ADVANCED TECHNIQUES FOR THE CHARACTERIZATION OF HYDRIDED ZIRCONIUM ALLOY

by

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Abstract

Zirconium alloy pressure tubes are an important component in CANDU nuclear reactors. During operation these tubes can pick up hydrogen as a result of a corrosion reaction, which can eventually lead to the precipitation of a secondary, brittle zirconium hydride phase. Hydrides tend to first form at flaws (stress concentrations), and when they fracture can initiate a time-controlled crack growth mechanism known as delayed hydride cracking (DHC). Since DHC is a known failure mechanism for pressure tubes, and an ongoing concern in the nuclear industry, more fundamental knowledge is required about the behaviour of hydrides precipitated at flaws. Several approaches were employed in this thesis to better characterize the effects and behaviour of hydrides at such stress concentrations.

High energy X-ray diffraction, as well as in-situ SEM testing coupled with digital image correlation, were used to map the strains around stress concentrations where hydrides were present. These studies highlighted important differences in the behaviour of the hydride phase and the surrounding zirconium. To gain greater insight into hydride morphology, neutron tomography was used in an attempt to measure the through-thickness hydride distribution at flaws. A finite element model was also developed and verified against the X-ray strain mapping results. This model provided greater insight into details that could not be obtained directly from the experimental approaches, as well as providing a framework for future modeling to predict the effects of hydride precipitation under different conditions. Taken as a whole, these studies provide important information for improving service guidelines and avoiding conditions that favour embrittlement due to hydride precipitation.
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<td>Acoustic Emission</td>
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<tr>
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<td>AFM</td>
<td>Atomic Force Microscope</td>
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<tr>
<td>APS</td>
<td>Advanced Photon Source</td>
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<td>BCC</td>
<td>Body Centered Cubic</td>
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Chapter 1

Introduction

1.1 Zirconium Alloys in Nuclear Reactor Design

The harsh environment within the core of a nuclear reactor creates challenges in material design and selection not encountered in other engineering applications. Any material selected for use must be capable of withstanding high temperatures, pressures, prolonged exposure to intense radiation fields, and the corrosive environment within the reactor. In addition, the effect of a material on neutron economy within the operating reactor must be considered. A material selected for structural core components must have low thermal neutron absorption, in addition to meeting the requirements for mechanical properties. Most traditional engineering materials fail the requirement for either neutron permeability (steel, titanium) or mechanical properties (aluminum, magnesium). Zirconium is unique in its ability to meet the requirements for in-reactor structural components [1, 2]. Alloys of zirconium generally fall into two categories: α-Zr single-phase alloys (Zircaloys), and α/β-Zr dual-phase alloys (Zr-Nb alloys). A listing of common alloy compositions is shown in Table 1-1 [1], with mechanical properties for some alloys listed in Table 1-2 [1].
Table 1-1: Chemical compositions of common zirconium alloys for nuclear applications [1]

<table>
<thead>
<tr>
<th>Alloy element</th>
<th>Zircaloy-2</th>
<th>Zircaloy-4</th>
<th>Zr-1Sn-1Nb</th>
<th>Zr-2.5Nb</th>
<th>Zr-1Nb</th>
<th>Excel</th>
<th>Zr-Nb-Cu</th>
<th>Otherrnite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn (wt.%)</td>
<td>1.2-1.7</td>
<td>1.2-1.7</td>
<td>0.9-1.1</td>
<td></td>
<td>0.9-1.1</td>
<td>3.5</td>
<td></td>
<td>0.2</td>
</tr>
<tr>
<td>Fe (wt.%)</td>
<td>0.07-0.2</td>
<td>0.18-0.24</td>
<td>0.1</td>
<td>&lt;650 ppm</td>
<td>&lt;500 ppm</td>
<td>3</td>
<td></td>
<td>0.1</td>
</tr>
<tr>
<td>Cr (wt.%)</td>
<td>0.05-0.15</td>
<td>0.07-0.15</td>
<td></td>
<td>&lt;100 ppm</td>
<td>&lt;200 ppm</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni (wt.%)</td>
<td>0.03-0.08</td>
<td></td>
<td></td>
<td>&lt;35 ppm</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O (ppm)</td>
<td>&lt;900-1300</td>
<td></td>
<td>900-1300</td>
<td>&lt;1000</td>
<td>&lt;1000</td>
<td>&lt;1000</td>
<td>&lt;1000</td>
<td></td>
</tr>
<tr>
<td>N (ppm)</td>
<td>&lt;80</td>
<td>&lt;65</td>
<td>&lt;65</td>
<td>&lt;65</td>
<td>&lt;60</td>
<td>&lt;65</td>
<td>&lt;65</td>
<td></td>
</tr>
<tr>
<td>Nb (wt.%)</td>
<td></td>
<td></td>
<td></td>
<td>0.9-1.0</td>
<td>2.4-2.8</td>
<td></td>
<td>0.8</td>
<td></td>
</tr>
<tr>
<td>Cu (wt.%)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.0</td>
<td></td>
<td>2.4-2.8</td>
</tr>
<tr>
<td>Mo (wt.%)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.3-0.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H (ppm)</td>
<td>&lt;25</td>
<td>&lt;25</td>
<td>&lt;20</td>
<td>&lt;15</td>
<td>&lt;25</td>
<td>&lt;25</td>
<td>&lt;25</td>
<td></td>
</tr>
<tr>
<td>C (ppm)</td>
<td>&lt;270</td>
<td>120-400</td>
<td>&lt;125</td>
<td>&lt;200</td>
<td>&lt;270</td>
<td>&lt;270</td>
<td>&lt;270</td>
<td></td>
</tr>
<tr>
<td>Cl (ppm)</td>
<td>&lt;20</td>
<td>&lt;10</td>
<td>&lt;10</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

