] confirmed that increasing peak temperature that a DHC sample was cooled from was directly correlated with increased crack velocities as a result of the increased hydrogen supersaturation. Shi et. al [134] identified the temperatures that cracking initiated upon cooling from above the solvus, and the arrest temperature upon heating from that point, both of which are below the temperatures assumed to be the TSSD for those conditions. They also suggest a mechanism for low temperature crack growth where the balance between the TSSD of the bulk hydrides, TSSP of a precipitating hydride and the hydrostatic stress at the crack tip governs crack growth. Shek later suggests in Ref. [45] that the reason DHC is not predicted upon heating may be due to the fact that TSSD curves extrapolated to lower temperatures may not be representative of the real hydride dissolution behaviour at lower temperatures. Later, Kim et. al have presented several papers suggesting alternative mechanisms for low temperature DHC and the crack arrest temperature upon heating. Kim et al. [158] indicates that DHC upon heating is possible at low temperatures as a result of a stress-induced transformation from $\gamma$ hydride to $\delta$ hydride based upon the observation that the DHC arrest temperature in slow cooled samples was near the reported $\gamma \rightarrow \delta$ phase boundary. This was also
It has been demonstrated that the amount of hydrogen in solution can significantly affect cracking behaviour including arrest temperature $T_{arr}$, crack incubation time, cracking velocity $DHC_v$ and the occupance of DHC and is known to be shifted based upon the thermal history of the specimen. Therefore, if the dissolution behaviour of certain bulk hydrides can be related to DHC behaviour, the understanding of DHC mechanisms could be improved. Therefore, in the present work, DHC is tested primarily with hydride distributions produced under four test conditions:

1. Coarse slow cooled hydride platelets known to be $\delta$ fcc phase tested upon heating to the test temperature.

2. Fine ice brine quenched hydride needles known to be $\gamma$ fct phase at room temperature and transforming to $\delta$ upon heating to temperatures over 100 deg. C tested upon heating to the test temperature.

3. Coarse hydrides slow cooled under an applied hoop stress known to orient the hydride platelet normals in the axial-radial plane tested upon heating to the test temperature.

4. Samples the same as in (1) that were cooled to the test temperature under maximum hydrogen supersaturation conditions.

All three hydride samples tested upon heating should have different accommodation energies ($w_{inc}$) and may have different effects on the interaction energies $w_a$ under DHC conditions. The study of DHC behaviour in these samples at low test temperatures ($< 200\,^\circ$C) provides a forum to examine the effects of different bulk hydrides on DHC.
5.2 Materials and Samples

In order to study the effects of different bulk hydride phases on DHC appropriate samples were created. Material taken from Zr-2.5 wt% pressure tube CC097-89 (described previously in Sec. 3.2.1.3) was electrolytically hydrided to nominal 100 ppm H at Chalk River Laboratories in a rig similar to the one described in Sec. 3.2.2 but designed to hydride full pressure tube ring sections. Samples were then machined into two different sample geometries for measuring DHC in both axial and radial pressure tube directions. In the present work, a sample referred to as an axial sample means that the crack growth occurs in the axial direction with the crack plane being the axial-radial plane as shown in Fig. 5.1. A sample referred to as a radial sample has crack growth in the radial direction with the crack plane also in the axial-radial plane as shown in Fig. 5.2. It is of most interest to industry to study these two cracking directions as the direction of highest applied stress in an operating pressure tube is in the hoop direction, and therefore the radial-axial plane is the most susceptible to DHC. In addition, there are notable differences in the crack path through the microstructure between the radial and axial cracking directions, which can affect DHC.

5.2.1 Sample Geometries

Two different sample geometries were used in order to measure DHC properties in the axial and radial pressure tube directions. Nearly all previous axial DHC experiments on Zr-2.5 wt% Nb pressure tube material have used 1 of 3 different sample geometries: a Curved Compact Toughness sample (CCT), a mechanically flattened and annealed CT sample and a machined CT sample which were discussed previously in Sec. 4.4.2.2.
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Figure 5.1: Schematic of an axial crack growing in a pressure tube section showing hoop-stress loading direction (black arrow), crack growth direction (white arrow) and crack plane.

Figure 5.2: Schematic of an radial crack growing in a pressure tube section showing hoop-stress loading direction (black arrow), crack growth direction (white arrow) and crack plane.
In general, most experimenters have not used the mechanically flattened and annealed samples because changes in the microstructure, texture and dislocation density of the sample may affect DHC properties, in addition to the fact that a specific apparatus is required for the flattening operation. CCT samples are perhaps the most ideal samples for industry run tests as well as they most closely conform to conditions a real pressure tube is subjected to (ie. thickness, microstructure, oxides ect.) and likely most representative of real in-reactor DHC characteristics. However, the shortcoming of this sample geometry lies in the fact that a more complicated loading apparatus is required to load the samples for fatigue and DHC loading as well as the fact that the stress intensity at the crack tip may not be uniform due to the offset loading axis. Also, while these samples are sufficient for making DHCv measurements at high values of $K_I$ where the velocity is basically independent of load, they may be unsuccessful at making appropriate measurements of $K_{IH}$ and $DHC_v$ at low loads due to the additional moments induced by the curvature. This can apparently be accounted for with the use of tapered loading pins (personal communications with Shek). More commonly, DHC is usually studied in with the crack plane growing in the radial crack growth direction. This is usually one with cantilever beam or C-shaped geometries machined from pressure tube sections.

In the present work, axial crack growth samples were Electron Discharge Machined (EDM) at Twin City EDM in Minnesota, USA from the hydrided pressure tube rings into micro CT specimines with an EDM notch machined in the radial axial plane of the pressure tube. This geometry requires that the sample be thinner (~3mm as opposed to the 4.2mm thickness of a full pressure tube ring) than the pressure tube section in order to accommodate the curvature of the ring. Consequently, the present samples
may be further away from the plane strain condition than the full thickness tube (see Sec. 4.4.2). This is however, dependent upon a combination of the 'critical load', temperature and thickness. Plane strain fracture toughness measurements require the condition in Eq. 4.12 to be satisfied. However, during a DHC test, since the maximum load is far less than $K_{IC}$, the stress intensity factor can then be replaced by a lower value corresponding to the load that the test is operated at. This allows plain strain to be maintained for the thinner test sample thicknesses at $K_I \leq 20 \text{ MPa}\sqrt{m}$ and $T \leq 200 \, ^\circ\text{C}$, which was the initial intent for these tests. This was maintained in all axial tests and most radial tests with the exception two samples that had $K_{IH}$ slightly above $20 \text{ MPa}\sqrt{m}$. However, those tests still remained very close to satisfying the conditions required and this was not believed to affect the results significantly (see Sec. 4.4.2.2). Ultimately, the advantages of the selected machined axial crack growth sample is the fact that there is complete maintenance of the pressure tube material (microstructure, texture, dislocation density etc.), simple load frame (not available with curved geometry) and improved confidence in low $K_I$ parameter measurements. Fig. 5.3 is a drawing of an axial sample with the crack plane in the radial-axial direction and the crack growth occurring in the axial direction.

The radial crack growth used a curved pressure tube ring with a broached notch. Broaching is a technique where a toothed tool with a defined tip radius size is repeatedly (over the course of several hours) dragged across a surface with a decreasing tip radius in order to create a sharp notch. This procedure is required to make a precisely oriented almost sharp notch from which to initiate a crack. The samples were machined and broached at Kinetics Inc. The broach itself has been shown to have a 15 $\mu$m root radius at the notch tip; Fig. 5.4 is a schematic of a radial crack
5.2.2 Metallographic Examination of Hydride Phases

In order to confirm the outcome of the thermo-mechanical processes carried out to generate the different hydride populations, metallographic examination of the hydride phases was completed. Both furnace cooled δ and reoriented δ hydrides were easily examined with optical microscopy, but the γ hydrides formed upon the quench were very small (on the order of the grain size, 200nm -20µm, although usually on the order of nm due to elongated plate-like grain shape) and often only resolvable in Transmission Electron Microscopy (TEM). Since slow cooled hydrides generally consist of large ‘macro’ platelets consisting of a number of smaller platelets, in the δ and reoriented hydride samples, Scanning Electron Microscopy (SEM) was used to examine some fracture surface details. The following sections describe all the steps taken in order
Figure 5.4: Schematic drawing of radial crack growth sample. All dimensions are in millimetres.
to image hydrides \textit{in general} but for some of the more specific applications, some or alternative steps were taken and described accordingly. For organisational reasons, although the procedures are described presently, the metallography is included and discussed in the following Sec. 5.2.3 which describes the different hydride populations.

\section*{5.2.2.1 Grinding}

Samples for metallography were first encased in epoxy combined with an edge retainer. All samples were subsequently ground with increasingly fine sandpapers including 220, 320, 500, 800 and 1200 grit. The sample was ground until all of the grind marks were in the same direction of a given grit level, and then rotated 90 degrees and ground until the grind marks were again all in the same direction. This was done twice on the finest paper (1200). Samples were then ultrasonically cleaned in ethanol.

\section*{5.2.2.2 Attack Polishing}

Following grinding, samples were attack-polished on a rotary wheel. Attack polishing is used to remove material deformed during the final mechanical polishing stages and generally produces a 'mirror' finish. With the polishing wheel spinning at low-medium speed, a solution containing 3-4 drops of attack-polish solution composed of of 5\% $H_2O$, 5\% $HF$ (concentration \~48\%-52\%), 5\% $HNO_3$ and 5\% $H_2O_2$ with colloidal silica was used. Samples were slowly rotated opposite the direction of the wheel while adding some of the attack-polish solution and colloidal silica approximately every 30 seconds. Polishing continued until all scratches and pits were removed sufficiently at which point it was rinsed in water and wiped with a soapy cotton swab.
5.2.2.3 Etching

In the case where hydrides were imaged either optically or with Secondary Electron Imaging (SEI) in the SEM, etching was required to bring out the hydride microstructure. Etching was done in a solution of 50% $\text{HNO}_3$, 45% $\text{C}_3\text{H}_6\text{O}_3$ (lactic acid) and 5% HF (concentration 48%-52%). Samples were submerged between 30 and 50 seconds to produce the appropriate results. If hydrides were imaged with Backscatter Electron Imaging (BEI) in the SEM, this step was unnecessary. It should also be pointed out that some of the finer sub-platelet structures of the macro hydrides can become obscured by the etching. Shek [45] recommended an anodizing procedure to image the finer details of the hydride sub-platelets, but this was unnecessary for the present work because crack tip hydride detail was not studied.

5.2.3 Thermo-Mechanical Processing

In order to test the effect of bulk hydrides on DHC (see Sec. 4.1) it was necessary to produce samples with the same hydride content, but different hydride morphologies. More specifically, attention was given to producing hydrides with levels of matrix constraint. The general nature of hydrides in zirconium has been fully described previously in Chap. 2 and Chap. 3. Three different hydride populations were selected for DHC testing upon heating: furnace cooled $\delta$, $\gamma$ quenched and reoriented $\delta$ bulk hydrides.

5.2.3.1 $\delta$ Hydride

The first hydride population created for the present work was that of coarse $\delta$ phase hydrides in their natural orientation. Samples from the hydrided ring described
previously were heated to 350°C, held for 24 hours and then cooled at a rate of 1°C/minute. This cooling rate is expected to produce coarse δ-phase hydrides. Diffraction measurements made at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratories in Upton, New York, USA were used to confirm the predominance of δ hydride and were described previously in Chap. 3. The diffraction spectra for this sample is shown in Fig. 5.5. It was shown that the hydrides had a natural orientation that is dictated by the ability of the matrix to accommodate the hydride strains [58, 60, 61, 159]. In cold drawn pressure tube, this results in hydrides that exist in the transverse-axial plane in the absence of applied stresses [58, 61, 62]. Conformation of the hydride morphology was completed by optical metallography, and is shown in Fig. 5.6. Large macro hydrides visible in the images confirm radial-axial platelet like morphologies with flat extensions of hundreds of μm in the axial direction and more varied extensions of tens of μm in the radial plane. It is suggested that the geometry of the hydrides is related to the grain structure of the pressure tube material, with the more extended flat directions in the axial direction corresponding to the long axis of the grains. Throughout the remainder of this paper, this hydride population will be simply referred to as furnace cooled δ hydride.

5.2.3.2 γ Hydride

One set of samples was subjected to a heat treatment known to produce fine distributed γ hydrides. Sections of the hydrided Zr-2.5 wt% Nb pressure tube were slowly heated to 350°C in a tube furnace and then quenched in chilled brine. The solutionisation temperature of 350°C is well above the dissolution solvus for the present hydride concentration and therefore all of the hydrogen is assumed to be in
Figure 5.5: Diffraction spectra of slow cooled hydrided Zr 2.5wt% Nb pressure tube taken at NSLS in Upton, NY, USA showing the presence of a significant δ hydride peak and absence of any γ hydride peak.
CHAPTER 5. EFFECT OF BULK HYDRIDES ON DHC

Figure 5.6: Optical metallography of $\delta$ hydride material
solution at the time of the quench. The hydrides themselves were examined with Transmission Electron Microscopy (TEM) due to the fact that they were too small to be reliably observed with optical or the Scanning Electron Microscope available to the experimenter. Fig. 5.7 shows two TEM images of typical hydrides observed in the the quenched pressure tube. Nearly all hydrides were acicular precipitates measuring approximately 100-300 nm by about 10 nm across. The hydrides appear to nucleate at the $\alpha/\beta$ phase boundaries and grow into the alpha grains until they either reach another boundary or cease in the grain. The hydride population was measured to be nearly all $\gamma$ phase hydride through synchrotron diffraction, shown in Fig. 5.8 and described previously in Sec. 3.2.4.

5.2.3.3 Reoriented Hydride

One section of pressure tube ring was subjected to a thermo-mechanical process with the intention on creating a population of presumed $\delta$ hydrides oriented in the radial-axial plane. Although the natural orientation of hydride platelets in Zr 2.5wt% Nb pressure tube are in the axial-transverse plane, there have been many well documented accounts of hydrides reorienting themselves with the platelet normals aligned in the direction of the greatest applied stress. For more information on reoriented hydrides in general refer to Sec. 2.3.

For the present study, one ring of the Zr 2.5wt% Nb pressure tube previously described in Sec. 3.2.1.3 was heated up to 350°C, held for several hours to ensure dissolution of all hydrides, and then slowly cooled (1°C/minute) under an applied hoop stress near 300 MPa at Kinetics Inc in Toronto, Canada. This resulted in a hydride population with a bimodal distribution with large hydrides in the radial
Figure 5.7: TEM image of water quenched $\gamma$ hydrides in Zr-2.5wt% Nb pressure tube. Courtesy of A. Barrow.
Figure 5.8: Diffraction spectra of brine quenched hydrided Zr 2.5wt% Nb pressure tube taken at NSLS in Upton, NY, USA showing the presence of a significant $\gamma$ hydride peak and absence of any $\delta$ hydride peak.
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axial plane (reoriented) and smaller naturally orientated hydrides as visible in Fig. 5.9. There is a greater quantity of reoriented hydrides than naturally oriented ones and analysis in Ref. [30] suggests that greater than 80% of the hydrides would be expected to be oriented near the radial-axial plane at this stress based upon the use of micro-pressure tubes with similar microstructure and texture to full-size pressure tube. Although not implicitly measured, the phase is assumed to be the stable $\delta$ fcc phase, due to the fact that the cooling rate was slow and the physical morphology is similar to that of $\delta$ hydrides in Zr 2.5wt% Nb. However, TEM measurements by Northwood and Gilbert [59] in a similar material confirmed over 90% of the reoriented hydrides in Zr-2.5 wt%Nb pressure tube were $\delta$ hydride. The $\{111\}_\delta//\{0002\}_\alpha$ orientation relationship in reoriented hydrides with the matrix was also apparently confirmed by selected area diffraction.