|              | Fuel tube and plug material for BWR, PHWR | Fuel tube and plug material for PWR, and PHWR | Experimental fuel tube alloy | Pressure tube material for PHWR | Fuel tube and end plug in VVER | Experimental pressure tube Alloy | Garter spring material for PHWR |

* All the alloys contain Al < 75 ppm, B and Cd < 0.2 ppm, Cu and Mg < 20 ppm, and Hf < 50-150 ppm.

Table 1-2: Mechanical properties of common zirconium alloys for nuclear applications [1]

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Temperature</th>
<th>0.2% yield strength (MPa)</th>
<th>Tensile strength (MPa)</th>
<th>Percent elongation (TCE in %)</th>
<th>Fracture toughness</th>
<th>Creep strain rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure Zr</td>
<td>Room temp</td>
<td>80</td>
<td>220</td>
<td>45</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zircaloy-2</td>
<td>Room temp</td>
<td>45</td>
<td>120</td>
<td>55</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zircaloy-4</td>
<td>Room temp</td>
<td>275</td>
<td>435</td>
<td>20 (18)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zr-1Nb (Annealed)</td>
<td>Room temp</td>
<td>205</td>
<td>272</td>
<td>28</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zircaloy-2</td>
<td>Room temp</td>
<td>127</td>
<td>145</td>
<td>33</td>
<td>K_{IC} = 55-65 MPa.m^{0.5}</td>
<td></td>
</tr>
<tr>
<td>Zr-2.5Nb (Cold worked)</td>
<td>Room temp</td>
<td>270</td>
<td>330</td>
<td>12</td>
<td>K_{IC} = 60-75 MPa.m^{0.5}</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Room temp</td>
<td>600</td>
<td>650</td>
<td>12</td>
<td>J_{IC} = 120-160 kJ.m^{-2}</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>325</td>
<td>460</td>
<td>14</td>
<td>K_{IC} = 6-9 MPa.m^{0.5}</td>
<td></td>
</tr>
</tbody>
</table>

Nuclear reactors operating in Canada use the CANDU (CANada Deuterium Uranium) design. A simplified schematic showing the basic components of a CANDU type reactor core is shown in Figure 1-1 [3]. All the fuel channels in a CANDU reactor run through the reactor vessel, known as the calandria. This vessel is filled with D₂O moderator at ~70°C, which surrounds the fuel channels and thermalizes the high energy neutrons released from fission reactions in the uranium fuel in order to maintain the nuclear chain reaction. The outermost tube of the fuel channel is the calandria tube. Concentric within the calandria tube is the pressure tube, which
contains high pressure (~9.9MPa outlet and ~10.5MPa inlet [4]) D₂O coolant to transport heat produced during the fission of the fuel to the steam generators. The pressure and calandria tubes are separated by spacers, and the annular space is filled with flowing CO₂ in order to insulate the hot pressure tube (temperatures of 250 to 310°C) from the much cooler moderator. Inside the pressure tube sits the fuel bundles, each of which contains an array of elements consisting of UO₂ pellets inside tubular fuel cladding.

Figure 1-1: Simplified illustration showing the arrangement of key components in a CANDU reactor core [3]

In order to maintain neutron economy, which allows the use of natural uranium fuel, the calandria tubes, pressure tubes, and fuel cladding are all made of zirconium alloys. The calandria tubes are Zircaloy-2, the pressure tubes are Zr-2.5Nb, and the fuel cladding is Zircaloy-4. These alloys have the strength and corrosion resistance required for in-reactor operation, as well as low neutron capture cross-sections. This body of work will focus on the behaviour of the
Zr-2.5Nb pressure tubing, which has a nominal composition by weight of Zr-2.5Nb-0.1O-0.1Fe as per CSA Standard N285.6 [5].

1.2 Hydrogen Embrittlement and Delayed Hydride Cracking (DHC)

Hydrogen ingress into zirconium alloy reactor components can have a negative impact on their performance. Low solubility of hydrogen in zirconium results in excess hydrogen precipitating out in the form of brittle hydride phases (ZrH$_x$) [2]. This may lead to degradation in mechanical performance and premature failure of reactor components. In Zr-2.5Nb pressure tubes this is of particular concern due to the high pressure and temperature heavy water coolant that they serve to contain. Corrosion occurs at the interface between the pressure tube and heavy water, freeing hydrogen (deuterium), of which a portion may enter the pressure tube. Noting that hydrogen and deuterium are chemically indistinguishable isotopes, this reaction can be described as:

\[
\text{Zr} + 2D_2O \xrightarrow{\text{yields}} ZrO_2 + 4D
\]

During reactor shutdown, hydride formation can be a particularly damaging problem due to the sharp decrease in hydrogen solubility with temperature. Failure of pressure tubes can also be caused by the time-dependent cracking mechanism known as delayed hydride cracking (DHC), which can occur even in isothermal conditions [6, 7]. DHC can initiate when hydrides form in the region of a sharp flaw or crack. Hydrogen is an interstitial solute, and will diffuse to areas of high hydrostatic tensile stress, and hence hydride formation is favoured at these locations. Whether or not DHC cracking will initiate at a notch depends on whether the stress intensity at that location exceeds the critical value for the onset of DHC, $K_{\text{int}}$; this value is dependent on
temperature and size of the hydride. Once the stress is sufficient, the hydride fractures and the resulting crack propagates through the brittle hydride until it reaches zirconium metal, where its progress is arrested. Subsequently, hydrogen will then diffuse to the new crack tip location, and once the terminal solid solubility for precipitation (TSSP) is again exceeded more hydride will begin to form and will subsequently fracture once a critical size has been reached; this allows the crack to progress further into the material in a stepwise, time-dependent manner which can eventually lead to failure of the pressure tube when the crack is large enough that $K_{IC}$ of the zirconium is exceeded.

1.3 Research Objectives and Thesis Format

The primary objective of the research discussed in this thesis is the characterization of hydrides formed at flaws in Zr-2.5Nb pressure tube material using several complementary techniques. Precipitation and fracture of hydrides at stress concentrations is the first step in DHC, and as such gaining new insight into the fundamentals of hydride behaviour in this condition is important for developing models to evaluate the life of currently operating pressure tubes, as well as making improvements to reduce DHC susceptibility in future pressure tube designs. Since several distinct approaches were applied to understanding the behaviour of hydrides at flaws, each chapter discussing one of these sets of results is written as its own self-contained body of work (Chapters 3-6). While each of these chapters contains a review of literature relevant to the technique used therein, a general review of zirconium and hydride behaviour and metallography will be presented in Chapter 2. The relevance and interplay of these approaches to the overall theme of hydride characterization is discussed in Chapter 7, along with potential avenues for future work in this area.
Chapter 2

Literature Review

The purpose of this literature review is to provide background information on zirconium and zirconium hydride, which is relevant to all studies presented in this thesis. Each of the following chapters containing results from the different studies on hydrided Zr-2.5Nb (Chapters 3-6) contains additional information on literature and experiments pertaining specifically to the methods used in those chapters (e.g. diffraction, modeling).

2.1 Zirconium Crystallography

Dilute zirconium alloys exists predominantly in a HCP α-phase crystal structure below 862°C (pure Zr), and can transform into a BCC β-phase at higher temperatures [8]. There are fewer slip systems in HCP metals than in those with a BCC or FCC structure, and these are anisotropically distributed. In HCP metals with a lower than ideal c/a ratio (1.633), such as zirconium (1.593), slip occurs primarily on \(\{10\bar{1}0\}\) prism planes along the \(\{1\bar{2}10\}\) directions [2]. Slip has also been observed to a lesser extent on the basal \(\{0002\}\) planes in the \(\{1\bar{2}10\}\) directions, as well as on \(\{10\bar{1}1\}\), \(\{1\bar{1}2\}\) and \(\{1\bar{1}2\}\) pyramidal planes in the \(\{1\bar{1}\bar{2}3\}\) directions. Twinning can occur readily in HCP metals, and plays an important role in the deformation of zirconium due to limited slip systems in the crystal c-direction. Tensile loading along the c-axis activates \(\{10\bar{1}2\}\{\bar{1}011\}\) twins, and to a lesser extent \(\{1\bar{1}2\}\{\bar{1}1\bar{2}6\}\) twins. Under compressive loading \(\{1\bar{1}2\}\{\bar{1}1\bar{2}3\}\) twins are dominant, with \(\{10\bar{1}1\}\{\bar{1}012\}\) twins observed at high temperature. Operable slip and twinning systems are shown in Figure 2-1 [2]. Twinning results in large lattice rotations, where the basal poles tend to align with the direction of compressive force [8].
Deformation due to twinning means that it is common for significant crystallographic texture to develop in zirconium and zirconium alloy components during manufacture; this is strongly influenced by the fabrication route [9].