Ultimately, the purpose of this process is to make a bulk hydride population with possibly different dissolution or interaction behaviour upon heat up. Since the hydrides themselves are in a metastable state of reorientation, it is suggested that they may be under a different matrix constraint than the naturally oriented $\delta$ hydrides due to the fact that the natural orientation preferentially forms due to strain accommodation. Consequently, different amounts of hydrogen in solution may be expected relative to naturally oriented hydrides. The study by Ambler in Ref. [157] calculated the expected accommodation energy for radial-axial hydrides was slightly larger than half of the reported value for naturally oriented hydride. This hypothesizes that the hydride orientation has an effect on the TSSD.
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Figure 5.9: Optical metallography of reoriented hydride material
5.2.4 Differential Scanning Calorimetry

Differential Scanning Calorimetry is a technique that can be used to infer phase transformation temperatures by relating inflections in a heat flow curve during the constant increase in temperature in a small piece of material. In general, the heat flow to increase the temperature of the small piece of material (in the present case, a piece of hydrided zirconium measuring approximately $4 \times 4 \times 5$ mm) is measured as a function of the temperature and compared to a well defined reference sample. When a phase transformation occurs in the sample of interest, either more or less heat will be required, and an inflection in the heat flow curve is observed. In the case of hydrogen in zirconium there is a noticeable difference in the amount of heat absorbed when the hydrides dissolve or precipitate and this inflection can be related to the Heq content using established TSSD curves. Two samples of each hydride population were tested on a DSC machine by colleagues at Atomic Energy of Canada Limited Chalk River Laboratories. Samples were thermally cycled at $10^\circ$C/minute heating and cooling rate while the heat flow was measured three times in order to remove bias associated with differences in the hydride themomechanical effects and consequently the TSSD and TSSP were all measured three times. Fig. 5.10 shows a typical DSC curve with temperatures of interest highlighted. 'Peak Temperature' is the temperature where the heat flow into the sample reaches a maximum and 'Maximum Slope Temperature' is the temperature where the derivative of the heat flow is the maximum. Experimental work by Khatamian has shown that the inflection labelled peak temperature is the most appropriate temperature to use as a measure of TSSD for Heq calculations [37] but the maximum slope temperature has also been
used by other authors. Khatamian’s conclusions were based upon comparisons between DSC tests and chemical VHEMS (Vacuum Hot Extraction Mass Spectroscopy) tests. Ultimately, it depends upon which part of the heat signal (maximum slope or peak temperature) what calibration curve (ie. Arrhenius curve relating temperature and hydrogen in solution) is used to relate the measured TSSD to an appropriate hydrogen content. The Terminal solid solubility in Eq. 5.4 is most often described as:

\[ TSS(\text{wtppm}) = A \exp\left(\frac{\Delta H}{RT}\right) \]  

(5.4)

where \( A \) is a pre-exponential term, \( \Delta H \) is the process enthalpy of hydride dissolution or precipitation, \( R \) is the gas constant and \( T \) is absolute temperature. Large ranges of numbers have been cited for the pre-exponential and enthalpy terms in pressure tube material for dissolution, with reported pre-exponential values ranging from 63576-81900 ppm H, and \( H_s \) ranging from 33.5-38.8 kJ/mol [46,89,160] and even wider ranges for other alloys. Ultimately, given the wide ranges of Arrhenius values cited previously, for a transition temperature of 330°C, Heq could be inferred to be anywhere from 28 - 102 ppm H, which is unacceptable for even a remotely accurate determination of hydrogen contents, let alone, which transition temperature to use (see Table 5.1), which cites Heq estimations corresponding to a peak temperature of 330°C and a maximum slope temperature of 340°C. The reason for the significant discrepancies in these measured or interpolated values is likely due to varied thermo-mechanical processes occurring pre-dissolution as a result of the varied constraints on different hydrides. Evidence of this in Table 5.2, where the experimentally measured TSSD1, the first of three successive TSSD measurements (ie. TSSD2 represents the second temperature cycle); the peak temperature measurements were considerably
different from the measurements from later thermal cycles. This combined with the fact that the hydrides are known to have experienced different thermo-mechanical processes before the first measurement, suggests that slight changes in the heating rates could result in different measured dissolution temperatures. Selection of appropriate values for the determination of Heq as a function of the measured TSSD is thus best done by those who have actually made the measurements directly with the given material or in contrast to another measurement method such as VHEMS. In the present case, this hydrided material was shown to contain 100 ± 5 ppm hydrogen by VHEMS, and therefore the closest measurements appeared to come from the Kearns curve for unalloyed Zr for the peak temperature, and the CSA standard or Slattery parameters for the maximum slope temperature. In reality, the outcome of this work does not require exact knowledge of the hydrogen content of all samples past a reasonable range (85-100ppm) and verification that the content is the same in all samples. Although not inherently important for the present work, Table 5.3 show the measured TSSP of all three hydride populations for three consecutive thermal cycles between room temperature and 400°C.

<table>
<thead>
<tr>
<th>Author</th>
<th>A</th>
<th>$\Delta H_s$</th>
<th>Heq PT</th>
<th>Heq MST</th>
<th>method</th>
<th>comment</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CSA N285.8</td>
<td>81900</td>
<td>34500</td>
<td>84.2</td>
<td>94.2</td>
<td>PT</td>
<td></td>
<td>[89]</td>
</tr>
<tr>
<td>Singh</td>
<td>63577</td>
<td>34500</td>
<td>65.4</td>
<td>73.1</td>
<td>dilatometry</td>
<td>PT</td>
<td>[46]</td>
</tr>
<tr>
<td>Pan</td>
<td>80800</td>
<td>34520</td>
<td>82.7</td>
<td>92.6</td>
<td>DEM</td>
<td>PT</td>
<td>[33]</td>
</tr>
<tr>
<td>Kearns</td>
<td>120000</td>
<td>35900</td>
<td>93.3</td>
<td>104.9</td>
<td>dilatometry</td>
<td>low alloy Zr</td>
<td>[39]</td>
</tr>
<tr>
<td>Slattery</td>
<td>68600</td>
<td>33570</td>
<td>84.9</td>
<td>94.7</td>
<td>dilatometry</td>
<td>CW rod</td>
<td>[161]</td>
</tr>
</tbody>
</table>

Due to the close match between the predicted Heq values calculated from the CSA standard Arrhenius parameters and the maximum slope temperature and the
CHAPTER 5. EFFECT OF BULK HYDRIDES ON DHC

Figure 5.10: Typical DSC curve for Zr-2.5 wt% Nb pressure tube sample hydrided ~100ppm H and heated at 10 °C/minute showing 'Peak Temperature' and 'Maximum Slope Temperature'

Table 5.2: TSSD measurements during thermal cycling between room temperature and 400 °C measured with Differential Scanning Calorimetry. All temperatures in degrees Celsius

<table>
<thead>
<tr>
<th>Hydride</th>
<th>Test</th>
<th>TSSD1</th>
<th>TSSD2</th>
<th>TSSD3</th>
<th>TSSD1</th>
<th>TSSD2</th>
<th>TSSD3</th>
</tr>
</thead>
<tbody>
<tr>
<td>δ</td>
<td>A</td>
<td>325.1</td>
<td>329.8</td>
<td>330.4</td>
<td>340.5</td>
<td>340.6</td>
<td>340.9</td>
</tr>
<tr>
<td>δ</td>
<td>B</td>
<td>325.2</td>
<td>328.1</td>
<td>328.2</td>
<td>340.4</td>
<td>339.2</td>
<td>340.9</td>
</tr>
<tr>
<td>γ</td>
<td>A</td>
<td>304.0</td>
<td>330.1</td>
<td>330.4</td>
<td>341.8</td>
<td>342.2</td>
<td>342.7</td>
</tr>
<tr>
<td>γ</td>
<td>B</td>
<td>303.8</td>
<td>330.4</td>
<td>330.8</td>
<td>341.3</td>
<td>342.9</td>
<td>343.4</td>
</tr>
<tr>
<td>Reoriented</td>
<td>A</td>
<td>330.7</td>
<td>330.7</td>
<td>330.5</td>
<td>349.6</td>
<td>343.6</td>
<td>344.2</td>
</tr>
<tr>
<td>Reoriented</td>
<td>B</td>
<td>328.3</td>
<td>330.7</td>
<td>331.1</td>
<td>348.2</td>
<td>342.4</td>
<td>343.7</td>
</tr>
</tbody>
</table>
results from the VHME measurements (which are commonly accepted to be the best measurements), these parameters were used to evaluate the TSSD of all hydride populations. The hydrogen equivalent or Heq of these samples can thus be inferred using well established curves relating the TSSD to the Arrhenius curve for dissolution of pressure tube hydrides in Table 5.5 and the measured TSSD from the third cycle or TSSD3, which is the measurement that is representative of hydrides cooled at 10 degrees Celsius per minute.

Table 5.4: Heq of Zr-2.5 wt% Nb pressure tube DHC samples from DSC based 'Max Slope' TSSD measurements

<table>
<thead>
<tr>
<th>Hydride</th>
<th>Heq (± 5)</th>
</tr>
</thead>
<tbody>
<tr>
<td>δ</td>
<td>94.5</td>
</tr>
<tr>
<td>γ</td>
<td>97.1</td>
</tr>
<tr>
<td>Reoriented</td>
<td>97.4</td>
</tr>
</tbody>
</table>

5.2.5 TSSD analysis

Although the TSSD measurements made with DSC do offer some quantitative insight into the amount of hydrogen content in the sample, they do not allow accurate determination of hydrogen in solution as a function of temperature. Knowledge of
how much hydrogen is in solution is required to predict cracking behaviour as described in Chap. 4. The TSSD curve used to measure the hydrogen content in the CSA standard is known to represent hydride dissolution in pressure tube upon slow heating and slow cooling, which is the thermo-mechanical process that the furnace cooled $\delta$ hydride population underwent. Therefore, this TSSD curve is used throughout the remainder of this document to describe the amount of hydrogen in solution for the furnace cooled $\delta$ hydride samples. The dissolution curve for $\gamma$ quenched hydride population is not well defined in the literature, especially due to the fact that $\gamma$ hydride phase stability is inconclusive, Chap. 2. Experimental measurements of the dissolution behaviour of a sample of the $\gamma$ quenched material was completed as a part of the NSLS experiment described in Chap. 3. The experimental beam setup was for the most part, identical to the setup in Sec. 3.2.4 and therefore the details of the experiment are not described here. A vacuum chamber containing a heatable copper block was constructed (Fig. 5.11) to allow synchrotron measurements in the aforementioned reflection geometry as the sample was heated up. Measurements were made at room temperature, and then the samples were heated up to an elevated temperature. At the elevated temperature, measurements were made 3 times, with the first measurement occurring 5 minutes after the sample reached the temperature, and 2 others occurring at intervals of 30 minutes past that point. Measurements were made at 100, 150, 200, 250 and 300°C and select diffraction images are shown in Fig. 3.11 to illustrate the changing intensities of $\delta$ and $\gamma$ hydride peaks. The hydrogen contents were estimated using the same procedure described in Sec. 3.2.4 with the temperature factor accounted for using measurements in Ref. [88], which was also described in Sec. 3.2.4 for organisational reasons. In order to extract some knowledge
of the concentration of hydrogen in solution, the hydrogen volumes measured with synchrotron diffraction were converted into weight content of hydrogen that existed in hydride form for a given temperature. This amount was subtracted from the initial concentration in order to compute the concentration of hydrogen in solution. The following Fig. 5.12 is a plot of the natural log of hydrogen in solution measured from the \textit{in situ} heating experiment and the reciprocal temperature. The slope of this plot is related to the activation energy for the dissolution of the $\gamma$-quenched hydrides and the intercept can be related to the pre-exponential term. The measured TSSD curve appears to match the TSSD measured with DSC within a reasonable range of error. Since several measurements were made during each temperature hold, only those that appeared within the measurement error of each other were included in Fig. 5.12, meaning the dissolution curve is representative of pseudo-equilibrium conditions. It should also be noted that a measurement of the dissolution behaviour of a $\delta$ cooled sample was attempted, but a measurement that was not representative of the bulk hydride was obtained. This was likely due to a bad statistical sampling. Poor statistics were likely due to the fact that no x-y stage rastering ability was available and a limited beam sampling area was available. A dissolution measurement sample of reoriented hydride was not attempted.

Fig. 5.13 shows a plot of all of the dissolution behaviour collected for the purposes of this project including the three 'Peak Temperature' DSC TSSD1 measurements representing the general dissolution behaviour of each hydride population, three 'Max Slope Temperature' DSC TSSD measurements representing the hydrogen contents, the measured dissolution curve of the $\gamma$ hydride population, the established $\delta$ hydride curve [89], which is expected to be similar for the reoriented sample as hydride size
Figure 5.11: *in situ* heating chamber used in synchrotron dissolution curve measurement
Figure 5.12: Arrhenius plot for $\gamma$ hydride measured \textit{in situ} with synchrotron diffraction

\[ y = -2.71709632x + 9.10971 \]

$R^2 = 0.99623$
and phase are the same and the DSC TSSD measurements (Table 5.2) were similar. The amount of hydrogen in solution at a given temperature is important for the prediction of DHC parameters as described in Chap. 4. These curves will be subsequently used throughout the remainder of this chapter to estimate the amount of hydrogen in solution during certain test conditions. The same figure also contains the plot of the TSSP of hydrogen in Zr 2.5wt% Nb PT, which is also of interest for the evaluation of theoretical DHC behaviour, which is independent of the thermo-mechanical processing before testing.

![Table 5.5: Arrhenius parameters of TSSD and TSSP curves in pressure tube](image)

<table>
<thead>
<tr>
<th>Hydride</th>
<th>A</th>
<th>Q</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>δTSSD</td>
<td>81900</td>
<td>34500</td>
<td>CSA N285.8 [89]</td>
</tr>
<tr>
<td>γTSSD</td>
<td>9043</td>
<td>22726</td>
<td>Measured with synchrotron diffraction</td>
</tr>
<tr>
<td>Reoriented TSSD</td>
<td>81900</td>
<td>34500</td>
<td>DSC TSSD measure indicates similar to δ</td>
</tr>
<tr>
<td>TSSP</td>
<td>41100</td>
<td>28000</td>
<td>CSA N285.8 [89]</td>
</tr>
</tbody>
</table>

5.3 Experimental Methods

This describes the procedures used to collect and analyse DHC related parameters. Specifically, the applied stress intensity to initiate DHC, $K_{IH}$ and the crack velocity due to DHC, $DHC_V$.

5.3.1 Crack Growth Monitoring

A method to monitor cracking in the samples throughout the duration of testing was required. This was necessary to allow the calculation and measurement of various
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Figure 5.13: Dissolution and precipitation behaviour of different bulk hydrides showing measurements of the TSSD and TSSP from DSC (PT = Peak Temperature, MST - Maximum Slope Temperature), established dissolution curve for $\delta$ hydride, measured dissolution curve for $\gamma$ hydride from in situ synchrotron diffraction, estimated reoriented hydride dissolution curve and the established curve for TSSP [89]
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DHC parameters related to the cracks length and when crack propagation was occurring. Previously, authors have used combinations of Crack Mouth Opening Displacement (CMOD) monitoring, acoustic emission (AE) [45, 157, 162–165], and potential drop (PD) methods [45, 68, 69, 104, 109, 122, 123, 147–149, 166–169] in addition to post facto fracture surface analysis to determine both when crack growth occurred and the crack position during the test.

5.3.1.1 Crack Mouth Opening Displacement Method

The Crack Mouth Opening Displacement (CMOD) is perhaps the least sophisticated method of monitoring crack growth in solid materials. This method relates the geometry of the opening at the mouth of a crack to the length of the crack using continuum mechanics. Where this method of crack growth measurement is suitable for many applications, it is more difficult to implement in applications with significant temperature transients or where the crack mouth is not readily observable, such as in the case of a DHC test, where the sample is suspended in a furnace and subject to temperature changes. It was therefore, not used for the present experiment.

5.3.1.2 Acoustic Emission Technique

Acoustic Emission (AE) methods measure the acoustic waves produced when a material undergoing a mechanical load is subjected to an irreversible energy release such as a propagating crack, plastic deformation or a phase transformation. The permanent deformation results in a release of elastic energy which manifests itself as an elastic stress wave. An appropriate piezoelectric sensor secured to the material can
detect these waves and be used in order to both monitor when deformation (particu-
larly cracking) occurs as well as quantitatively infer information about crack location
and growth extent. AE counts are measured as a crack propagates, and the magni-
tude of the acoustic fluctuation can be related to the extent of the crack growth or
to indicate when cracking is occurring. AE methods have been used successfully in
many materials and applications other than the present work [162–165]. It is quite
often used to monitor DHC behaviour in both laboratory and industrial applica-
tions [45,68,69,104,109,122,123,147–149,166–170] as a result of its relatively simple
set-up and operation.

5.3.1.3 Potential Drop Technique

Perhaps the best method for monitoring crack growth is through the use of the Direct
Current Potential Drop (DCPD) method. This was first adapted to measuring crack
growth from DHC in Ref. [171]. In its simplest form, DCPD makes use of Ohm’s law
to relate the change in resistance across a crack mouth to the extent of crack growth.
For the schematic circuit diagram in Fig. 5.14, I represents a constant current source,
R represents a resistor and V is a measurement of the potential drop across the
resistor. Ohm’s law is:

\[ V = IR \]  \hspace{1cm} (5.5)

Thus, if a constant current of I is maintained, a resistor of resistance \( R \) will have
a potential drop of voltage \( IR \). If the resistance changes from \( R \) to \( R + R_1 \), then
the potential drop voltage becomes \( I(R + R_1) \). This is the basis that potential drop
crack growth monitoring is based upon. In the case of monitoring crack growth a
sample is connected in such a way that the constant current is forced to pass through
an area where crack growth is speculated to occur and voltage measurement leads are secured across a crack mouth such as in Fig. 5.15. The sample is effectively the resistor in Eq. 5.5, and an increase in crack length (Fig. 5.15(a) and Fig. 5.15(b)) results in an increase in resistance, and therefore an increase in measured voltage. This relationship is especially convenient for several reasons. First, the extent of crack growth (crack area) is linearly related to the change in resistance, and hence measured voltage via a calibration factor that is experimentally determined. Secondly, the calibration factor is independent of temperature, meaning crack growth can be easily monitored at several temperatures without recalibration. Although the preceding description is a simplification of the measurements actually made (measurements of the electrical potential field around the crack tip are what is actually measured), it serves the purpose for the present description. This principal has been used to monitor creep [172], corrosion [173], fatigue crack [174] and environment cracking experiments such as DHC [155,171] in addition to long term crack monitoring in operating metallic structures [175,176]. One other fact that should be noted is that additional resistance in series with a given sample do not affect the voltage measurement in the first sample and consequently one current source may be used for multiple samples wired in series. There are two main ways that potential drop monitoring has been used and the method heavily affects what kind of measurements are collected. One style of measurements uses the potential drop method to indicate only when cracking occurred such that the crack length measured following the test can be directly related to the cracking time and an average cracking velocity can be collected. This is the method most commonly favoured by industry as it produces very robust measurements due to the fact that no inferences need to be made with respect to the potential drop signal.
other than time the sample spent cracking. The trade off is that few measurement can be made per sample and constant stress intensities are not often maintained (although manually dropping the load throughout the test is common) [45].

\[ V = IR \]

**Figure 5.14:** Schematic used to describe Ohm’s law

(a) The voltage across the crack tip is measured as \( V = IR \)

(b) Crack growth results in an increase in resistance across the crack tip, therefore, the measured potential drop increases

**Figure 5.15:** Schematic used to describe how Ohm’s law can be applied to crack growth monitoring
5.3.1.4 Potential Drop Method Calibration for DHC tests

Crack growth in the sample geometries described previously in Sec. 5.2.1 was related to the potential drop across the crack tip. This has been done in numerous publications [45, 69, 174] and was originally adapted for zirconium DHC tests in Ref. [171]. The calibration can be done in several ways. Probably the best and most accurate potential drop monitoring method relates the crack extension for a sample of constant thickness to the potential drop normalised to a reference voltage measured before the test as shown in Eq. 5.6.

\[ a = \left( \frac{V - V_o}{V_o} \right) A \]  

(5.6)

Where \( a \) is the crack length inferred to from the potential drop, \( V \) is the measured voltage, \( V_o \) is a reference voltage taken before the test corresponding to a certain starting crack geometry and \( A \) is the calibration factor relating normalised voltage to crack length with dimensions of length. The main advantage of this method is the fact that it accounts for variances in the placement of the voltage and current leads, resulting in more accurate estimation of the crack lengths. The most significant drawback to this method is \( V_o \) must be recalculated any time a significant load or temperature change occurs, as the measured crack voltage is a function of both parameters. Therefore, for a test with limited test variables or crack segments, or where possible, this is generally the preferred method.

Another method used more commonly in larger samples, relates the crack growth to the voltage at the crack tip normalised to a voltage measured in the same sample at a location not affected by crack growth as described by Eq. 5.7

\[ a = \left( \frac{V}{V_{ref}} \right) A \]  

(5.7)
$V_{ref}$ is the voltage measured either on an alternative sample or an area not affected by crack growth. This method takes into account variances and drift in the current signal which is otherwise assumed to be constant. It is suggested that $V_{ref}$ be at least 2 times the voltage measured at the crack tip. This was not feasible to achieve in the present DHC tests due to the small sample geometry. One attempt was made, but $V_{ref}$ was several times smaller than $V$, and the measurement appeared worse.

The simplest method is to infer crack extension (where crack extension is representative of crack area) and relate it to the measured voltage across the crack tip, herein called the direct potential drop method. This ultimately results in a factor that directly relates crack extension to a change in the measured voltage by a factor with dimensions of length/voltage, or as it relates to the present sample, mm of crack growth per millivolt of potential drop (Eq. 5.8).

$$\Delta a = \Delta VA$$ (5.8)

A linear relationship between crack extension and potential drop is possible. However, differences in the locations of wires, which is inevitable with spot welds is not accounted for, and although the crack length potential drop calibration remains linear, differences in actual crack length and inferred crack length are more likely. However, provided the amount of total crack growth is relatively low (few mm) and points on the fracture surface can related to measured crack growth segments, real crack growth behaviour can still be correctly determined. The advantage of this method is that it makes test operation significantly more simple due to the fact that no reference voltage is required for a given geometry, and therefore, nothing needs to be re-calculated during a significant load or temperature change. Therefore, for tests facilitating a
significant number of load and temperature changes, the cumulative errors of peri-
odically re-calculating $V_o$ would require fracture surface crack re-evaluation anyways, and thus the direct potential drop method is preferred.

There are a number of factors to consider when securing the current and voltage wires to the samples. Many of the initial studies that used potential drop to monitor crack growth secured the wires to the the sample mechanically with screws. The biggest advantage of this is that it produces a high repeatability in the electrical potential field around the sample. However, satisfactory results can also be achieved by instead spot welding wires directly to the sample surface. The actual electrical potential field produced from the current wires is not likely to be significantly shifted more by this securing method provided the experimenter ensures that it is centered relative to the sample width and far enough from the crack tip. In all instances of the present work, the current carrying wire was approximately 1\text{mm} \phi Pt coated Nb wire spot welded near the center (relative to sample thickness) and approximately 5\text{mm} away from the crack mouth in the axial sample geometry as shown in Fig. 5.16 and approximately 10\text{mm} away from the crack mouth in the radial samples as shown in Fig. 5.17. Two considerations worth noting when it came to selecting the location of the crack tip voltage leads. In general, most potential drop literature suggests that more accurate crack growth inferences are possible by both maximising the total potential drop across the crack tip as well as increasing the change in voltage across the crack tip for a given crack extension. Maximising the total potential drop across the crack tip can be done by securing the voltage leads across the crack tip in opposite directions. However, due to the enclosed nature of the DHC oven interior, it was very difficult to repeatably secure voltage leads while running the wires in opposite
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directions and therefore, wires were always welded in the same direction (Fig. 5.16, Fig. 5.17). In order to maximise the change in potential drop with a given crack extension, it is of interest to weld the voltage leads as close as possible to the crack tip. However, there are two major problems with this approach. First, there is a risk of having the welds short circuit the crack mouth. Second and more importantly, although the sensitivity of the results increases as the leads approach the crack mouth, the repeatability of the measurements decreases significantly. Consequently, locating the leads approximately 1 mm away (no closer) from the crack tip provided sufficient sensitivity and repeatability in the crack growth measurements. Special attention was also paid to ensure that a good weld was achieved (principal point of electrical contact) immediately at the area where the wire led from the sample towards the digital multimeter to ensure that a similar voltage measurement position was maintained in all tests.

For the present study axial crack growth was calibrated in terms of both direct and normalised potential drop methods and radial crack growth was calibrated in terms of normalised potential drop. This was done primarily by growing a crack segment in tensile fatigue on an INSTRON mechanical test rig, measuring the potential drop across the crack tip corresponding to a $3.00A$ applied constant current with a Keithley 2701 Digital Multimeter, marking the crack position with a 'heat tint' oxidation treatment ($300^\circ$C for 3 hours). The fatigue crack was grown by cycling the load on the sample between stress intensities of 1 and 11 MPa $\sqrt{m}$, which is an average stress intensity used in the present DHC tests. This process was repeated usually three times for each calibration sample. Following the growth of all crack segments, each crack position was measured with optical microscopy. Due to the curved nature of
Figure 5.16: Locations of spot welds on axial crack growth samples
Figure 5.17: Locations of spot welds on radial crack growth samples
the crack front, 9 equidistant lines along the crack surface were averaged in order to describe an ‘average crack length’ (see figure Fig. 5.18). In addition, calibrations were also possible by relating DHC crack growth segments to the measurement of the cracks following the tests. Fig. 5.19 contains the direct calibration curve used in axial crack growth samples. Fig. 5.20 is the normalised calibration of the radial samples. Temperature calibration was done primarily by measuring the voltage signal at several temperatures and was also determined to be linear, as has also been observed by other authors. Special note is made in Fig. 5.19, where sample of similar geometry to the present work (labelled as Kerr and Kerr250) underwent similar calibration crack segments at room temperature in fatigue and 250°C in DHC. This confirmed that the calibration factor is independent of temperature. It is also noted presently, that the wires were attached in a slightly different manner to the calibrations completed by the author, and therefore the calibration factor from the Kerr samples and those in the present sample are not the same.

Since the current work is the first in our laboratory to utilize the present sample geometries, ongoing updates to the calibration factors were made based upon comparisons between the inferred crack lengths (inferred meaning length determined during DHC test from potential drop changes) and crack lengths measured following a test by optical examination and our database of pd to crack growth data. In addition, it is also recognised that some scatter in the calibration factor still exists between the multiple samples, likely a result of material variability, spot welds and experimental errors associated with crack and voltage measurements. Following every DHC test, the fracture surface was examined and features representing known crack
**Figure 5.18:** Average crack length measurement made with 9 equidistant lines across the crack surface measured from the EDM notch.

**Figure 5.19:** Potential drop calibration for axial crack growth samples. Kerr and Kerr250 are slightly different geometries at room temperature and 250 °C respectively. Symbols in legend are arbitrary labels. Equations represent the linear fit for each line and are intended for reference purposes.
Figure 5.20: Normalised potential drop calibration for radial crack growth samples. Symbols in legend are arbitrary labels. Equations represent the linear fit for each line and are intended for reference purposes.

segments were recognised, measured and the inferred crack length was linearly corrected (Sec. 5.3.3.3) to reflect the real crack length, which would be done regardless of whether or not scatter existed. Consequently, a good crack length calibration really only affects how accurate the knowledge of the stress intensity is during a given test (which affects how accurately a constant $K$ measurement can be made).

There is a finite length of crack growth that can be reasonably accurately measured by the potential drop method. Most publications on the subject indicate that the crack length voltage relationship should be linear for a range of ratios of $a/W$, where $a$ is the crack length and $W$ is the distance from the loading axis to the back face of the crack. The ASTM standard in Ref. [132] suggests that these values are valid in CT geometries for $a/w$ ratios of up to $0.25 \rightarrow 0.75$. In general, the tests were grown from threshold of $a/w = 0.3$ (edm notch) to approximately $0.5 \rightarrow 0.6$ which was conservative by ASTM recommendations. Regardless, a linear voltage crack length
measure was observed in the range used in the experimental potential drop work reported here. The radial samples were not subject to any other measure of crack growth reliability past the experimental calibrations completed in the present work. Consequently, most tests were stopped after the crack length approached $a/w = 0.5$.

5.3.2 DHC Testing

5.3.2.1 Fatigue Pre-Cracking

Growing a crack by DHC requires a significant initial flaw that can be controllably loaded such as an Electron Dispersion Machined (EDM) notch in the case of the axial samples or a broached notch in the case of the radial samples. However, using either of these flaw geometries poses two significant problems. First, a measurement of the critical stress intensity that needs to be exceeded for DHC to occur, or $K_{IH}$, which will only be valid for that particular crack geometry as crack initiation is a function of flaw geometry, [100, 134, 177–179]. In general, the more blunt the flaw, the higher $K_{IH}$ for that flaw is. Although understanding crack initiation from flaws of different geometries is of interest to the nuclear industry, it is not relevant for the present study. Secondly, crack initiation from blunt flaws generally requires a significantly increased incubation time before a crack actually propagates. For these reasons, sharp cracks created by fatigue crack growth were used to provide starter cracks for DHC that could then be repeatably measured. This is because the crack produced following a DHC crack growth segment, is essentially a sharp crack. For a vast majority of literature studies on DHC, cracks are initiated and grown from a fatigue crack. The other main consideration to account for during both fatigue cracking and DHC operations is the plastic zone size at the crack tip. In general,
plastic zone size increases with increased applied load and lowered yield stress. $K_{IH}$ is known to be sensitive to whether or not the load in excess of $K_{IH}$ was approached from a stress intensity above or below and what the previous 'highest' stress intensity was prior to a $K_{IH}$ measurement (see Sec. 4.4.2 and Ref. [99, 134]). Consequently, there are several different types of $K_{IH}$ measurements: those measured upon loading assuming that the plastic zone size is representative of that critical load and allowing creep, and those measured with the plastic zone size representative of a larger load. For reasons described in Sec. 4.4.2, measurements in increasing load mode, assuming that the plastic zone size would be representative of the applied load were attempted, and therefore a sharp crack with a final applied stress intensity lower than that of the expected $K_{IH}$ values was required.

In the present work cracks were grown in the DHC samples in tensile fatigue on an INSTRON alternating between a high and low stress intensity ($K_{max}$ and $K_{min}$ respectively) at 4Hz. $K_{max}$ is assumed to be representative of the final stress intensity. The experimental setup is shown in Fig. 5.22. Fatigue cracks were grown in all axial samples by first alternating loads between 11 and 1 MPa $\sqrt{m}$ for approximately 250$\mu$m of crack growth, reducing $K_{max}$ to 8 MPa $\sqrt{m}$ for approximately 100$\mu$m of crack growth and reducing $K_{max}$ to 6 MPa $\sqrt{m}$ for an additional 100$\mu$m of crack growth. Ultimately fatigue cracks that were approximately 400–500$\mu$m were typically created with the plastic zone at the crack tip smaller than the plastic zone of the predicted $K_{IH}$ at the first test temperature. Given the fact that the lowest measured $K_{IH}$ values were around 6-7 MPa $\sqrt{m}$ and they were measured at high temperature where the lowered yield stress and creep relaxation increases the plastic zone size, this is a reasonable approach. The stress intensity factors for axial and radial crack
growth samples were calculated using the relations in Eq. 5.9, Eq. 5.10 and Eq. 5.11, Eq. 5.12 respectively with the terms defined in Fig. 5.21. For CT specimens:

\[ K = \frac{P}{B\sqrt{W}} \left( 2 + \frac{a}{W} \right) f \]  \hspace{1cm} (5.9)

where

\[ f = 0.886 + 4.64 \left( \frac{a}{W} \right) - 13.32 \left( \frac{a}{W} \right)^2 + 14.72 \left( \frac{a}{W} \right)^3 - 5.6 \left( \frac{a}{W} \right)^4 \]  \hspace{1cm} (5.10)

and for C-shape specimens:

\[ K = \frac{P}{B\sqrt{W}} \left( \frac{3X}{W} + 1.9 + 1.1 \frac{a}{w} \right) \left[ 1 + 0.25 \left( 1 - \left( \frac{a}{w} \right)^2 \right) \left( 1 - \frac{r_1}{r_2} \right) \right] g \]  \hspace{1cm} (5.11)

where

\[ g = \left[ \frac{\sqrt{\frac{3.74 - 6.30\left( \frac{a}{w} \right) + 14.72\left( \frac{a}{w} \right)^2 - 2.43\left( \frac{a}{w} \right)^3}{(1 - \frac{a}{w})^2}}} \right] \]  \hspace{1cm} (5.12)

Crack growth was monitored with the same method described in Sec. 5.3.1.3 and

**Figure 5.21:** Geometrical assignments for stress intensity calculations
the final crack sizes, which were the initial inputs into the DHC tests, were usually evaluated with the normalised voltage calibration, which was thought to be the most accurate. Fatigue cracks were also grown in the radial crack growth samples by the same procedure, but since the radial thickness is 3.5mm from the end of the broach to the outer diameter, a smaller starter crack totalling 250–300µm was grown. Fig. 5.23 shows a typical plot of a fatigue crack grown in an axial crack growth sample. The potential drop signal for all crack segments are marked. A similar curve was produced for all radial samples with fatigue cracks (not shown because it is very similar).

5.3.2.2 DHC Test Rig

Test ovens were copied from similar ovens developed at Kinectrics Inc to facilitate many forms of thermo-mechanical loading with a particular emphasis on DHC testing and shown in Fig. 5.24. Four loading frames were run through a large Applied Test Systems test oven capable of holding temperatures in excess of 400°C for extended periods of time. Each load rig began with a mounted load cell connected to a universal joint, connected to a grip, which secured to a sample, to a grip, to a second universal joint and then to a lever arm tensioned by a stepper motor as shown in Fig. 5.25. The load signal from the load cells was routed into a control system in Labview that adjusted the stepper motor location until a pre-programmed set point (load) was reached. The stepper motors with a step size of 2µm operating at the end of a ∼5:1 lever arm provided more than sufficient resolution for the intended load ranges. Each oven had 4 load rigs with the capability of being independently loaded. In order to monitor crack growth, the potential drop method was used as described in Sec. 5.3.1.3. Kepco ATE 6–5DM power supplies supplied a constant current.
Figure 5.22: Axial sample undergoing fatigue pre-cracking on INSTRON load frame
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![Typical fatigue pre-cracking voltage signal showing areas of different load cycles for axial crack growth sample](image)

**Figure 5.23:** Typical fatigue pre-cracking voltage signal showing areas of different load cycles for axial crack growth sample

of 3.00 A through Pt clad Nb wires spot welded to the test samples in a simple series circuit. Due to the nature of a series circuit, all samples experience the same (constant current), so as long as complete sample failure does not occur. However, due to the occasional failure of a Pd wire usually only 1 or 2 samples were wired in series. This meant that should a wire fail, the crack length voltage signal would not be lost in all samples. Pt coated Nb wires were used because a thick (current carrying, φ apx. 1mm) wire needed to be spot welded and thick zirconium wire was difficult to reliably spot weld. Thin zirconium leads were spot welded across the crack mouth and the voltage was measured with a Keithley 2701 Digital Multimeter operating with a Keithley 7700 data logger. The voltage leads were placed on opposite sides of the crack mouth approximately 1mm away from from the crack edge. Both leads were secured across the mouth in the same direction (Fig. 5.22) due to the fact that the enclosed space inside the ovens made it very difficult to accurately spot weld in a certain area. The specifics of the crack tip spot welds were described in
more detail previously in Sec. 5.3.1.4. Additionally, a K-type thermocouple was spot-
welded either on (radial samples) or near the test sample and constantly monitored. 
Ultimately, an apparatus that allowed the simultaneous control and/or measurement 
of temperature, load and potential drop across the crack tip for four samples was 
constructed. All measurement systems were controlled by a graphical user interface 
in Labview. This provided the ability to control and measure all aspects of the 
thermo-mechanical testing required for DHC experimentation. Since DHC depends 
upon the stress gradient between the bulk and the crack tip, maintaining a constant 
stress intensity is preferred to maintaining either a constant displacement or constant 
load. The unfortunate consequence of crack growth measurements is that the stress 
intensity at the crack tip is always increasing during a test run at a constant load, and 
always decreasing during a test that is run at constant displacement. A constant load 
test, the crack would accelerate until fracture and in a constant displacement test, 
the crack would decelerate until arrest. Consequently, these methods require the 
measurement of ‘average crack velocity’ which is undesirable. At stress intensities 
corresponding to stage II crack growth, this is less of an issue (which is also the 
realm of most literature $DHC_v$ tests). It is actually ideal to study DHC under 
constant stress intensity conditions because crack growth rates are constant for a 
given stress intensity. Therefore, a constant K control loop was setup between the 
measured potential drop across the crack tip and the load control system. As the 
 crack propagated through the sample, potential drop changes would be related to the 
change in crack length described by the potential drop calibration (Sec. 5.3.1.3) and 
the load would be backed off accordingly. This provided the functionality to study 
crack initiation by automatically ramping up the stress intensity factor at intervals
of constant K until cracking occurred and subsequently measure crack velocity as a function of applied stress intensity factor. The one limitation of this procedure is the reality that the re-evaluation of crack lengths following a test results in change in $K_I$ due to the nature of the relationship between crack length and stress intensity factor (further described in Sec. 5.5.1). Consequently, the velocity must be described in terms of $K_{avg}$ or the average K with an uncertainty associated with the range of K over that crack segment. In the present study, as more tests were run, the range of K was minimised due to improvements in our crack length prediction ability. In general, K was maintained within approximately 0.5 MPa $\sqrt{m}$ or better during most crack segments.