![Figure 2-1: (a) slips systems in α-Zr (top) with slip planes for (c+a) Burgers vectors (bottom); (b) twinning systems in zirconium [2]](image)

### 2.2 Zr-2.5Nb Pressure Tubes

Pressure tubes in CANDU nuclear reactors are fabricated from Zr-2.5Nb (see Table 1-1). As an alloying agent, the Nb allows metastable β-phase to be retained in the alloy at room temperature, which would otherwise revert entirely to α-Zr below ~850°C. This alloy composition containing Nb with a two-phase microstructure at low temperature was found to have a marked improvement in corrosion resistance over Zircalloys [2]; in pressure tubes this is important due to their susceptibility to hydrogen embrittlement stemming from corrosion. A
phase diagram for the Zr-Nb system can be found in Figure 2-2 [10]. Note that in the real system there are other impurities that would shift the lines in the phase diagram somewhat.

The manufacturing of these tubes involves extrusion at 815°C in the two-phase \(\alpha+\beta\) region; the ratio of \(\alpha\) to \(\beta\) at this temperature is \(\sim 60:40\). Following extrusion, the tubes are cold-worked to 27% and stress-relieved at 400°C for 24h before being installed in the reactor [11]. The microstructure resulting from this process consists of \(\alpha\)-Zr grains elongated in the extrusion (axial) direction, and surrounded partially by a grain boundary network of BCC \(\beta\)-Zr filaments [12]. These \(\beta\)-Zr filaments contain \(\sim 50\%\) Nb and are metastable (slowly transforming to \(\beta\)-Nb).

Current pressure tube designs have a crystallographic (0002) texture (\(\alpha\)-Zr) that is primarily transverse, i.e., the majority of the basal (0002) planes have their normals (poles) closely aligned with the circumferential (hoop) direction of the pressure tube. Very few poles are oriented in the axial direction. A typical pressure tube pole figure is shown in Figure 2-3 [4].

**Figure 2-2: Zirconium-Niobium phase diagram [10]**
Figure 2-3: (0002) pole figure for a typical CANDU pressure tube [4] (A=axial, R=radial, T=transverse)

2.3 Zirconium Hydride

2.3.1 Terminal Solid Solubility

The terminal solid solubility (TSS) as it relates to hydrides is the concentration of hydrogen at a given temperature within the zirconium alloy, above which hydrides will precipitate, or below which they will dissolve. For hydrides formed in zirconium alloys, it is well known that there is a significant hysteresis between the temperatures for precipitation and dissolution [13-15]. The reason for this hysteresis is thought to be due to the accommodation energy of hydrides that is necessary due to the misfit strains with the surrounding zirconium matrix resulting from the volume change during hydride precipitation. The nucleation of very small hydrides involves purely elastic accommodation, and the solvus for hydride nucleation \( C_{H}^{nuc} \) can be described with respect to the stress-free, equilibrium solvus \( C_{H}^{S} \) by the relation [14]:

\[
C_{H}^{nuc} = C_{H}^{S} + \Delta C
\]
\[ C_{H}^{nucl} = C_{H}^{S} \exp \left[ \frac{\bar{W}_{el}^{inc}}{RT} \right] \]

wherein \( R \) is the gas constant and \( T \) is the temperature. This describes how the reversible, elastic work necessary for hydride nucleation alters the threshold hydrogen concentration required for precipitation. In order for hydrides to grow to larger (micron) sizes, plastic deformation becomes necessary to accommodate the volume change of the plastic region. Plastic deformation represents irreversible work done by the precipitating hydride, and is the primary reason for the hysteresis in TSS. The solvus upon cooling/precipitation \( (C_{H}^{cool}) \) and heating/dissolution \( (C_{H}^{heat}) \) can be described by the relations [14]:

\[ C_{H}^{cool} = C_{H}^{S} \exp \left[ \frac{(\bar{W}_{el,p}^{inc} + \bar{W}_{p}^{inc})}{RT} \right] \]

\[ C_{H}^{heat} = C_{H}^{S} \exp \left[ \frac{(\bar{W}_{el,p}^{inc} - \bar{W}_{p}^{inc})}{RT} \right] \]

where in these equations \( \bar{W}_{el,p}^{inc} \) is the remaining elastic contribution to the accommodation energy, and \( \bar{W}_{p}^{inc} \) is the plastic component of the total accommodation energy. Experimental techniques using differential scanning calorimetry, dynamic elastic modulus, and small angle neutron scattering have been used to study the problem of solubility hysteresis for dissolution (TSSD) and precipitation (TSSP). Figure 2-4 shows a comparison of solubility limits determined by Pan et al. [13] with the results from some other studies.
2.3.2 Hydride Phases