Figure 5.24: DHC oven setup showing key components
Figure 5.25: Interior of DHC test oven showing 4 independent loading rigs
5.3.3 DHC Measurements

Since the intention of this study is to characterise DHC behaviour as a function of different bulk hydrides, measurements of DHC parameters at low temperatures (\(<\ 220^\circ C\)) was the primary objective. The critical stress intensity for DHC or $K_{IH}$ and the advancing crack velocity, or $DHC_v$, were measured for the axial crack growth direction at 140, 160, 180, 200 and 220\(^\circ\)C upon heating for $\delta$, $\gamma$, and reoriented $\delta$ hydride samples (Sec. 5.2.3) and upon cooling for $\delta$ hydride samples. These parameters were also measured in the radial crack growth direction and at 140, 180 and 220\(^\circ\)C for furnace cooled $\delta$, $\gamma$ quenched and reoriented hydride samples upon heating. This temperature range is also of further interest in efforts to describe the effects of hydride phase on cracking due to the inference that the disputed $\gamma$ hydride phase boundary exists around 180\(^\circ\)C, which was also confirmed in the synchrotron diffraction measurements in Fig. 3.12(b). Consequently, measurements at 140\(^\circ\)C are expected to be in the regime where $\gamma$ hydride may be stable, and measurements at 220\(^\circ\)C will be in the regime where $\delta$ hydride is definitely stable.

5.3.3.1 Axial DHC

This section describes procedure undertaken in the present study for all axial crack growth samples. The sample geometry allowed a significant amount of crack growth (~2mm) under DHC from the point where the fatigue crack began to the point where crack growth or potential drop measurement may have been affected by the back of the sample. Therefore, a procedure was adopted that allowed measurements of $K_{IH}$ and $DHC_v$ for several temperatures on the same sample. Thus, measurements could be made on multiple samples of the same type in order to get an idea of the variances
in the test method and crack mechanism. Axial crack growth samples were tested in DHC as follows:

1. Samples were EDM machined from the pressure tube rings to the specifications described in Sec. 5.2.1.

2. Samples with the $\gamma$ hydride population were quenched as described in Sec. 5.2.3. The reoriented samples were already in their test form before machining. The furnace cooled $\delta$ hydride samples were subjected to a 'standard thermal cycle' consisting of heating to 350°C over the course of 6 hours, holding for 24 hours and then cooling back to room temperature in 6 hours.

3. Samples were hand ground to 2.78 ± 0.2 mm in decreasing grits of sandpaper with the final finish on both sides attributable to that of 1200 grit sandpaper.

4. A 400-500 $\mu$ m fatigue crack of was grown in each sample on an INSTRON test rig as described in Sec. 5.3.2.1.

5. Samples were loaded into the DHC oven as described in Sec. 5.3.2.2.

6. The DHC oven was heated to the lowest test temperature, 140°C, and held for a minimum of 24 hours to ensure the uniform distribution of dissolved hydrogen representative of that temperature and hydride population.

7. Samples were loaded to a stress intensity factor below the expected $K_{IH}$ and crack growth was monitored using the direct calibration method described in Sec. 5.3.1.3.

8. After 24 hours the stress intensity factor was automatically increased by 1 MPa $\sqrt{m}$. 
9. This process repeated itself until approximately 0.3 mm of inferred crack growth from the potential drop measurements was observed at which point the sample was unloaded to a nominally small tensile load. In some cases, if $K_I$ significantly exceeded $K_{IH}$, a crack with a $K_I$ slightly higher than $K_{IH}$ was used to grow a ‘relief’ crack in attempt to alleviate the plastic zone.

10. Once all samples had cracked the desired amount, the test oven was heated to the next temperature, changing the thermal conditions to those of that temperature.

11. Items 6-10 were carried out at 140, 160, 180, 200, and 220°C or suspended if crack growth approached the limits defined in Sec. 5.3.1.3.

12. Additionally, one set of $\delta$ samples was tested with the same loading procedure but following a thermal cycle to 350°C with a hold of 60 minutes and a heating and cooling rates of 60°C/hour.

13. In order to confirm the presence of the ‘knee’ in the $K_I/DHC_v$ relationship in Fig. 4.15 one of each sample was subjected to crack growth of approximately 0.3 mm at a stress intensity of approximately 18 MPa $\sqrt{m}$ to characterise the terminal crack velocity characterised by stage II crack growth.

Ultimately, for a given axial DHC test, cracking was not observed at the first testing temperature until a stress intensity factor higher than $K_{IH}$ was reached. At this point, usually several crack segments were measured within the ~0.3 mm of crack growth at several stress intensities and consequently, overlap from all samples of the same type provided data containing the stress intensities where no cracking occurred, and the $DHC_v$ at several stress intensities slightly higher than $K_{IH}$.
5.3.3.2 Radial DHC

Radial crack growth was also measured in attempt to investigate possible differences in the crack growth as a result of texture and microstructural differences in the radial crack growth direction. Due to the fact that the trackable distance in the radial crack growth direction was significantly less (~1mm) than the axial samples, a different procedure was used to measure the same parameters.

1. Samples were EDM machined from the pressure tube rings to the specifications described in Sec. 5.2.1 and a broached notch was placed on the inner diameter of the sample to serve as a crack initiation point.

2. Samples with the $\gamma$ hydride population were quenched as described in Sec. 5.2.3. $\delta$ and reoriented samples were already in their test form before machining.

3. Samples were hand ground to 3.15 mm ± 0.2 mm in decreasing grits of sandpaper with the final finish on both sides attributable to that of 1200 grit sandpaper.

4. A 250 – 300 $\mu$m fatigue crack was grown in each sample on an INSTRON test rig as described in Sec. 5.3.2.1.

5. Samples were loaded into the DHC oven as described in Sec. 5.3.2.2.

6. The DHC oven was heated to the test temperature, either 140, 180 or 220°C, and held for a minimum of 24 hours to ensure the uniform distribution of dissolved hydrogen representative of that temperature and hydride population.

7. Samples were loaded to a stress intensity factor below the expected $K_{IH}$ and the crack was monitored using the normalised calibration method described in
Sec. 5.3.1.3 due to the fact that no temperature changes and few significant load changes would be experienced by the present test.

8. After 24 hours the stress intensity factor was automatically increased by 1 MPa \( \sqrt{m} \).

9. This process repeated itself until approximately 0.6 mm of inferred crack growth from the potential drop measurements was observed at which point the sample was unloaded to a nominally small tensile load.

10. Once the \( DHC_v \) at several stress intensities had been recorded, the sample was loaded to a stress intensity well above \( K_{IH} \) for that temperature and the crack was grown for a further 0.3 – 0.4 \( mm \) in order to establish the terminal crack velocity characteristic of stage II crack growth, which usually ended up being above 20 MPa \( \sqrt{m} \).

Ultimately, the crack velocity for all hydride populations in the radial crack growth direction was measured at increasing increments of \( K_I \) from below \( K_{IH} \) to well above the crack velocity knee in Fig. 4.15 for 140, 180 and 220°C.

5.3.3.3 Crack Measurements

Following all DHC tests, the fracture surface was examined with optical microscopy in a stereo-microscope in order to measure crack segments. Due to the fact that minor to significant crack tunneling was present in nearly all samples, 9 equidistant lines were drawn perpendicular to the crack mouth from either the EDM notch or the back face of the sample and turned into a measure of the average crack length (see Fig. 5.18). A typical fracture surface for an axial crack growth sample is shown in
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Fig. 5.26. All major crack segments were measured and differentiated due to colour as a result of 'heat tinting' oxidation behaviour of zirconium or the presence of a 'stretch mark' indicating an abrupt change in load. These absolutely known real crack lengths were then replaced into their respective locations on the inferred crack length measurements from the DHC test, and the crack growth was scaled linearly between known points based upon the assumption that although the total crack length may not have been inferred perfectly, the potential drop/crack length linear relationship described in Sec. 5.3.1.3 was maintained between each known crack length. At a minimum, both the end of the fatigue crack and the end of the DHC crack (often marked with a fatigue post-crack) were used. Following the crack corrections, $K_I$ needed to be re-evaluated. This was done by relating the scaled real crack length to the measured load and calculating $K_I$ using Eq. 5.9 or Eq. 5.11. The degree of error this resulted in was a function of how accurately the inferred crack was predicted during the DHC test, which improved throughout the course of the experiments.

![Figure 5.26: Typical axial sample fracture surface showing different crack segments.](image)
5.4 Results

5.4.1 Axial DHC

The following figures contain all of the V-K plots\(^1\) for 140, 160, 180, 200 and 220°C test temperatures. Each value of velocity was calculated by fitting a linear function in MATLAB to the corrected crack length signal for each stress intensity region as shown in Fig. 5.27. Consequently, any areas that either did not experience crack growth measured either a very low or negative crack velocity (Fig. 5.28) were determined to have no crack growth and assigned a value for having not experienced significant crack growth. In general the scatter about zero where no crack growth was actually occurring suggested a cutoff of \(5.0 \times 10^{-10} m/s\) below which, no crack growth could be consistently determined and above which reliable measurements could be made. It is noted that this number is not representative of the resolution of the crack measurement system but an arbitrarily assigned threshold. Accurate measurement of lower crack velocities would require longer periods of crack growth than the 24 hours used in the present experimental method. Usually, a velocity measurement was collected based upon the entire 24 hours that the crack spent at that particular stress intensity. However, in some cases, cracking initiated part way through a loading step, and only the constant crack growth section was used. For nearly all velocity measurements, the cracking appeared to be mostly continuous as observed from the potential drop signal as opposed to the obvious piecewise cracking characteristic of the precipitation, growth and fracture of a crack tip hydride. However, due to the cracking conditions,

\(^1\)V-K plots meaning crack velocity plotted depending on the stress intensity factor, which is a representation of the raw data
this was reasonable and is discussed further in Sec. 5.4.3. In the cases where piecewise crack growth did occur (DHC upon cooling) a suitable cracking section was fit in the same manner. Ultimately, any crack velocity fit was associated with its total crack growth length, cracking time, an $R^2$ value based upon its residual in addition to the minimum, average and maximum stress intensities. For crack velocities past the threshold described previously, a velocity measurement was kept if the following criteria was met

- Significant crack growth occurred over the crack growth period. This was subject to the measured crack velocity, with less crack growth being acceptable for lower crack velocities, and therefore a case by case discretion was employed. As a general rule, at least tens $\mu m$ of crack growth was required.

- Significant enough cracking time occurred to ensure a suitable average crack velocity for the test conditions, again at the experimenter discretion. Usually the full 24 hours of crack growth at a given load was preferred. Some exceptions were made in the cases where the velocity was high and constant.

- For crack velocities that were high enough an $R^2$ cutoff of 0.80 was used to eliminate bad data fits. However, even though a fit at a low crack velocity might be very correct, $R^2$ values can be quite low due to the fact that the noise in the data is a similar order of magnitude as the change in velocity producing a very low $R^2$ value, and consequently these were ignored. In general, cracking event outputs such as the one in Fig. 5.27 had $R^2$ values well above this range.

- The stress intensity factor remained within a reasonable range. Due to the nature of the crack corrections described in Sec. 5.3.3.3, K was re-calculated from
the updated crack length and consequently K in some cases went from constant amongst an uncertainty to a range due to the over or under-prediction of the crack length during the test. This is the reason that the maximum, minimum and average stress intensities were recorded. Thus, on the V-K plots below, the plotted data point is the average $K_I$, and the horizontal error bars are 1.5 times the maximum and minimum stress intensities observed in the crack segment. The extra 1.5 times multiplier was added in attempt to account for variances in the shape of the crack front and is an attempt to be conservative.

Figure 5.27: Typical crack growth linear fit showing variance in $K_I$ (top), crack length (with green linear fit, middle) and fit residual (bottom)
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Figure 5.28: Typical output for a data point taken to be representative of no crack growth
The V-K plots collected for the axial crack growth samples with bulk furnace cooled δ, quenched γ and reoriented δ hydrides for DHC upon heating and furnace cooled δ hydrides upon cooling are shown below in the following sections. If no significant crack growth was observed, the data point was placed below the horizontal red line (located at $y = 2 \times 10^{-10}$) indicating a real data point that no cracking was observed at. The solid vertical line represents the value of the of the lowest measured value of $K$ for which significant crack growth occurred and the vertical dotted lines represents the range between the highest value of $K$ for which no crack growth was observed and lowest value of $K$ that cracking was observed giving an upper and lower bound for the experimental data set. This was done in opposition to the extraction of one $K_{IH}$ data point from each individual sample which would be a function of the size of the step increase in $K_I$ which varied with the corrected crack lengths. Consequently, the range specified by the vertical lines is representative of the range that $K_{IH}$ lies for all of the tested samples and is how crack initiation is represented in the current work.

5.4.1.1 DHC upon cooling

Fig. 5.29 shows all of the V-K plots measured for an axial crack growth sample that had experienced a thermal cycle by heating from room temperature to 350 °C for 60 minutes and then slowly cooled to the test temperature to ensure maximum hydrogen supersaturation. The results on each plot are the data points taken to be reliably extracted from the data sets of 3 individual samples. In general, cracking occurred at high velocity (in general on the order of $5 \times 10^{-9} \text{m/s}$ at the $K_I$ immediately above $K_{IH}$), which was expected from a test sample that had high hydrogen supersaturation
and is consistent with the measures made by Ambler [157] amongst other studies. The range of $K_I$ values associated with crack initiation in addition to cracking velocity both appear to have increased slightly with increasing temperature.

5.4.1.2 Furnace cooled $\delta$ DHC upon heating

Fig. 5.30 shows the V-K plots of DHC from samples with furnace cooled $\delta$ hydrides upon heating to the test temperature. Each plot is the combination of data points from 4 V-K samples and one terminal velocity sample. A significant increase in the applied stress intensity required for crack initiation with increasing temperature was observed. Terminal crack velocities were similar at all temperatures except for the lower temperature range, which was slightly lower. These crack velocity measurements are also similar to the results from the similar tests by Ambler [157].

5.4.1.3 $\gamma$ quenched DHC upon heating

Fig. 5.31 shows the V-K plots of DHC from samples with quenched $\gamma$ bulk hydrides upon heating to the test temperature. Each plot is the combination of data points from 4 V-K samples and one terminal velocity sample, with an exception of the 200 and 220°C test samples, which each only had two V-K test sample due to experimental issues (potential drop issues, max crack growth limit being reached). A minor increase in the applied stress intensity required for crack initiation with increasing temperature was observed. Terminal crack velocities increased with increasing temperature in a nearly identical manner to those cooled under maximum supersaturation, which is similar to the results in Ref. [157].
Figure 5.29: V-K plots of axial DHC upon cooling to the test temperature under maximum supersaturation conditions
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Figure 5.30: V-K plots of axial DHC with furnace cooled δ hydrides upon heating
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Figure 5.31: V-K plots of axial DHC upon heating with $\gamma$ quenched bulk hydrides
5.4.1.4 Reoriented DHC upon heating

Fig. 5.32 shows the V-K plots of DHC from samples with reoriented bulk hydrides upon heating to the test temperature. Each plot is the combination of data points from 6 total samples which are each only 1 test sample due to experimental issues (potential drop issues, max crack growth limit being reached). A significant increase in the applied stress intensity required for crack initiation with increasing temperature was observed. Terminal crack velocities were similar across the temperature range observed, with the highest measured values occurring at the mid test temperature of 180°C.

5.4.2 Radial DHC

The V-K plots collected for the radial crack growth samples with bulk furnace cooled δ, γ-quenched and reoriented δ hydrides are shown below in Fig. 5.33, Fig. 5.34, and Fig. 5.35. In the same convention as the axial crack growth results, all data points below the horizontal red line indicate no measurable crack growth was observed for the duration of 24 hours. Again, the error bars are representative of 1.5 × the actual measured differences in the inferred applied $K_I$. The solid vertical line represents the value of the lowest measured value that crack growth occurred at, and the vertical dotted line represents the highest value that no cracking occurred at, or the traditional representation of $K_{IH}$. The data set from each plot was created from only one sample, with an exception of both the reoriented and γ quenched 140°C V-K samples, where testing was carried out on an additional full sample to confirm the results and the terminal velocity measurement on the reoriented 220°C sample. The main advantage of the radial tests was the fact that only one crack initiation and one terminal velocity
Figure 5.32: V-K plots of axial DHC upon heating with reoriented bulk hydrides.
measurement was made for each sample. Consequently, errors associated with the potential drop method are expected to be minimised, which is in contrast to most of the axial crack growth samples, whose geometry allowed significantly larger cracks to be grown and were subject to measurements at several temperatures. Unfortunately, this meant that duplicate samples were not used (except for the 140°C γ quenched and reoriented samples, which were repeated and showed great repeatability).

![Figure 5.33: V-K plots of radial DHC upon heating at 140°C with furnace cooled δ hydrides, γ quenched hydrides and reoriented hydrides](image)

**Figure 5.33:** V-K plots of radial DHC upon heating at 140°C with furnace cooled δ hydrides, γ quenched hydrides and reoriented hydrides

### 5.4.3 Fractography

For nearly all velocity measurements, the cracking appeared to be mostly continuous as observed from the potential drop signal as opposed to obvious piecewise cracking characteristic of the precipitation, growth and fracture of a crack tip hydride. This was also observed by Shek [45] for cracking in similar conditions. The low cracking temperatures as well as low hydrogen saturation due to heating meant that critical
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Figure 5.34: V-K plots of radial DHC upon heating at 180°C with furnace cooled δ hydrides, γ quenched hydrides and reoriented hydrides.

Figure 5.35: V-K plots of radial DHC upon heating at 220°C with furnace cooled δ hydrides, γ quenched hydrides and reoriented bulk hydrides.
crack tip hydrides were not expected to be long and (except in the case of crack initiation) were very thin meaning any arrest event following a hydride fracture might not produce an appreciable enough change in potential drop. This was also reported by Shek [45] and Shi et. al [101] who theoretically calculate the critical hydride length to be $< 10\mu m$ at the highest test temperature in the present experiment, also observed on some of the present fracture surfaces. The exception was the DHC measurements upon cooling from an elevated temperature where fracturing thicker crack tip hydrides were likely to result in a more significant change in voltage signal.

Fracture surfaces were examined in both SEM and optically in a stereo-microscope (described previously in Sec. 5.5.1) in an attempt to both confirm the DHC mechanism as well look for any exceptional occurrences. Optical methods were used to characterise the presence of striations on the DHC fracture surface. Although several instances of striations were observed, there remained a significant number of samples that did not have readily visible striations, and accordingly, no complete striation data set is available for the present work. The striations were not visible in many cases due to a combination of factors compounded by small striation size, the decreased oxidation at low temperatures and over oxidation at higher temperatures. It was reported by Shek [45] that low temperature DHC striations could be made visible if subjected to a heat treatment at an elevated temperature, but this was only partially successful (notably not in the ‘over-oxidised samples’). However, sometimes the test conditions provided easy examination of striations and all hydride populations appeared to have similar length striations between 10 and 20 $\mu m$, which is expected at the test temperatures in this study.
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The following Fig. 5.36 shows some striations that were observed in two axial samples during the terminal velocity crack growth tests. Of the striations that are visible in equivalent sections, it is clear that the observable striations are similar between a furnace cooled δ and reoriented hydride sample. Fig. 5.37 is the same test sample and shows a difference between the samples with reoriented bulk hydrides that was notedly different from the other hydride populations. In both the fatigue pre-crack and the DHC fracture surface, there is some obvious effect on the crack surface and the crack front as a result of the reoriented radial-axial hydrides. This has made the crack front significantly less uniform and there may be an additional contribution to the crack velocity as a result of the interaction between the advancing crack front and the bulk hydrides. Fig. 5.38 shows a comparison between two radial DHC samples where the majority of the cracking occurred at 140 °C. Of note is again the differences between the fracture surfaces of samples with reoriented and naturally orientated hydrides. DHC growth in samples with reoriented hydrides appeared to have some interaction with the bulk radial-axial hydrides as shown by many of the fracture surface features whose size and orientation is representative of these reoriented hydrides.

Both axial and radial fracture surfaces were also examined with SEM in effort to further characterise the presence of DHC and the differentiation between samples with existing reoriented hydrides. Fig. 5.39 shows a characteristic image of a typical DHC fracture surface showing the presence of small regions of brittle fracture in addition to instances of plasticity associated with ductile tearing between hydride platelets (ridges and cliffs) and crack arrest (horizontal stretch marks). The fracture features on this length scale was fairly similar with both cracking directions and thus only one image is provided. Fracture surfaces imaged at lower magnifications, in the
SEM provided the ability to observe some of the notedly different fracture surfaces in samples with reoriented bulk hydrides.

For radial crack growth samples, the effects of the existing reoriented bulk hydrides were easily observed at lower magnifications as shown in Fig. 5.40. Here, significant ductile tearing is present in what appears to be the outlines of pre-existing bulk hydrides in the crack plane, especially in the second part of the DHC where crack growth was under higher applied stress intensities. Similar features are also visible in the optical images in Fig. 5.38. These features are not observed in the equivalent image of radial crack growth in samples with the hydrides in other morphologies as shown in Fig. 5.41. The fracture surfaces in the axial direction showed some similar differences between reoriented and normally oriented hydrides (shown in Fig. 5.42 and Fig. 5.43. The difference is that in reoriented axial samples the evidence of bulk hydride-crack interaction was minimised relative to that in the radial samples, with fewer and often smaller features.

5.5 Discussion

5.5.1 Crack Measurement Considerations

Plots of the terminal crack velocity $DHC_v$ and $K_{IH}$ in both axial and radial crack growth samples are shown below in Fig. 5.47, Fig. 5.48, Fig. 5.45, and Fig. 5.46; extracted from the appropriate plots in Sec. 5.4. There are several realities of these measurements that are presently addressed. First, it was often difficult to ensure that each terminal velocity measurement was made at the exact same applied stress intensity. This was due to the fact that the applied stress intensities were initially
Figure 5.36: Axial fracture surfaces in samples with bulk reoriented (left) and furnace cooled δ hydride (right) populations showing fatigue pre-crack, DHC crack segments differentiable by the characteristic oxide, fatigue post-crack and striations characteristic of DHC
measured based upon an inferred crack length that was subsequently corrected based upon the real crack length, shifting the applied stress intensity. However, since the crack velocity approaches a 'plateau' as described previously in Fig. 4.15, crack velocities measured at stress intensities well past the knee in the V-K plots in the previous Sec. 5.4 are representative of the terminal velocity within the expected uncertainty for the given cracking condition and these are the data points plotted in the present section. Initially, the intention of the V-K measurements was to make several measurements of velocity with increasing $K_I$ in hopes of identifying both $K_{IH}$ and $DHC_{vt}$ in the same test. However, this ultimately had to be confirmed by a second test at high $K_I$. Secondly, measurements of crack velocity in the present work are subject to uncertainties associated with several factors including cracked length, cracking time, crack front shape, potential drop calibration errors and crack correction errors. Due to the fact that DHC is characterised by piecewise cracking consisting of the repeated
**Figure 5.38:** Radial fracture surface showing a sample with $\gamma$ quenched (left) and reoriented bulk hydrides (right) showing different crack segments and differences in fracture surface and crack front morphology.
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Figure 5.39: SEM image showing the fracture surface features typical of DHC in all observed samples, 1000x.

Figure 5.40: SEM fracture surface of radial crack growth sample with reoriented bulk hydrides showing definitive instances of crack front-bulk hydride interaction, 40x
Figure 5.41: SEM fracture surface of radial crack growth sample with furnace cooled δ bulk hydrides showing no definitive instances of crack front-bulk hydride interaction, 40x

Figure 5.42: SEM fracture surface of axial crack growth sample with reoriented bulk hydrides showing definitive instances of crack front-bulk hydride interaction, 200x
growth and fracture of brittle hydrides, error associated with both over and under-predicting the crack length are possible if the cracked length used in the velocity measurement is similar to the critical hydride length. The critical hydride lengths in the present work at low temperature were on the order of 10 \( \mu m \), and even greater during crack initiation. Consequently, total measurements of at least tens of \( \mu m \) were required for a reasonably valid velocity measurement. This was really only an issue for the samples on the threshold of crack propagation, where the critical hydride length is larger and the amount of time required to grow the critical hydride is on the order of the 24 hours each load increment occurred for, as in the case of a very slow crack velocity. Unfortunately, this meant that experimenter discretion was occasionally required to determine if crack growth had occurred or not. The crack velocity acceptance criteria outlined in Sec. 5.4 is an attempt to make an unbiased
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ruling on valid crack velocities, but it has the possibility of rejecting otherwise real
crack growth due to low amount of growth over the measured time period or low
velocity. The obvious solution to this is to increase both the duration allowed at each
load step for cracking to allow either a larger crack, or more definite instance of crack
growth to occur in the low velocity regime. This however, can come at the cost of
making the test impractically long, which can cause other issues. The measurement
of crack length used by both the VI control system as well as any measurement made
on a crack surface is entirely idealised and not representative of the real shape of the
 crack front, which is always somewhat curved and can be subject to significant crack
tunnelling effects (see Fig. 5.44). Consequently, whenever crack size is measured, it
is described with an attempt to account for this curvature and is an averaged finite
crack length for use in calculations. This is a significant assumption, but also one
that is very difficult to account for and eliminate. This is most likely due to variations
in the stress across the sample thickness due to the presence of plane stress condi-
tions, where the hydrostatic stress in the through thickness centreline of the sample
is greater than the hydrostatic stress at the free surface. Consequently, the centre of
the sample is exposed to a higher effective $\Delta K_I$ in the fatigue cycles in addition to a
greater rate of diffusion of hydrogen towards the crack tip as a result of the increased
stress gradient. Therefore, the through-thickness centre section of the test sample is
expected to experience higher crack growth rates under both DHC and fatigue con-
ditions. Crack tunnelling is especially prevalent in samples where the stress gradient
required for DHC is relatively large, ie. that there is relatively low hydrogen super-
saturation. Here, the stress in the centreline may be above the threshold, and the
ligaments along the sides of the sample, in addition to the areas above and below the
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Table 5.6: List of samples and crack conditions resulting in significant crack tunnelling

<table>
<thead>
<tr>
<th>Crack Direction</th>
<th>Hydride</th>
<th>Temperature (deg. C)</th>
<th>Label</th>
</tr>
</thead>
<tbody>
<tr>
<td>Radial</td>
<td>$\delta$ - heating</td>
<td>220</td>
<td>2</td>
</tr>
<tr>
<td>Radial</td>
<td>reoriented - heating</td>
<td>220</td>
<td>20</td>
</tr>
<tr>
<td>Axial</td>
<td>reoriented - heating</td>
<td>200</td>
<td>B,D</td>
</tr>
<tr>
<td>Axial</td>
<td>reoriented - heating</td>
<td>220</td>
<td>B,D,J,G</td>
</tr>
<tr>
<td>Axial</td>
<td>$\delta$ - heating</td>
<td>220</td>
<td>R,P,S,T</td>
</tr>
</tbody>
</table>

crack plane, may be below the threshold for hydride precipitation, resulting in a very small area that can experience hydride accumulation, and therefore crack tunneling may occur. In the present work, the crack fronts were always slightly curved, but significant crack tunnelling occurred in the samples listed in Table 5.6.

Figure 5.44: Fracture surface showing crack tunnelling and no crack tunneling
It is clear from Table 5.6 that experimentally, significant crack tunneling only occurred in the samples when a large shift in the solubilities was required to initiate cracking. Consequently, velocities measured during crack tunneling are likely subject to larger uncertainties in crack velocity due to a more varied crack front resulting in deviations from a linear voltage calibration as well as the fact that the different sections of the crack front are advancing at different rates since different crack length implies a different K. It is therefore wise to apply additional consideration to the measured velocities. Two other possible sources of error are the errors associated with potential drop crack measurements. The first source of error is associated with any calibration based error. As seen in Fig. 5.19, crack length is always linear with respect to potential drop, but the calibration factor between samples does vary (likely due to variances in spot welds and voltage lead placement). This was primarily why the inferred crack lengths were always re-calculated based upon the real crack lengths measured from the fracture surface. However, even despite these best efforts, temperature, load, material, crack tunneling and other variables during testing are likely to have affected the accuracy of these crack measurements, which is a significant justification for much of the scatter in both the \( DHC_v \) and \( K_{1H} \) measurements. These errors were also compounded in many of the axial crack growth samples by the fact that several test temperatures (5 in some cases) and highly variable loads were used. Secondly, errors associated with correcting the initial data input containing the inferred crack length and real crack lengths are possible. Again, the beginning and end crack lengths of a crack correction were used to tune the inferred crack length to one representative of the real crack length. However, when the experimenter had confidence that a fracture surface feature corresponded to a feature from the test,
additional interpolation points were added to the crack correction, increasing the accuracy of all measured crack values. In the present work, this was really only practical in differentiating the $200^\circ C$ and $220^\circ C$ crack increments from those at lower temperatures because of the presence of brown oxides on those formed at the higher temperatures in place of blue at the lower temperature. A study to determine the oxide colours as a function of heat treatment was attempted, but was not conclusive due to the fact that oxide growth at lower temperatures is also significantly affected by time. Differentiation of crack segments is also possible through analysis of the striations (Sec. 4.4.3) in the test, with longest striations expected near the sections experiencing crack initiation, and increasing striation size with increasing temperature. Unfortunately, this proved more difficult to use as an analytical tool because the striations in most samples were very difficult to see, even following the heat treatment recommended by Shek [45]. This was especially true in most axial crack growth samples, which usually spent well over a month in the test oven and every crack section was exposed to $220^\circ C$. Some samples that were only tested for shorter cracking periods did end up with well defined striations and it is therefore assumed that the striations in most samples were obscured due to their long oxidation times (although still physically observable in SEM). One more option for marking the cracks (and hence improving measurement accuracy) would be to form a small fatigue crack after some test temperatures or subject the sample to a thermal cycle to significantly modify the oxide, which is the standard method used. Due to the fact that DHC was performed upon heating and that the bulk hydrides populations are sensitive to thermal manoeuvres, this was not done. Removing the samples and fatiguing them to mark crack sections is a viable option for DHC testing upon heating, but additional
errors would accumulate due to added crack segments and repeated and varied spot welds. This would really only affect the inferred crack length and could be corrected for following the test. In summary, the real crack lengths used in this study are those measured via the potential drop method (Sec. 5.3.1.3) corrected (Sec. 5.5.1) based only upon features on the fracture surface that the experimenter was absolutely sure were representative of a given part of the test. In retrospect, all of the errors associated with measuring crack lengths with the potential drop method can be easily minimised or eliminated by either minimizing the number of distinct crack segments on a given sample or by ensuring knowledge of several crack positions on the fracture surface are made more visible than they were in the present experiment. This is directly the approach that was taken in the set of radial samples which were tested after the majority of axial samples were tested, with each sample consisting only of one test temperature and one terminal velocity measurement. Thus the axial crack measurements are likely to be less accurate and is this is one of the main reasons for the increased measurement scatter (beyond inherent scatter).

Examination of all velocity plots indicates that the scatter in the measurements based upon repeat measurements is more than reasonable for drawing conclusions between the sample types, and therefore serves the purpose of this experiment. DHC velocity measurements in the literature still produces scatter on up to $1-2 \times 10^{-8}$ m/s, which is only slightly better than some of the present measures. In addition, the error associated with DHC upon heating should realistically be significantly higher due to the added uncertainties associated with a much larger stress shift to produce precipitation at the crack tip and lower crack velocities.
Figure 5.45: \( K_{II} \) measured in axial crack growth samples
Figure 5.46: $K_{IH}$ measured in radial crack growth samples
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Figure 5.47: DHC velocity measured in axial crack growth samples

- reoriented
- δ furnace cooled
- γ quenched
- cooling from 350 °C

Temperature (°C) vs. DHC (m/s)
Figure 5.48: DHC velocity measured in radial crack growth samples
5.5.2 Effect of Different Bulk Hydrides on $K_{IH}$

Plots of $K_{IH}$ as a function of temperature for both axial and radial crack growth geometries are shown below in Fig. 5.45 and Fig. 5.46 respectively. The x-axis error bars represent the ranges of the temperature throughout the test for all collective samples. This meant that the reported temperatures are actually nominal representations of the test temperature, when in reality due to variances in the ovens and the tests, a given plot is actually more accurately represented by a few degrees above and below the nominal temperature. The y-axis bars represent the range of average $K_I$ encountered between the highest $K_I$ that experienced no crack growth and the lowest $K_I$ that experienced measurable crack growth (representing the dotted lines in the V-K plots in Sec. 5.4). The y-bars cross the x-bars at the lowest value of K that DHC occurred at, which is also given by the solid vertical line in the V-K plots seen in Sec. 5.4. This was done because it best represents the $K_{IH}$ in the entire sample set and the more traditional description of $K_{IH}$ (stress intensity below which DHC will not occur) lies below it (e.g. accounting for all samples, not just taking one possible outlier data point as the value). Representing the data as a range of stress intensities was done because although the potential drop crack monitoring system works, it is not completely accurate and crack length can be over- and under-estimated resulting in variances in the step size of load increments. Consequently, by defining the value given for $K_{IH}$ over this range it does not penalise samples for slight differences in predicted crack length, instead providing the range that the true $K_{IH}$ should exist, pending the measurements made. It is also noted that the upper and lower y-axis values do not include the uncertainties in the $K_I$ plotted in the x-axis of the V-K plots (ie. the errors are considered independent). Scatter in the present measurements of
$K_{IH}$ are typical with comparison to reported literature values [45, 99, 102, 103, 141].

It is clear that in all test samples, $K_{IH}$ always increases with increasing test temperature, but the extent of this trend is very dependant on the hydride treatment. In the axial crack growth samples, $K_{IH}$ with bulk furnace cooled $\delta$ and reoriented hydrides upon heating increased from approximately $7 MPa\sqrt{m}$ at 140°C to $13 MPa\sqrt{m}$ at 220°C with no clear distinction between the two hydride populations. DHC upon heating from $\gamma$ quenched samples and cooling from 350°C also demonstrated a similar trend, but with $K_{IH}$ increasing from approximately $6 MPa\sqrt{m}$ at 140°C to near $8 MPa\sqrt{m}$ at 220°C. Radial crack growth samples showed similar trends to the axial samples with the exception that crack growth at 220°C with furnace cooled $\delta$ and reoriented bulk hydrides required stress intensities greater than $20 MPa\sqrt{m}$. The main characteristics in the $K_{IH}$ data are summarised as:

- An upwards trend in $K_{IH}$ with increasing temperature.
- $K_{IH}$ upon heating is similar in samples with bulk furnace cooled $\delta$ hydrides and bulk reoriented hydrides.
- $K_{IH}$ upon heating of bulk $\gamma$ quenched hydrides and $K_{IH}$ upon cooling under full supersaturation conditions are similar.
- Although similar behaviour is observed between the radial and axial crack direction samples, axial samples tended to crack at slightly lower stresses than radial samples, especially radial samples at higher temperatures.

Explanation of these trends requires understanding of the conditions required for the initiation of a delayed hydride crack (see Sec. 4.4.2). Qualitatively, the stress
gradient between the bulk and crack tip must be large enough to precipitate and grow crack tip hydrides and the crack tip stress intensity must be large enough to fracture the hydrided region at the crack tip. Shek [45] and other authors [101] observed that depending on the thermal treatment, either one of these factors could dominate. It was observed that in conditions where high hydrogen supersaturation was present, hydrogen precipitation was easily accommodated in the region around the crack tip (Fig. 4.14(a)) and the material properties of the hydrided region governed fracture. In conditions under low hydrogen supersaturation, the crack tip hydrides are limited to a narrow region ahead of the crack tip and it was observed that the hydride was often growth limited, requiring an increased stress gradient to produce a significant hydride at the crack tip. Therefore, the effects of the thermo-mechanical hydride treatments and direction of approach to test temperature and the test temperature itself on the ability of a hydrided region to form at a crack tip must be considered.