There are three hydride phases (ZrH$_x$) that have been identified in zirconium alloys: FCC δ-hydride ($x=1.6-1.7$), FCT γ-hydride ($x=1$), and FCT ε-hydride ($x=1.74-2$) [7]. In these hydride phases, the hydrogen atoms occupy the tetrahedral sites [7]. Information in the literature about which hydride phase is stable in different Zr-alloys under various conditions is unclear and often contradictory. Some have postulated that the γ-hydride phase is metastable and favoured by fast cooling rates (quenching) [16, 17], where δ-hydride is the more stable phase formed at slow cooling rates [7, 18]. This conclusion is supported by several X-ray diffraction experiments which found that δ-hydride was stable at room temperature after significant aging [18-20]. However, several other studies have found that the γ-hydride phase is stable below ~250°C [21-24]. It has also been suggested that zirconium alloy purity can have an effect on phase stability,
with the δ-phase favoured for alloys with a higher proportion of alloying elements [18]. In a set of experiments by Cann et al. [25], oxygen content was found to affect hydride phase stability, with higher oxygen concentrations favouring the δ-hydride phase. The authors postulate that the oxygen may have been changing the yield stress of the material, which could have affected which hydride phase was favoured by changing the plastic strain energy associated with hydride precipitation. A phase diagram for the zirconium-hydrogen system is shown in Figure 2-5 [26].

It is believed the hydrides formed in the studies discussed in this thesis were predominantly δ-hydride, given the slow cooling rates used and the general agreement in the literature; also, only δ-hydride peaks were detected in the X-ray experiments discussed in Chapter 3. For this reason, further discussion will focus primarily on the δ-phase.

Figure 2-5: Phase diagram for the zirconium-hydrogen system [26]
2.3.3 Hydride Morphology

Hydride platelets as seen in an optical microscope tend to precipitate in the axial-circumferential plane, referred to as the circumferential orientation (see Figure 2-6 [7]) in unstressed Zr-2.5Nb pressure tubes (PT). This orientation relationship is thought to be due to residual stresses from the PT manufacturing process (also affected by crystallography and grain structure), and it is possible for the hydrides to reorient under applied tensile hoop stress and thermal cycling to a more deleterious radial orientation, i.e. in the radial-axial plane [27, 28]. These large hydrides have been described as having a ‘cornflake’ morphology, or elongated, irregularly shaped plates. Examination by TEM has revealed that these large hydrides are actually composed of stacks of sub-platelets whose orientation does not necessarily correspond to the orientation of the macroscopic hydride [29] (see Figure 2-7). The α/β interface in Zr-2.5Nb appears to be a prevalent site for the nucleation of these hydride platelets, which then often grow trans-granularly. The origin of the stacks of hydride platelets is thought to be sympathetic nucleation events due to the strain fields produced during hydride precipitation [29].

Figure 2-6: Illustration showing different hydride orientations in a section of PT [7]
The transformation from HCP zirconium to FCC δ-hydride is hypothesized to be accomplished by a shear in the plane of the hydride platelet and a dilatation normal to it [29]. The habit plane for the hydride sub-platelets has a very close orientation relationship to the α-Zr basal plane, such that δ[111]∥α[0001] and δ[111]∥α[11$ar{2}$0] [30]. This relationship holds true for both inter- and intra-granular hydrides [29, 31]. In the absence of stress the texture of the Zr will thus have a strong effect on the predominant orientation of hydrides. The orientation of the sub-platelets does not necessarily correspond to the orientation of the macroscopic hydride; the sub-platelets tend to have the same orientation for both macroscopic radial and transverse hydrides (see illustration in Figure 2-8 [29]).

Figure 2-7: (a) optical micrograph showing macroscopic hydride distribution in coarse-grained Zr-2.5Nb material; (b) a closer TEM examination showing the stacks of hydride platelets [29]
Under applied (or residual) tensile stress, the hydrides tend to precipitate in locations and orientations that minimize the tensile stress. This reduction in stress is because the precipitation of hydride is associated with a ~17% change in volume (expansion) that occurs in the transformation of HCP Zr to less dense FCC δ-hydride [32]. Exactly how this dilatation is accommodated with respect to the principal directions of the macroscopic hydride (ie. in the plane of the macroscopic hydride plate or normal to it) is somewhat ambiguous in the literature, and is discussed in detail in Chapter 4, where it is very relevant to modeling the hydride precipitation process. Due to the brittle nature of hydrides, orientations where the macroscopic hydride is orientated perpendicular to the applied tensile stress have the most severe impact on mechanical properties, as is the case for hydrides formed at a tensile stress concentration.

### 2.3.4 Experiments Examining Hydride Mechanical Properties

Determining the mechanical behaviour of hydrides can be problematic, since they form embedded within zirconium metal, and isolating their response in any mechanical testing can be a challenge. One of the more widely used tools to measure the behaviour of hydrides in
zirconium alloys is acoustic emission (AE). In AE studies a microphone is attached to the hydrided sample, which is tuned to detect acoustic vibrations caused by fracturing hydrides. Simpson [33] used an AE technique to measure the fracture of hydrides oriented with their normals parallel to the direction of loading in Zr-2.5Nb PT alloy. By correlating the AE results with metallography, it was found that the AE technique was quite accurate in determining the onset of fracture for hydrides embedded in zirconium. Given the rapid increase in AE events after the onset of yield in the material (see Figure 2-9 [33]) the study concluded that some plastic deformation in the zirconium matrix appears to be prerequisite for large-scale fracture of hydrides; this is an observation that has been frequently reported in literature [34-37]. It was also found that the size of the hydrides does not appear to have a significant effect on fracture behaviour below 2 to 4µm.