5.5.2.1 Temperature Considerations

Increasing the test temperature increases the diffusion rate of hydrogen in zirconium, increases the hydrogen TSSP at the crack tip and lowers the yield stress of the zirconium metal. The effect of increased diffusion rate would only be expected to affect $K_{th}$ under very marginal conditions and is therefore not the explanation for this behaviour. An increased TSSP as a result of increased temperature would only affect crack initiation if it resulted in a decrease in the ability of hydrogen to diffuse to the crack tip due an increase in the difference between the hydrogen in solution and the TSSP, which is the case in DHC upon heating, or if the total hydrogen content in the sample was lower than the TSSP upon cooling to the given temperature. This
is expected to affect samples upon heating due to significant differences between the TSSP and the concentration of hydrogen in solution, with the difference increasing with increasing temperature. However, the fact that increasing $K_{IH}$ with temperature was still observed in the samples cooled to the test temperature under full supersaturation conditions, indicates that either the effect of the TSSP and the amount of hydrogen supersaturation or the decrease in yield stress with increasing temperature affects $K_{IH}$. An increase in temperature is expected to result in an increase in $K_{IH}$ due to the decreased crack tip stress, due to a lower yield stress and increased creep relaxation at the crack tip. This is expected to affect $K_{IH}$ under both high and low hydrogen supersaturation conditions, due to the fact that the change in crack tip stress will affect both the ability to fracture a crack tip hydrided region under high supersaturation conditions, as well as the ability of a crack tip hydride to grow to a significant size under low supersaturation conditions due to decreased peak stress. The experimental evidence of this lies in observations of striations which increase in width with increasing temperature [104] and decreasing yield strength [142]. The added effects from increased differences between the TSSP and the hydrogen supersaturation with increasing temperature would only be expected to have an effect on $K_{IH}$ if it contributed to the improved ability of a crack tip hydrided region to fracture, and therefore is not expected to be the major contributor to increasing $K_{IH}$ with increasing temperature under the high hydrogen saturation conditions.

5.5.2.2 Hydride Dissolution Considerations

Although all samples do experience a general trend of increasing $K_{IH}$ with increasing temperature, the increase is relatively large in the furnace cooled δ and reoriented
hydride samples and only slight in both the $\gamma$ quenched and cooled to test temperature samples. This difference is attributable to the differences between the amount of hydrogen in solution and the TSSP at a given temperature. Fig. 5.49 is a modified version of Fig. 5.13 showing dissolution behaviour of the hydride populations (previously described in Sec. 5.2.5). In this figure are an established line for the dissolution of pseudo-equilibrium hydrides (furnace cooled $\delta$), established precipitation solubility for cooling from above the hydrogen solubility limit (CSA standard N285.8 [89] for both) and measured solubility for dissolution of $\gamma$-quenched bulk hydrides (Sec. 5.2.3). As stated previously in Sec. 5.2.5, based upon DSC measurements showing no significant differences between the TSSD upon heating of furnace cooled $\delta$ and bulk reoriented hydrides, the dissolution behaviour of the bulk reoriented hydrides is expected to follow a similar trend to that of the furnace cooled $\delta$ hydride solubility. In the case of both furnace cooled $\delta$ and reoriented bulk hydrides, the stress gradient between the crack tip and the bulk must be large enough to overcome the solubility differences between the hydrogen in solution in the bulk (represented by the red $\delta$ solubility line) and the concentration required to precipitate a crack tip hydride (represented by the pink TSSP line). Under these conditions, the applied stress intensity will need to be relatively large in order to provide the condition where a hydride can precipitate at the crack tip, and consequently, $K_{IH}$ is reflective of the condition where the applied stress intensity is large enough to provide significant growth of a crack tip hydride. As the temperature is increased from $140\degree C$ to $220\degree C$, the solubility difference that must be overcome to grow a significant hydride trebles. In contrast, the bulk solubility of a hydride upon cooling from above the solvus follows the pink TSSP line and the solubility of $\gamma$ quenched bulk hydrides follows the green line in Fig. 5.49.
Consequently, in the case of DHC upon cooling and $\gamma$ quenched bulk hydrides upon heating at lower temperatures, the stress gradient between the crack tip and the bulk only needs to be small in order to precipitate hydrides in the region near the crack tip and slightly larger at higher temperatures in the $\gamma$ quenched condition. Even at $220^\circ C$ in the $\gamma$ quenched condition upon heating, the solubility difference between the bulk and a precipitating hydride at the crack tip is still much less than that of the furnace cooled $\delta$ bulk hydrides upon heating. $K_{IH}$ in these samples is thus a result of the ability to fracture the hydrided region at the crack tip due to the fact that hydride precipitation is easily accommodated. Consequently, the evidence from the present study indicates $K_{IH}$ experiences significant increases in the samples where there is a large difference in the amount of hydrogen in solution and the precipitation solvus. When no significant difference exists, such as in the case of the $\gamma$ quenched upon heating and DHC upon cooling, $K_{IH}$ increases with temperature only at a rate associated with material property changes with temperature (e.g. yield stress).

5.5.2.3 Hydrogen Stress Shift

The closest comparison in the literature is a series of data sets produced by Shek in Ref. [45] where $K_{IH}$ was measured under varied thermal conditions including different amounts of hydrogen supersaturation as a function of thermal cycle temperature, hydrogen supersaturation as a function of test temperature, and test temperature under maximum hydrogen supersaturation; described previously in Sec. 4.4.4. Here exists a large data set that, as independently as possible, attempts to isolate the effects of diffusible hydrogen and test temperature. Of most interest to the present work is the
fact that measurements of $K_{IH}$ were made on samples with various amounts of hydrogen in solution relative to the TSSP required for DHC. Hydrogen supersaturation, which is again defined as the amount of hydrogen in solution in excess of the TSSD (Sec. 2.2.1), is deemed to be representative of the amount of diffusible hydrogen in solution and a trend between $K_{IH}$ and hydrogen supersaturation is drawn. However, this may not be the best way to look at the data set. It makes sense that since the hydrogen concentration at the crack tip must surpass the bulk material TSSP as a result of the stress gradient, that $K_{IH}$ may be better described instead by the difference between the present amount of hydrogen in solution and the concentration required for hydride precipitation at the crack tip. This can be implicitly tested by combining the data set produced by Shek with the present work which significantly varies the amount of hydrogen in solution as a result of the varied hydrides upon heating to the test temperature. Fig. 5.50 shows the combination of the three aforementioned Shek data sets overlapped with the present work plotted as a function of the difference between the amount of hydrogen in solution and the TSSP, referred to as Hydrogen Stress Shift, or the change in the concentration of hydrogen at the crack tip as a result of the stress gradient that must occur in order for cracking to occur. First, it is clear that under conditions where the amount of hydrogen in solution is close to the TSSP as a result of either cooling from above a certain temperature or the thermal process ($\gamma$ quenching, and DHC upon heating), $K_{IH}$ lies within a reasonable range expected for both the varied test temperatures and test methods in the presented data sets. This, and other samples with slightly higher stress shift values, are representative of the values where crack tip precipitation is easily facilitated in the high stress region around the crack tip and $K_{IH}$ is governed by the ability of the hydrided region to
fracture. Consequently, as the stress shift increases, there is an upwards trend in the $K_{IH}$ which can be explained by the fact that the applied stress intensity required to precipitate a significant crack tip hydride is greater than that required to fracture it, and $K_{IH}$ is thus increased. There appears an intermediate range, and this effect appears to take a greater effect past a stress shift of $\sim 15$ ppm H, which is expected to be the point where the fracture behaviour shifts from fracture controlled to more growth controlled $K_{IH}$. This suggests that having a parameter (supersaturation) defined based on a dissolution solvus is flawed due to the fact that it can be shifted significantly and is not the correct basis for assessing DHC susceptibility. Instead, the observed behaviour is better explained by comparing the amount of hydrogen in solution (diffusible hydrogen) to the TSSP. These data sets include studies where the diffusible hydrogen has been varied by different test temperatures, different thermal cycles and now different bulk hydrides upon heating.

5.5.3 Effect of Different Bulk Hydrides on $DHC_{vt}$

The crack velocity during DHC is loosely defined as the rate of advancement of a crack front. In the case of DHC this means the crack velocity can be modelled based upon the rate of hydrogen accumulation near the crack tip as described previously in Sec. 4.5.3.1. This rate of accumulation is driven by the diffusion properties of hydrogen in zirconium, the amount of hydrogen in solution, the TSSP of hydrogen in the crack tip region and the corresponding stress gradient between the stress raiser and the bulk. The present work seeks to test further test this claim past the measurements and analysis that have been previously made by Ambler [157], described previously in Sec. 5.1.
Figure 5.49: Hydride solubilities at experimental DHC temperatures
Figure 5.50: Effect of the difference between hydrogen in solution and TSSP on $K_{IH}$. Shek 250°C is data from a study with different thermal cycle temperatures on DHC at 250°C, Shek 43ppm is DHC with 43ppm in solution at different test temperatures, Shek full supersaturation is DHC upon full supersaturation at different temperatures [45], and Tulk is the axial data from the present study, with the data points represent the location of the solid line in the V-K plots in (Sec. 5.4), of which the traditional definition of $K_{IH}$ (No DHC, used by Shek) is below, and is the most reliable measurement in the present work.
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The basic crack velocity model scales the difference between the stress shifted solvus lines by terms characteristic of the diffusivity of hydrogen and some experimentally determined critical crack tip hydride. Consequently, if $K_{IH}$ is exceeded, and DHC is possible in a particular case, then the crack velocity will be representative of the difference between the solvus of the precipitating hydrided region and either the hydrogen in solution or the solvus of the dissolving hydrides. Consequently, the present experiment provides test conditions with identical precipitation behaviour, but different dissolution behaviour.

Fig. 5.47 shows the axial crack velocities measured in the present study. It is clear that the crack velocities observed in the samples with bulk furnace cooled $\delta$ and reoriented hydrides are similar and that the crack velocities in the samples with bulk $\gamma$ quenched and those cooled to the test temperature are similar. This is in full support of the argument that the amount of hydrogen in solution is primarily what affects the crack velocity. This is because the amount of hydrogen in solution for furnace cooled $\delta$ and reoriented bulk hydrides upon heating are similar, and lower, than the amount of hydrogen in solution for $\gamma$ quenched bulk hydrides upon heating and in solution upon cooling to the test temperature. Consequently, it does not appear that there is any significant effect of the ability of hydrogen to dissolve from the remaining bulk hydrides. If there was an appreciable effect on this, the $\gamma$ quenched and cooled samples as well as the furnace cooled $\delta$ and reoriented hydride populations would be expected to have different cracking behaviour.

The crack velocity equations shown in Eq. B.8 and Eq. 5.1 contains two distinct factors. The first term is some representation of the ability of hydrogen to diffuse to the crack tip (increasing with temperature) and critical crack tip hydride size
(increasing with temperature). Alternatively, the bracketed factors represents the chemical potential driving hydrogen diffusion between the bulk and the crack tip with a large chemical potential resulting in a large hydrogen flux towards the crack tip, and consequently, a high crack velocity. Thus, for conditions where only a small stress is required to produce a significant hydrogen flux towards the crack tip, the first term dominates and crack velocity increases with increasing temperature primarily due to increased hydrogen diffusion rate. However, under conditions present in DHC upon heating, the flux of hydrogen is increasingly hindered by the increasing gap between the amount of hydrogen in solution, and the TSSP with increasing temperature. Thus, it appears that the 'plateau' of constant crack velocity with increased temperature in furnace cooled \( \delta \) and reoriented bulk hydride samples upon heating is a point where the increase in crack velocity associated with the increased diffusivity of hydrogen is similar to the decrease associated with the lowered chemical potential due to increasing differences between the amount of hydrogen in solution and the TSSP.

Examination of the data collected from the radial samples shows a slightly different result. First, the samples with bulk \( \gamma \) quenched and furnace cooled \( \delta \) bulk hydrides behave similarly to those in the axial crack growth data set. However, the bulk reoriented hydrides provide significantly different cracking behaviour, with crack velocities being repeatably higher than even the \( \gamma \) quenched samples at 140°C and consistently higher than the furnace cooled bulk \( \delta \) hydrides. This result is not consistent with either the axial crack growth data, or the hypothesis that hydrogen in solution relative to the TSSP is the main factor controlling crack velocity. There are several possible explanations for this behaviour. There is a possibility that the crack
velocities determined in the axial crack growth data set are not correct due to the additional uncertainties associated with the crack measurement methods relative to the radial data set. However, due to the fact that within the axial data set several samples were tested at different times, and the upper end of the range of the data is consistently below the $\gamma$ quenched crack velocities and is directly within the range of the furnace cooled samples indicates that this effect was uniquely observed only in the reoriented radial samples. We therefore believe the effects are real. The potential contributing differences between the axial and radial sample crack growth geometries are summarised by the following:

- The diffusion of hydrogen is anisotropic in Zr-2.5 wt% Nb due to texture and $\beta$ filaments. This may contribute to differences in the cracking behaviour between the axial and radial samples.

- The sample geometry of the axial samples is such that the entire crack plane is subjected to tensile stresses when loaded in a test. This is however not true in the radial crack growth samples due to the samples curvature producing a compressive bending stress at the back half of the crack plane. This has the possibility of increasing the stress gradient between the hydrogen in solution/dissolving bulk hydrides and the precipitating hydride at the crack tip.

- The sample thickness of the radial samples was 3.15mm and the sample thickness of the axial samples was 2.78mm, although this is not expected to result in appreciable change in crack behaviour.

- The hydride morphology is different in each pressure tube direction. There is a possibility of an interaction between a growing or cracking hydrided region and
the bulk hydrides.

Of these we believe that there are two possible explanations to cause these observed differences in the radial geometry samples. One is the possibility that the compressive stresses in the back half of the sample are affecting the chemical potential driving hydrogen diffusion in the reoriented bulk hydrides to a greater extent than any of the other hydride populations. Considering the fact that the applied stress associated with the precipitation of reoriented bulk hydrides is perpendicular to the hydride platelet, the applied compressive stresses would act in direct opposition to the stresses that shifted the hydride stability from the axial-transverse plane to the radial axial plane. Therefore, in the case of bulk reoriented hydrides, the compressive stresses would change the stress gradient between the dissolving bulk hydride and the crack tip hydride. This can be contrasted with the case of the furnace cooled δ hydrides, of which only in hydride-plane stresses and hydrogen in solution would be affected by the compressive stress. Since the stresses surrounding the reoriented hydrides are tensile, these constraint stresses would therefore relax, which would actually lower the stress gradient, and therefore decrease the crack velocity. Consequently, this isn’t expected to be a major contributor to the experimental data. The compressive stresses at the back of the radial sample would also affect the stress in the hydride, by increasing the compressive stresses that would otherwise be present. The effects of this are unknown, but it is postulated that this could affect the hydride solvus. This suggests that the hydride interaction energy, $w_a$ may have an effect on the ability to remove hydrogen out of bulk hydrides. At the moment this inference is purely speculative, but could be studied by measuring the strain evolution of hydrides under the physical conditions in this experimental work. The other reasonable cause is that the bulk hydrides had an interaction with the advancing crack front resulting in an elevated crack velocity in
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the reoriented hydride radial samples relative to the axial samples. This interaction could be a mechanism where a hydrided region fractures deeper into the crack plane due to a favourably aligned hydride resulting in more cracked area for some segments of the crack section. There is some evidence of crack-hydride interaction in both the radial and axial samples, but the effect appears to be greater in the radial crack growth samples. However, for any conformation, this must be quantifiable different between the radial and axial samples. Fig. 5.9(b) and Fig. 5.9(c) show the reoriented hydrides that would directly influence the propagating crack in the radial and axial cracking directions respectively. Although there does not appear any appreciable differences in average hydride length between the axial and radial directions of the reoriented hydrides, there is a distinct difference in the hydride morphology. The reoriented radial-axial hydrides remain very straight but are out-of-plane across the crack in the axial crack growth direction and are significantly less straight but in-plane across the crack in the radial direction. Consequently, increased crack velocities may be expected in the radial crack direction due to the increased likelihood of the growing crack intersecting a bulk hydride. Unfortunately, the magnitude of difference expected between each cracking direction is difficult to estimate and the differences between axial and radial samples are hard to quantity. This effect may actually be accentuated by the fact that most radial samples had their terminal velocities measured at stress intensities between 20 – 25 MPa√m in contrast to the axial samples that were generally measured below that, usually around 17 – 18 MPa. Where the increased stress intensity is not expected to affect the chemical potential between the bulk and the crack tip at high stresses, it may provide an increased ability to fracture the radial-axial hydrides, and thus increase the crack velocity due to increased
amounts of bulk hydride fracture. Unfortunately, it is difficult to assign a complete description to the differences between the axial and radial reoriented data sets beyond the preceding speculation without further experimentation. All that can be concluded is the fact that the bulk reoriented hydrides do affect the geometry of the crack front (Fig. 5.37/Fig. 5.38) and fracture surface (Fig. 5.40/Fig. 5.42) and that this is likely to increase the crack growth rates of these samples. These effects are significantly more prevalent in the radial reoriented samples, and therefore we believe are the main reason for the reoriented hydride samples cracking faster than the $\gamma$ quenched samples at 140°C and always faster than the furnace cooled $\delta$ samples in the radial sample geometry. The reason this was not prevalent in the axial samples was because these effects were minimised by the fact that $DHC_v$ measurements were made at lower stress intensities and that the bulk hydrides were less likely to interact with a growing crack due to their flat morphology. This is also supported by the fact that the bulk hydride-crack interactions became more prevalent when the stress intensities were highest in the reoriented radial samples.

5.5.4 Modelling

A brief modelling attempt was undertaken using the model developed by Puls using some inputs from Ambler [157] and following the general structure of the calculations in Mieza et al. [69]. Using all of the parameters described previously in the section on dissolution, Sec. 5.2.5, and velocity equations and parameters in Sec. B.3, Fig. 5.51 was created. Sec. B.3 contains all of the parameters and measurements used in the calculation of these values. Here it is observed that the model correctly captures the similarities between the $\gamma$ quenched and cooled samples as well as the
furnace cooled and δ samples. While it captures the increase of crack velocity with increasing temperature and similar magnitude to the experimental data, it fails to accurately predict the plateauing and eventually ceased crack growth with increasing temperature in the furnace cooled δ and reoriented hydride samples. Manipulation of several parameters reveals that capture of the plateau and arrest behaviour is possible through manipulation of the dissolution solvus, which is essentially what Ambler does to match his data set in Ref. [157]. This reveals just how sensitive the model can be to the dissolution and precipitation solvi used. A change in the solvus by a few ppm H can change the outcome of model from predicting crack arrest to a valid and stable velocity. Therefore, no additional distinction can be made regarding the justification for the observed behaviour without further physical evidence.

There are several possibilities as to why the present formulation of the model does not correctly predict the plateau and arrest behaviour. Perhaps the most likely cause is the fact that the established dissolution curve used to represent the dissolution of furnace cooled δ and reoriented hydride is not entirely accurate. Given the fact that the γ quenched samples had a markedly different dissolution solvus measured by synchrotron diffraction, it seems likely that TSSD behaviour is easily and significantly shifted based upon the hydride population. Consequently, until some justification for all of the varied dissolution curves of furnace cooled hydrides (several are listed in Sec. 5.2.5) is understood or an experiment is run in a setup that allows measurement of dissolved hydrogen during DHC, can this suggestion be verified. Another suggestion is the possibility that the stress induced chemical potential driving DHC is defined incorrectly. The original paper discussing the stress gradient was developed with steels in mind and although the formulation may be correct of zirconium, this
Figure 5.51: Predicted crack velocities from implementation of Puls model
is not supported by any evidence. Direct evidence of this would mean a physical measurement of the shift of hydrogen concentration as a result of applied and measured stresses. Measurement of this in zirconium would allow confirmation of this parameter. The final inference was the postulation that the initial crack tip hydride is of $\gamma$ phase, which could possibly shift the effective the TSSP low enough to make cracking possible. However, if this were the case, there would likely be a difference in the test results of all samples at 140°C and 220°C not directly linked by the general thermodynamic approach (ie. solubility differences and temperature).

5.5.5 General Discussion

The present work provides further insight into the currently debated models for DHC. This data set provided measurements of both the terminal crack velocity, the critical stress intensity required for crack growth and some instances of the stress-velocity relationship for stage I crack growth for DHC with three distinct hydride populations upon heating and DHC upon cooling under full supersaturation conditions in two pressure tube directions. Experimentally, the results are consistent with a similar study conducted by Ambler [157] and a large number of the experimental results produced by Shek in Ref. [45] based upon diffusible hydrogen content, amongst other studies.

Although DHC upon cooling to the test temperature has been studied extensively, this study sought to observe DHC primarily under conditions of heating, for which few studies have been completed. The unique feature of DHC upon heating was the possibility of varying the amount of hydrogen in solution due to the different dissolution behaviour of different bulk hydrides at the same test temperature while maintaining
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the same TSSP. This is an alternative means to Shek’s test method which varied the concentration of hydrogen in solution by first heating to various temperatures to dissolve a certain amount of hydrogen then cooling to the given test temperature. The first intention is to verify that the amount of diffusible hydrogen in solution is the main factor contributing to DHC upon heating. This was verified by producing three different hydride populations, observing or inferring the hydrogen dissolution behaviour upon heating to a test temperature (to estimate the concentration of hydrogen in solution), and measuring cracking parameters.

Crack initiation in this study is easily explained using a similar methodology to that of Shek [45] in his experiments varying the dissolved hydrogen concentration with thermal manoeuvres. Shek cited two distinct conditions for $K_{IH}$, one where the crack tip hydrided region is ‘fracture’ limited and one where the hydride is ‘growth’ limited. Conditions where the crack tip region is primarily fracture limited occurred when the chemical potential between the bulk and crack tip was high due to the easily accommodated precipitation of hydride at the crack tip hydrided region. Therefore, the fact that $K_{IH}$ was nearly identical and increased only slightly with increasing temperature in both the $\gamma$ quenched sample upon heating and for the sample cooled to the test temperature indicates that these cracking conditions were ‘fracture’ controlled. This is consistent with the the hydrogen in solution conditions expected from these thermal manoeuvres, as the heated $\gamma$ quenched samples and those cooled to the test temperature had hydrogen contents in solution at or near the TSSP required for hydride precipitation. Consequently, although only a slight stress would be required to setup a hydrogen chemical potential in these samples, a larger stress intensity between $6 - 8MPa\sqrt{m}$ was required to fracture the hydrided regions. In contrast, the
samples containing furnace cooled δ and reoriented hydrides experienced a rapidly increasing $K_{IH}$ with increasing temperature due to the fact that applied stress required to produce a chemical potential gradient large enough to precipitate crack tip hydrides is greater than the critical hydride size characteristic of the material conditions in a fracture controlled hydride. This is consistent with the inferred hydrogen dissolution behaviour, as there is expected to be a significant difference between the amount of hydrogen in solution and the TSSP in these samples. Ultimately, it appears that $K_{IH}$ is best represented by the difference between the amount of hydrogen in solution and the TSSP at the given test temperature. This is relevant for both DHC upon heating as shown in the present study, but also in all conditions demonstrated by Shek during cooling [45] (Fig. 5.50). The combined results of these studies indicate that there is a critical chemical potential difference required to have enough hydride precipitation to result in a 'fracture' controlled $K_{IH}$ and is estimated to be what amounts to approximately 15 wt ppm H. Otherwise, the hydride may be in a growth limited cracking condition, and $K_I$ needs to be higher for DHC to occur.

The crack velocity data can also be described with a similar explanation. The present data indicates that crack velocity can increase as a result of two main factors. Increasing temperature results in increasing diffusion rates of hydrogen, and therefore elevated hydrogen flux and crack velocity. Increasing the chemical potential difference between the bulk and the crack tip also results in an increase in the hydrogen flux and consequently crack velocity.

This is directly observable in the present work. During stage II crack growth, the peak hydrostatic stress in all samples is expected to be similar, due to the fact that the crack tip hydride is fully contained in the crack tip plastic zone, and consequently
the stress gradient between the bulk and crack tip should be similar in all samples. This is also true of the TSSP required for precipitation of a crack tip hydride, which is not expected to be change between any of the hydride populations. In contrast, the concentration of hydrogen in solution at each given test temperature is different in the different cracking conditions. Consequently, although the stress gradient in all test conditions was similar, the chemical potential gradient was not. Therefore, conditions where the concentration of hydrogen in solution is close to the TSSP at a given temperature will produce an elevated chemical potential gradient and thus greater crack velocity. In the current work, this was observed as elevated and increasing crack velocities with temperature in the $\gamma$ quenched upon heating and cooled samples which correlates with the fact that the concentration of dissolved hydrogen in both samples is nearly the same as the TSSP. In the furnace cooled $\delta$ and reoriented hydride samples have significantly lower amounts of diffusible hydrogen in solution and therefore, their crack velocities are lower. In addition, due to the fact that the difference in the TSSP and hydrogen solubility in these samples increases with temperature, the chemical potential decreases with increasing temperature, which effectively works in opposition to the improved diffusion abilities, leaving similar crack velocities at all tested temperatures.

Ultimately, a reasonable prediction of DHC behaviour is possible purely by knowing the concentration of hydrogen in solution and the conditions for hydride precipitation at the crack tip (TSSP in this case). The present study proves that the magnitude of the effective solubility differences between the crack tip and the bulk can sufficiently describe both $K_{IH}$ and $DHC_{vt}$ for samples regardless of their heat treatment. This work is, in general, consistent with the current understanding that
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the chemical potential difference between the bulk and the crack tip is the driving force for DHC.

One final considerations should be addressed. No evidence of an apparent stress induced phase transformation at the precipitating crack hydride was observed. This is because the cracking behaviour at 140°C and 220°C was basically predictable with respect to the thermodynamic approaches described previously. Most sources that indicate $\gamma$ hydride stability (including the present measurements, which shows stability up to 150°C) suggest that $\gamma$ hydride is likely stable below 140°C on heatup from a quench and $\delta$ phase is definitely stable at 220°C. Therefore, since there is no obvious difference between the cracking behaviour at these two temperatures, a contribution to DHC upon heating as a result of a possible $\gamma$ phase crack tip hydride is unlikely.

5.6 Conclusions and Recommendations

The following conclusions can be made from the present experiments:

1. $\gamma$ quenched hydrides were observed to dissolve in greater amounts at lower temperatures than that of furnace cooled $\delta$ hydrides. Although the direct reason for this is not known, it it suggested this may be due to the reduced matrix constraint on the $\gamma$ hydride phase due to differences in the volume expansion, the hydride morphology or the hydride microstructure. Regardless, this is evidence that the measured TSSD can be very sensitive to the prior thermomechanical treatment. The dissolution behaviour of samples with reoriented bulk hydrides was observed to be similar to that of the naturally orientated hydrides with a
similar hydride phase and size distribution. The different amounts of hydrogen in solution were found to affect DHC.

2. Crack initiation was found to depend on the difference between the amount of hydrogen in solution and the TSSP in addition to the test temperature. In the cases where the amount of hydrogen in solution is similar to the TSSP, crack initiation occurred at stress intensities in excess of \(6 \leq 8 MPa \sqrt{m}\), which is the result of \(K_{IH}\) not being constrained by the stress gradient but by the fracture properties of the crack tip hydrided region. Conversely, in the cases where the concentration of hydrogen in solution was significantly less than the TSSP, the stress gradient required to produce a significant crack tip hydrided region was greater than that required to fracture the hydrided region, and consequently, \(K_{IH}\) increased from 7 to 15\(MPa \sqrt{m}\) in the axial samples and 7 to 23\(MPa \sqrt{m}\) in the radial samples.

3. Stage II crack velocity was also determined to be primarily affected by the difference between the amount of hydrogen in solution and the TSSP, and the test temperature. In the cases where the concentration of hydrogen in solution was similar to the TSSP, the chemical potential gradient driving hydrogen diffusion to the crack tip was high and therefore a higher crack velocity was observed. These velocities also increased with increasing temperature due to the elevated hydrogen diffusion properties. In contrast, when the amount of hydrogen in solution was significantly lower than the TSSP, the chemical potential gradient was greatly reduced under the same stress gradient and crack velocity was decreased and the temperature did not strongly affect the crack velocity.
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4. In some cases, the crack velocity in the samples with hydrides oriented in the crack plane had crack velocities that were higher than the thermodynamic model would suggest. This was suggested to be a result of an interaction between the advancing DHC front and the existing bulk radial-axial hydrides. This was more prevalent in both the radial crack growth samples, and at higher stress intensities.

5. No evidence of crack tip $\gamma$ hydrides or a proposed stress induced $\gamma \rightarrow \delta$ phase transformation was observed. Due to the fact that the TSSD was highly variable between the established furnace cooled $\delta$ TSSD curve and the measured $\gamma$ quenched hydride TSSD curve, and that several TSSD measurements in the literature have produced different results and that small solvus uncertainties (ie. 2-3 ppm H) can directly shift the predicted behaviour, it seems that hydride dissolution is likely not correctly captured in many experiments.
Chapter 6

Concluding Thoughts

I used to bulls-eye whomp rats in my old T-16 and they’re not much bigger than 2 metres

— L. Skywalker

The present work discussing bulk hydrides and their effects on delayed hydride cracking (DHC) are additions to the long running work on the zirconium hydrogen system and its engineering applications. Taken as a whole, these studies indicate that although there is substantial understanding of the zirconium hydrogen system. However, many factors are not yet explained

6.1 Bulk Hydrides

The work on bulk hydrides in Chap. 3 serves to indicate that both the phase and morphology of bulk hydrides in zirconium are sensitive to several factors including alloy, hydride heat treatment, microstructure and yield strength. Unfortunately, the
contributions from all of these factors on the hydride phase and morphology remain unclear. Ultimately, there are several drivers to further understanding of zirconium hydrides. First, knowledge of how the mechanical properties of a component are affected by bulk hydrides and certain conditions are required in order to prevent failures in zirconium components. Accurate prediction of this is only possible by determining the general nature of zirconium hydride precipitates. Most of the discussion in Chap. 2 and Chap. 3 suggested that the bulk hydride phase is probably affected by the conditions around the nucleating hydride precipitate and whether or not there is a high or low hydrogen saturation. The literature covering the phase stability of zirconium hydride in particular is extensive and often contradictory. Although the present study was designed with the intention of answering some of the questions, in reality, it appears as if this study has actually raised more questions than answers. Due to the sensitive behaviour of hydride phases, a more organised approach is required in place of numerous studies that attempt to isolate specific features. A suggested path forward is to continue work to quantify the thermodynamical conditions surrounding the zirconium-hydrogen system. This is likely the best way to alleviate the individual effects from standard metallurgical conditions such as grain size, grain shape, phase boundaries and hydrogen distribution/segregation. A likely candidate study would be to further develop some of the phase field models developed in Ref. [180–186] to allow the precipitation of different hydride phases (presently only $\gamma$ hydride is considered) and alloy. Synchrotron diffraction techniques can be used for making average bulk measurement for many of the required parameters including phase, hydride strains, hydride content, texture and even grain/phase shapes. Optical microscopy appears to
be the best method to determine macro hydride morphology and TEM studies provide the details contained in the individual precipitates. This coordinated approach of all of these techniques with an appropriate phase field model has the ability to offer the complete solution to the confusion associated with the zirconium hydrogen system. Obviously, this study is a large undertaking, but the upside is the possibility of actually understanding zirconium hydrides.

The second main benefit of additional studies on bulk zirconium hydrides is the possibility of better understanding dissolution and precipitation behaviour. This is most important for the engineering justification behind DHC mitigation due to the fact that understanding of the conditions for precipitation and the concentration of hydrogen in solution (given by the dissolution or precipitation behaviour) are required for reliable DHC modelling.

6.2 Delayed Hydride Cracking

6.2.1 General Conclusions

The work in Chap. 5 contains a data set that primarily observes crack initiation and crack velocity as a function of different bulk hydrides upon heating which resulted in different amounts of hydrogen in solution during the same test temperatures. The data set is consistent with commonly cited DHC models indicating that the stress induced chemical potential is the driver for DHC. In this study, both crack initiation and crack velocity were shown to be affected primarily by the difference between the expected concentration of hydrogen in solution and the expected TSSP. Several of the DHC models approach the same hydrogen flux equation with significantly
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varied levels of detail. Ultimately, it appears that these models, particularly the most recent (and) complex iteration published recently by Puls in Ref. [49], may be overcomplicating things by attempting to account for both dissolving bulk hydrides and the supposed existence of a 'stress free solvus'. Instead, it appears as if DHC could be modelled purely by knowing the amount of hydrogen in solution, the effect of the hydrostatic stress gradient on the chemical potential and the TSSP at a stress raiser. This inference is primarily made because samples with similar amounts of hydrogen in solution and very different bulk hydrides do not appear to affect DHC. This brings into question exactly which terms are relevant in the most recent iteration of the Puls model. This has actually been somewhat indirectly brought to attention by the other recent work by McRae et al. [113]. As declared by Puls himself [49]:

McRae and co-workers refer to their DHC propagation rate model as a Diffusion First Model (DFM) suggesting that it is a refinement of the original Dutton-Puls model, the latter of which they claim is flawed because...shows that the DFM is identical to the Dutton-Puls model.

which suggests that both models are essentially the same. The main difference is that Puls seems to attempt to model from a very theoretical basis encompassing everything from determining the effective solubilities by relating a 'stress free hydrogen solvus', to work terms associated with hydride accommodation and interaction energies. In contrast, the McRae et al. approach appears to instead require only knowledge of the stress gradient, the concentration of hydrogen in solution and the concentration required for hydride precipitation. The Puls model may be correct in its theoretical basis, but it may introduce terms that are not required to accurately predict DHC behaviour given the level of variability associated with DHC and lack of physical
knowledge of several parameters within the Puls formulation. Consequently, minor changes in any of the large number of parameters (especially difficult to measure ones including interaction and accommodation energies for dissolving and precipitating and hydrides) in the Puls model could produce either more accurate, or more tunable results (for better or worse). The present study suggests that some of the terms in the Puls equation may be negligible (given the different hydride work terms do not result in different DHC behaviour, as it appears it would in the case of the Puls version of the model).

6.3 Experimental Recommendations

The following are some general recommendations regarding some of the shortcomings in Chap. 5 which could be later addressed in effort to further solidify the conclusions from that study and DHC testing in general:

1. In many cases, the data from the tests on samples with reoriented hydrides were subject to test conditions which may have complicated the results.
   - Since bulk hydrides were oriented in the crack plane, and they appear to have interacted with the advancing crack front, these results are not entirely representative of the pure thermodynamic bulk hydride dissolution response as intended. Consequently, although it is concluded that the reoriented hydride cracking behaviour in the thermodynamic sense is the same as the furnace cooled $\delta$ hydrides, this may not be entirely the case. Unfortunately, the use of a radial-axial hydride as a source of dissolving hydrogen is subject to this complication, and elimination of this effect would be very difficult.
CHAPTER 6. CONCLUDING THOUGHTS

• The dissolution behaviour of the reoriented hydride population in the present study is entirely inferred based upon established pseudo-equilibrium dissolution of furnace cooled hydrides (via CSA N297.8) and the TSSD measurements with DSC indicated the overall dissolution behaviour was similar (within a few degrees at the given hydrogen concentration) to the furnace cooled material. However, this may not necessarily be the case due to the fact that the hydrides in the reoriented hydride material are bi modal (small natural orientation hydrides and large reoriented hydrides) and therefore a varied dissolution behaviour should be expected and may be significantly different from the furnace cooled hydrides. Therefore, it is recommended that a dissolution curve be established for this hydride population using a synchrotron diffraction experiment similar to that of the $\gamma$ quenched hydride population in this study, or alternatively with neutron diffraction techniques.