![Figure 2-9: Typical loading curve with AE event rate from the study by Simpson [33]](image)

Other studies correlating AE results to metallography (post fracture or from interrupted tests) found that hydrides accelerate fracture by nucleating voids in the material [36]. These voids are created when the hydrides fracture, and can grow when subjected to further loading. In an AE
study on notch-tip hydrides, Sagat et al. [38] confirmed that hydrides with their normals parallel to the direction of tensile loading have a marked negative effect on ductility, and hydride fracture accelerates rapidly beyond a threshold stress; in this study, the threshold stress (peak applied stress) was estimated to be between 675 and 750MPa. In another AE study by Cui et al. [39] looking at hydrides formed at stress concentrations, it was found that the stress under which the hydrides are formed has an effect on fracture resistance, with the stress for hydride fracture decreasing with increasing formation stress. Other factors were found to influence the fracture behaviour of notch-tip hydrides including flaw geometry, thermal history and hydrogen content.

Choubey et al. [34] used AE to study hydrided Zr-2.5Nb PT material at different temperatures, with the hydride plates initially oriented with their normals parallel to the applied stress. The observation was made that between 100 to 150°C the AE event rate increased rapidly once yield was reached in the material, consistent with other studies; hydride fracture strength at 100°C was estimated to be ~520MPa. It was also found that in regions of multi-axial stress (ie. flaws) hydrides fracture at a lower stress than under uniaxial loading. At temperatures beyond 150°C there was a significant decrease in the number of AE events, indicating hydrides were much less likely to crack at elevated temperatures. Metallographic examination showed that at high temperatures hydrides were able to reorient parallel to the applied load, providing some evidence for hydride plasticity.

The results obtained from AE studies are qualitative in nature, in that they do not provide a direct measure of hydride mechanical properties; observations are inferred indirectly by
correlating AE events with other aspects of the experiment (i.e. load, yield strength, temperature). For more direct measures of the mechanical behaviour of hydrides in zirconium, in-situ SEM techniques have been utilized. Grange et al. [35] used in-situ SEM testing to examine the mechanical response of hydrides precipitated in Zircaloy-4 sheet material. In these tests, some indication was found that the hydrides were able to deform with the surrounding zirconium, which would imply some plastic deformation can occur in hydrides at low temperatures. Specifically, this was evidenced by slip bands observed to run continuously through a transgranular hydride (see Figure 2-10 [35]). The authors postulate that deformation of these transgranular hydrides is due to transmitted slip, possible due to the crystallographic relationship between the zirconium and the hydride. The observation that intergranular hydrides tended to fracture before transgranular hydrides in the tests seems to corroborate this view, since the slip systems of the grains bracketing the hydride may not share the same orientation relationship. Similar experiments by Arsene et al. [40] also revealed such slip band continuity for hydrides and the surrounding matrix in Zircaloys. Both of the in-situ studies [35, 40] seemed to confirm results from AE experiments that incidence of hydride fracture increases dramatically with increasing plastic deformation of the matrix, and that hydrides with their normals in the direction of the applied load are much more susceptible to fracture.
Even for in-situ SEM techniques on hydrided zirconium exact values for mechanical properties (i.e. elastic modulus) cannot be directly measured because the hydrides are small inclusions in a zirconium matrix. A method that has been used to obtain direct measurements of the mechanical properties of zirconium hydride is by tests on ‘bulk’ polycrystalline hydride material created by reacting zirconium with hydrogen at high temperature (~800°C). Tests by Barraclough et al. [41] found that there was no measurable plastic strain in the hydrides in tension at temperatures ranging up to 500°C. This extreme brittle behaviour in tension was at least partly due to the difficulty in growing crack-free bulk hydride polycrystals. In compression tests, no plastic deformation could be measured below ~100°C before fracture, which would indicate that at low temperatures hydrides are entirely brittle. At higher temperatures, some plastic deformation was detected before fracture; results for the hydride mechanical response at different temperatures are shown in Figure 2-11 [41]. When plastic deformation was detected in these tests, it was associated with slip on the \{111\} planes (\delta\text{-ZrH}_{1.66}). In a more recent study by Puls et al. [42] the properties of solid hydrides grown from Zr-2.5Nb material were determined using microhardness testing, as well as confined and unconfined compression
tests. Cracking of the hydrides during their formation was minimized by carefully controlling the hydrogen ingress and cooling rate, though some subsurface cracks were still detected. Direct measurements of Young's modulus found that the elastic response of solid hydride was almost identical to the original pressure tube material for hydrogen compositions up to ZrH$_{1.6}$.