2. Crack tunnelling was commonplace in many of the samples observed in the present study. Reduction or elimination of these considerations from future tests is only possible by ensuring either pure plane stress or pure plane strain conditions, which would both favour a uniformly growing crack. Plane strain conditions would probably be preferred due to the validity of plane strain linear elastic fracture mechanics and the large crack area would provide the ability to produce more accurate crack measurements, especially in tests where understanding of critical crack tip hydrides and the plastic zone is desired. Most DHC testing is done with pressure tube material, and therefore, the thickest samples are around 4.2mm, well below the threshold typically required for valid plane strain measurements ($12^+\text{mm}$ at the presently tested temperatures).
3. Nearly every single study of DHC that uses the currently developed thermodynamic models make the assumption that the peak hydrostatic stress driving the chemical potential gradient of hydrogen during DHC is representative of the plane strain condition of the peak hydrostatic stress being $2.4\sigma_{ys}$. Unfortunately, it appears that these authors fail to note that plane strain in zirconium at DHC test temperatures requires excess of $12mm$ of sample thickness. Consequently, differences between experiential results (where thicknesses tested are between $3 - 4.2mm$) and modelling attempts (particularly in those that indicate DHC is not possible, such as DHC upon heating) may be sensitive to this assumption. Additionally, under conditions that require a large stress shift such as DHC upon heating, this means that the crack front is subjected to a non uniform peak stress distribution resulting in crack tunneling, which can skew the modelling results even further. It is advised that a study to either understand the depth resolved stress field for samples of different thicknesses or a laboratory investigation of DHC with samples that satisfy the plane strain criterion is undertaken in order to provide verification of suggested DHC stress conditions.

4. Of additional interest is the conditions required for crack arrest upon heating. This is expected to occur when the stress gradient governed by yield stress is not enough to shift the chemical potential gradient enough to produce appropriate diffusion of hydrogen towards the crack tip. Since this difference between the amount of hydrogen in solution and the TSSP increases with temperature upon heating, at some point this difference cannot be overcome by the applied stress gradient, and crack arrest is postulated to occur. This was observed by Ambler.
and some of the data points in the present work. However, a more detailed study on the present samples would complete the present data set, and identify the effective critical hydrogen concentration difference for DHC upon heating, providing further justification for the conclusions already made. This will also have a role in defining the critical stress shift that is possible for DHC to occur, which will be an indirect measurement of the effect of the stress gradient on the chemical potential.

5. The conclusions made in this study are formed by correlating measured or inferred hydrogen dissolution measurements with separately measured DHC behaviour. Unfortunately, this remains indirect evidence of the present justification behind the DHC mechanism. In fact, this argument can be extended to majority of the parameters used in the steady state DHC models. An \textit{in situ} study of DHC in a synchrotron beam could provide the means to almost simultaneously measure the concentration of hydrogen in solution in the bulk and hydride content at the crack tip (inferred if precipitated hydrides exist), the stress in the bulk hydrides, the stress at the crack tip and the stress in the zirconium matrix near the bulk. Such a study could provide definitive verification of the stress shifted chemical potential gradient, concentration of hydrogen in solution and several of the work terms used in the various forms of the chemical potential based models. Since slight variations in several of the terms can shift the outcome of the thermodynamic models, the fact that this study measures many of the parameters at the same time (in place of several educated guesses) could more definitively determine which terms are the most important.
References


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REFERENCES


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REFERENCES


Appendix A

Symbols in Chemical Potential Gradient Equations

- $\mu^D_H$: Chemical potential driving diffusion of hydrogen
- $p$: Average Hydrostatic Stress difference between crack tip and bulk
- $\mu^o_H$: Hydrogen chemical potential at zero stress
- $T$: Temperature
- $R$: Ideal gas constant, usually $8.312 \, J/molK$
- $C^H_D$: Amount of diffusible hydrogen in solution
- $V_H$: Molar volume of hydrogen in zirconium
- $C^H_P$: Concentration of hydrogen at a stress raiser
- $C^S_H$: Equilibrium hydrogen solvus concentration under zero stress
- $J_H$: Flux of hydrogen towards the crack tip
- $D_H$: Diffusion coefficient of hydrogen in zirconium
- $\Omega_{Zr}$: Atomic volume of zirconium
- $\phi(l, L)$: Hydrogen concentration gradient, $\ell(L/\ell)$
- $\nabla^D_H$: chemical potential gradient
Appendix B

Sample Calculations

B.1 Hydride Expansions

The volume expansion of $\delta$ hydride is 17.2% relative to the zirconium matrix.
The volume expansion of $\gamma$ hydride is 12.3% relative to the zirconium matrix.
The hydrogen enrichment of $\delta$ hydride is approximately $\text{ZrH}_{1.66}$.
The hydrogen enrichment of $\gamma$ hydride is approximately $\text{ZrH}$.
Normalising the expansion for each hydrogen atom:
For $\delta$ hydride:
$17.2%/1.66 = 10.36 \%$
For $\gamma$ hydride:
$12.3%/1 = 12.3\%$

Therefore, although the unit cell of $\delta$ hydride is larger, there will be more total hydride volume in a sample containing $\gamma$-hydrides because there will be more 'unit cells' of $\gamma$ hydride for the same hydrogen content.
B.2 Hydride Volume Fraction to wt ppm

For a sample of hydride containing a volume fraction of $\delta$ hydride $V_{\delta}$, volume fraction of $\gamma$ hydride $V_{\gamma}$, and volume fraction of alpha zirconium $V_{\alpha}$, where $V_{\delta} + V_{\gamma} + V_{\alpha} = 1$. The mass of hydrogen is given by the expression:

$$m_H = V_{\gamma}\rho_{H,\gamma} + V_{\delta}\rho_{H,\delta}$$ (B.1)

The mass of zirconium is given by the expression:

$$m_{Zr} = V_{\gamma}\rho_{Zr,\gamma} + V_{\delta}\rho_{Zr,\delta} + V_{\alpha}\rho_{Zr,\alpha}$$ (B.2)

where $\rho(x,y)$ is the density of species $x$ in crystal $y$.

$$\rho(x,y) = \frac{m_{x,y}}{V_y} = \frac{N_x M_x}{N_A V_y}$$ (B.3)

where $m_{x,y}$ is the mass of species $x$ in the unit cell of $y$, $N_x$ is the number of atoms of species $x$ in the unit cell, $M_x$ is the molar mass of species $x$ and $N_A$ is Avogadro’s number. Thus, using the unit cell and crystal structures listed in Table 2.1, the partial densities $\rho$ can be calculated. $\rho_{H,\gamma}$ represents the density of hydrogen in fct $\gamma$ hydride with a hydrogen enrichment of $ZrH$ and lattice parameters a=0.4596 nm and c=0.4969 nm. Since the fct unit cell contains 4 lattice (Zr) atoms, the stoichiometric ratio between Zr and H is 1:1, Eq. B.3 becomes:

$$\rho(H,\gamma) = \frac{N_x M_H}{N_A V_\gamma}$$ (B.4)
APPENDIX B. SAMPLE CALCULATIONS

\[ \rho(H, \gamma) = \frac{4.101 \text{g/mol}}{0.02 \times 10^{23} \text{mol}} \times 0.4596 \times 0.4596 \times 0.4969 \text{nm}^3 \] (B.5)

which can be when subbed back into Eq. B.1 to solve for \( m_H \). A similar procedure is used to evaluate \( \rho \) for all other parameters. Once all \( \rho \) terms have been evaluated, the weight fraction of H in Zr can be computed by dividing Eq. B.1 by Eq. B.2 such that:

\[ \text{ppm}[H] = \frac{m_H}{m_{Zr}} \] (B.7)

B.3 Crack Velocity

The theoretical DHC velocity (Puls Model) is calculated by relating the flux of hydrogen diffusing from dissolving hydrides located at L to a precipitating crack tip hydride at \( \ell \) (in accordance with Fig. 4.1) to estimates of the 'critical crack tip hydride size'. The velocity is calculated with the relation in Eq. B.8:

\[ DHC_v(T) = \frac{2\pi D}{\Omega_{Zr} \Phi t_h N_H x} \{ E_L - E_i \} \] (B.8)

Where D is the diffusion coefficient of hydrogen in zirconium, \( \Omega_{Zr} \) is the atomic volume of zirconium, \( N_H \) is the atomic density of hydride, \( t_h \) is the thickness of the crack tip hydride at fracture, \( \Phi \) is the hydrogen concentration gradient, and \( x \) is the concentration of hydrogen atoms in the hydride \( ZrH_x \). \{ \( E_L - E_i \) \} represents the extent of hydrogen solubility differences as a result of the stress gradient between
dissolved or dissolving and precipitating hydrides at distances $L$ and $l$ from the crack tip, respectively. Combining all of the first terms into a temperature dependant value $C(T)$ and in Eq. B.9 produces the following representation.

\[ DHC_v(T) = C(T) \{E_L - E_\ell\} \]

The parameters $E_L$ and $E_\ell$ are essentially representations of the hydrogen concentrations surrounding dissolved or dissolving and precipitating hydrides respectively as a result of the stress gradient and have been represented in several different manners throughout the development of steady state DHC models, with their first application in Ref. [43]. Specifically, $E_L$ represents the solubility of hydrogen in the bulk of the material affected by the stresses at $L$ such that, in the general case:

\[ E_L = C_H \exp \left( \frac{w^a}{RT} \right) \]

\[ E_\ell = C_C \exp \left( \frac{w^a}{RT} \right) \]

where $C_H$ is the solubility of hydrogen in the presence of the hydrides at $L$ upon heating and $w^a_i$ is the total interaction energy per mole H due to hydride formation at $L$ or $\ell$. The interaction energy term $w^a_i(L)$ and $w^a_i(\ell)$ are described as follows:

\[ w^a_i = -\frac{\nabla_{zr}}{x} \sigma^a_{ij} e^T_{ij} \]

Where $\nabla_{zr}$ is the partial molar volume of zirconium, $x$ is the hydrogen enrichment in the hydride, $\sigma^a_{ij}$ is the applied external stresses and $e^T_{ij}$ is the stress free hydride transformation strains. It is presently noted that the values at $L$ and $\ell$ are different.
Table B.1: Terms used to calculate the interaction energy due to hydride formation under external stress. Stresses are justified in Ref. [43] and strains are justified in Ref. [51].

due to the different stresses and strains. $\sigma_{ij}^a$ has been be calculated in the literature to hold for plane strain conditions and is justified in Ref. [43] and the stress free hydride transformation strains are justified in Ref. [51] and the value for $\bar{w}_i^a$ is the summation over the repeated indices [69]. Although plane strain conditions are not met in virtually any DHC experiment (~12 mm thickness is required) the plane strain values are used to stay consistent with the literature up to the present date (described previously).

$C_H$ is very sensitive to the parameters described previously in Sec. 2.2, but in short, the hysteresis in the solubility of hydrogen in zirconium means that the solubility of hydrogen at any given point will be a result of the thermal history. If the hydride in question is approached from below the test temperature, hydrides will be dissolving
APPENDIX B. SAMPLE CALCULATIONS

and the solubility can be written as:

\[ C_H = C_S \exp\left(-\frac{\overline{Q}_{\text{heat}}}{RT}\right) \] (B.13)

Alternatively, if the hydride is precipitating the solubility is \( C_C \) and the equation becomes:

\[ C_C = C_S \exp\left(-\frac{\overline{Q}_{\text{cool}}}{RT}\right) \] (B.14)

Where \( C_S \) is the stress free equilibrium solvus, \( \overline{Q}_{\text{heat}} \) is equal to \( \overline{w}_{\text{inc},p} - \overline{w}_{\text{inc}} \), \( \overline{Q}_{\text{cool}} \) is equal to \( \overline{w}_{\text{inc},p} + \overline{w}_{\text{inc}} \), where \( \overline{w}_{\text{inc}} \) is the plastic component of the accommodation energy per mole H and \( \overline{w}_{\text{inc},p} \) is the remaining elastic contribution. This is due to the fact that there is no contribution of the plastic component of the accommodation energy on heating (plastic work is not reversible on dissolution). Consequently, if the test temperature is reached upon cooling from a higher temperature, then \( C_H \) is calculated based upon the work required to precipitate hydrides, and \( \overline{Q}_{\text{heat}} \) is substituted with \( \overline{Q}_{\text{cool}} \), which is the sum of \( \overline{w}_{\text{inc},p} \) and \( \overline{w}_{\text{inc}} \). However, since the present work deals primarily with DHC upon heating, the equation in Eq. B.13 the present case will be used. This requires the accurate determination of either the elastic-plastic and plastic accommodation energies or either of the dissolution/precipitation energies. Puls [43] attempts to determine these values by modifying the calculated accommodation energies of spherical particles described by Lee et. al [187]. The values for these as a function of temperature and two yield stresses are located in the Puls [43] reference and the values at 473K are included in Table B.2. \( C_S \), or the stress free solvus is made note of in Ref. [95] as being, at least, close to what is affectionately regarded by some DHC researchers as the 'Kearns' line [39] for hydrogen solubility in zirconium and is
equal to $9.9 \times 10^4 e^{-8250/RT}$ ppm H. However, both $C_H$ and $C_C$ can also be represented by the otherwise established TSSD and TSSP values for a given thermal treatment. Evaluation of $E_\ell$ and $E_L$ is therefore possible based upon substituting the solubilities of bulk and crack tip hydride solubilities at the given temperatures into Eq. B.10 and Eq. B.11. Therefore, if $E_L > E_\ell$, there will be a net flux of hydrogen towards the crack tip, and DHC will occur and the magnitude will be the C(T) term from Eq. B.9 multiplied by $\{E_L - E_\ell\}$. Consequently, the greater the chemical potential gradient, the greater the crack growth rate.
<table>
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<th>Meaning</th>
<th>Value</th>
<th>Source</th>
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<tr>
<td>D</td>
<td>Diffusion Coefficient (m/s²)</td>
<td>$2.9e^{-34700/RT}$</td>
<td>[144]</td>
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<tr>
<td>$\Omega_{Zr}$</td>
<td>Atomic Volume of Zr (m³/atom)</td>
<td>$2.3 \times 10^{-29}$</td>
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<tr>
<td>$t_h$</td>
<td>Thickness of critical hydride (m)</td>
<td>$1.5 - 1.7 \times 10^{-6}$</td>
<td>[98, 149]</td>
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<td>$\Phi$</td>
<td>Hydrogen concentration gradient</td>
<td>$6.13 \times 10^{28}$</td>
<td>[149]</td>
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<td>$N_H$</td>
<td>Atomic density of zirconium hydride (atoms/m³)</td>
<td>$1.66$ for δ hydride</td>
<td>[149]</td>
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<tr>
<td>x</td>
<td>hydrogen atoms in the hydride $ZrH_x$</td>
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<td>-</td>
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<tr>
<td>T</td>
<td>Temperature (K)</td>
<td>8.314</td>
<td>-</td>
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<tr>
<td>R</td>
<td>Universal gas constant (J/mol K)</td>
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<td>-</td>
</tr>
<tr>
<td>$\overline{\omega}_{el,p}^{inc}$</td>
<td>Elastic accom. energy/mol. H w/ plasticity</td>
<td>See Ref. for chart, 0.67 kJ/mol H @473K</td>
<td>[43]</td>
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<tr>
<td>$\overline{\omega}_{p}^{inc}$</td>
<td>Plastic accom. energy/mol. H</td>
<td>See Ref. for chart, at 473K 0.8443 kJ/mol H</td>
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<td>$\overline{Q}_{heat}$</td>
<td>Energy to dissolve a hydride per mole H</td>
<td>$\overline{\omega}<em>{el,p}^{inc} - \overline{\omega}</em>{p}^{inc}$, -0.18 kJ/mol H @473K</td>
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<tr>
<td>$\overline{Q}_{cool}$</td>
<td>The energy to precipitate a hydride per mole H</td>
<td>$\overline{\omega}<em>{el,p}^{inc} + \overline{\omega}</em>{p}^{inc}$, 1.51 kJ/mol H @473K</td>
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<tr>
<td>$V_{hyd}$</td>
<td>Hydride volume per mole H</td>
<td>$16.3 \times 10^{-6}m^3/mol H$</td>
<td>[51]</td>
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<tr>
<td>$V_H$</td>
<td>molar volume of hydrogen</td>
<td>-</td>
<td>-</td>
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<td>$C_S$</td>
<td>Stress-free equilibrium solvus of hydrogen in Zr</td>
<td>$9.9 \times 10^4 e^{-34650/RT}$ ppm H,</td>
<td>[39, 95]</td>
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<td>$C_H$</td>
<td>TSSD of δ or reoriented hydride in PT</td>
<td>$81900 \ exp[-34500/RT]$</td>
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<td>$C_C$</td>
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<td>$\sigma_{ij}$</td>
<td>Applied external stresses</td>
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<td>$\epsilon_{ij}$</td>
<td>Hydride stress free transformation</td>
<td>see Table B.1</td>
<td>[51]</td>
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</tbody>
</table>

**Table B.2:** Parameters used in theoretical velocity calculation
Appendix C

Test Summary

The following Table C.1 and Table C.2 summaries all of the DHC tests from the present experiment. The indicator V-K means the test was of the style where load was increased stepwise and cracking velocity was measured as a function of stress intensity. $DHC_{vt}$ means that the test was a terminal velocity test, or an attempt to measure the stage II cracking velocity. cal. indicates that a sample was used to calibrate the potential drop signal, either in fatigue (most cases) or in DHC (some radial samples). Although other samples were tested in addition to those here, they were removed because of some experimental error or test failure.
### Table C.1: Summary of all axial DHC test samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Crack direction</th>
<th>Test</th>
<th>Hydride</th>
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</thead>
<tbody>
<tr>
<td>B</td>
<td>axial</td>
<td>V-K - heating</td>
<td>reoriented</td>
</tr>
<tr>
<td>C</td>
<td>axial</td>
<td>V-K - heating</td>
<td>reoriented</td>
</tr>
<tr>
<td>D</td>
<td>axial</td>
<td>V-K - heating</td>
<td>reoriented</td>
</tr>
<tr>
<td>E</td>
<td>axial</td>
<td>V-K - heating</td>
<td>reoriented</td>
</tr>
<tr>
<td>F</td>
<td>axial</td>
<td>$DHC_{vt}$</td>
<td>reoriented</td>
</tr>
<tr>
<td>G</td>
<td>axial</td>
<td>V-K - heating</td>
<td>reoriented</td>
</tr>
<tr>
<td>I</td>
<td>axial</td>
<td>V-K - heating</td>
<td>reoriented</td>
</tr>
<tr>
<td>J</td>
<td>axial</td>
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Table C.2: Summary of all radial DHC test samples

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<td>180 - broach, cal.</td>
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<tr>
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