Caution must be used when relating the results from ‘bulk’ polycrystalline hydrides to the smaller hydrides formed within a zirconium matrix, which is the situation of more realistic importance. The hydrides in the ‘bulk’ samples had an equiaxed structure, with a grain size of ~0.2-0.4mm. This is in contrast to the smaller hydrides formed within zirconium, which have a plate-like structure made up of smaller sub-platelets (see Section 2.3.3). The hydrogen concentration and ratio of the hydride phases present in the ‘bulk’ material is also not necessarily representative of hydrides formed within zirconium.

![Figure 2-11: Nominal compressive stress-strain curves for ‘bulk’ ZrH$_{1.6}$ at different temperatures [41]](image-url)
Chapter 3

Strain Mapping Using High Energy Synchrotron X-Ray Diffraction

3.1 Background

Synchrotron X-ray radiation has been used for decades to study materials. Modern synchrotron facilities make use of oscillating electric fields to accelerate electrons to energies in the GeV range and ultra-relativistic velocities. A sequence of magnets is used to bend and focus the accelerated electron beam around a closed loop. The highest achievable energy of such an accelerator design is ultimately limited by the size of the loop and the strongest achievable magnetic field [43]. The high-energy photons (X-rays) are emitted when the charged particles (electrons) are subjected to an accelerating field. When the field is electric, then radiation is called bremsstrahlung, and when it is magnetic is referred to as synchrotron. In modern synchrotron light sources, a periodic magnetic structure generating a sinusoidal magnetic field along the path of the electron beam is used to generate high intensity synchrotron X-rays with a narrow energy band; this magnetic configuration is called an undulator.

During the 1990s the third generation of synchrotron X-ray light sources came online making use of undulator technology, and proved to be a powerful tool in the fields of structural biology, condensed matter physics, and materials science [43]. Three high energy, third generation sources are currently in operation worldwide: the European Synchrotron Radiation Facility (France), Spring8 (Japan), and the Advanced Photon Source (USA). All high energy X-ray diffraction (HEXRD) experiments discussed in this chapter were conducted at the Advanced Photon Source (APS) using the 11D beamline. This beamline uses an undulator as its X-ray
source with X-Ray optics optimized to maintain brilliance during monochromatization of the X-Ray beam [44].

For the study of materials, the high energy (HE) X-rays produced at these facilities have many favourable characteristics. The absorption cross-sections for HE X-rays are much lower than traditional Cu lab based X-ray sources, resulting in significantly deeper penetration depths in materials [44]. For comparison, the transmission of HE X-rays as a function of atomic number is shown for several elements in Figure 3-1. For the experiments discussed in this chapter, the beam energy was 80keV, which has a 10% transmission thickness of ~2mm in zirconium. The other important characteristic of the X-ray beam produced by the APS undulator is its very high flux (photons/(s.mm².mr²)), as illustrated in Figure 3-2 for the 1ID beamline; this is ~8 orders of magnitude greater than a Cu lab based X-ray source. This allows for very small beam sizes to be used (as small as 20 x 20 µm) while still maintaining very short exposure times. For kinetic or mapping studies, this characteristic is very useful.
Figure 3-1: X-ray transmission as a function of atomic number [44]

Figure 3-2: APS 1ID beamline flux as a function of X-ray energy [44]
The fundamental basis [45] for all X-ray diffraction measurements in the experiments discussed in this chapter is Bragg’s law:

$$\lambda = 2d_{(hkl)} \sin \theta_{(hkl)}$$

This equation relates the wavelength ($\lambda$) of the incident X-rays to the interplanar spacing ($d$) and scattering angle ($\theta$) for a given set of crystallographic planes {hkl}. Diffraction from a set of planes within a crystal occurs when the orientation of the planes with respect to the incident X-ray beam satisfies this equation. The reality of what occurs as an X-ray beam passes through a material is rather complex, but this relatively simple expression describes the end result very well. For the experimental results presented in this chapter, a monochromatic X-ray beam (80keV) is used, which fixes the X-ray wavelength. The scattering angle for a given X-ray exposure is captured by the detector, which is then used to calculate d-spacing. Thus, changes in scattering peak position correspond to changes in d-spacing.

A number of factors can influence d-spacing, including applied or residual strains, temperature, and material chemistry. In order to make meaningful measurements of strain, it is important to have an appropriate reference d-spacing with which to compare to a measurement of interest. Small changes in chemistry can lead to non-negligible variations in d-spacing, and as such it is important that the reference spacing come not only from the same type of material, but also from the same source (ie. billet, tube, etc.). It has been found that a difference of only 30 wt-ppm hydrogen can produce an ‘apparent’ strain of $\sim$200E-6 [46] in zirconium. The temperature of the reference should also be as close as possible due to the effect of thermal expansion on lattice spacing. If an absolute measure of strain is desired, then the reference material should
be as close to stress-free as possible. Once a reliable reference has been obtained, the strain can be calculated by the equation:

\[ \varepsilon_{(hkl)} = \frac{d_{(hkl)} - d_{0(hkl)}}{d_{0(hkl)}} \]

where \((\varepsilon)\) and \((d)\) are the strain and d-spacing for the measurement location of interest, respectively, and \((d_0)\) is the reference d-spacing.

HEXRD, like all diffraction techniques, only gives a direct measurement of elastic strains, which are due to changes in interplanar spacing. Plastic strains which arise from dislocation motion do not contribute to shifts in peak position. Peak shape can be affected by changes in dislocation density as well as a number of other factors including: stacking faults, strain heterogeneities at the grain level (type-II stresses), steep strain gradients, as well as the set-up of the detector [45]. Deconvoluting these effects to determine the effect of dislocation density alone, and thus gaining direct information about plastic strain, is not a simple procedure. Studies relating to the changes in the X-ray peak shape from single grains [47] during plastic deformation have been conducted, but the situation becomes much more complex when using grain-averaged diffraction information. Mathematical models have been proposed that show promise in predicting dislocation density [48], but in general this is not straightforward. For these experiments only elastic strains are considered, though some information about the plastic behaviour of different phases in the material can be inferred from changes in elastic load sharing.

An excellent example of a study using HEXRD to study an engineering material is the work conducted by Turski et al. [49], the purpose of which was to examine the effects of creep.
damage driven by residual stress in AISI type 316 stainless steel in notched CT samples. Residual strains measured using HEXRD and neutron diffraction (ND) matched up very well, with the higher spatial resolution of the HEXRD evident in regions of high strain gradients. The HEXRD measurements were also used to validate a 3D finite element (FE) model, showcasing the usefulness of this tool for validating complex engineering models. A comparison of the mid-thickness residual elastic strains in the material for the three methods is shown in Figure 3-3.

Figure 3-3: Residual strains in the material tested by Turski et al. after pre-straining [49]

Crack tip mapping studies using HEXRD techniques have been reported for numerous materials including aluminum alloys [50, 51] and steels [52, 53]. In these studies, the high resolution of HEXRD measurements allowed for the characterization of strain fields ahead of fatigue cracks, which influences crack closure and the rate of fatigue crack propagation. This technique has also be applied to measure changes in strain and texture during crack propagation in NiTi shape-memory alloys [54]. In this material plastic deformation occurs primarily due to a detwinning
mechanism rather than dislocation-slip, and changes in texture as a result of this deformation mechanism during fatigue crack growth were observed.

3.2 Introduction

The experiments discussed in this chapter are a continuation of several studies by Kerr et al. [55-58] utilizing HEXRD to study strain evolution in zirconium alloys. The first of these [55] looked at the bulk strains in both tension and compression, in samples cut from rolled Zircaloy-2 plate material containing ~90wt-ppm hydrogen with zirconium hydrides present in the material. It was found that strain measurements in the hydride phase could be obtained even at this low hydrogen concentration, and the similar elastic moduli obtained for the Zircaloy-2 matrix and the hydride of ~100GPa showed good agreement with indentation experiments on solid zirconium hydride [42]. Strain saturation observed during the experiments was thought to be the result of hydride fracture, and this was supported by subsequent metallographic examination. Further studies showed the applicability of HEXRD for looking at the elastic strain fields at stress concentrations in Zircaloy-2 compact tensile (CT) samples. It was shown that this technique could be used to observe the elastic strain field around a sharp fatigue crack [56].

Kerr’s most recent studies used HEXRD to look at the distribution and subsequent redistribution of strains in notched, C-shaped Zr2.5Nb pressure tube (PT) material; this is the same material and sample geometry used in the experiments detailed in this chapter. Experiments examining PT material with ~100wt-ppm hydrogen and containing large (~100µm), pre-existing hydrides at a 15µm notch showed how in tension load is transferred to the hydrides until fracture occurs [58]. Hydride fracture was found to be resolvable in-situ after loading at room temperature to
of the load at which the hydride was formed; this was later confirmed by metallography, as seen in Figure 3-4. In the next step, experiments were performed [57] to observe hydrides forming in-situ at a 15µm notch in PT material containing ~60wt-ppm hydrogen. Hydride precipitation was observed at a temperature of 250°C. After precipitation, the sample was loaded at temperature to 125% of the load used to form the hydride. No hydride fracture occurred at this load, but the differential in strain between the zirconium and the hydride at this temperature (250°C) was found to be much less pronounced than at room temperature.

Figure 3-4: SEM micrograph confirming hydride fracture observed in-situ using HEXRD [58]

The purpose of the experiments detailed in this chapter is to gain further insight into hydride growth and subsequent fracture at stress concentrations in Zr-2.5Nb PT material. Several experiments were conducted to this end. Two notched, C-shaped samples with a hydrogen content of ~60wt-ppm were loaded in-situ and subjected to thermal cycling to promote the precipitation of hydrides at the notch while diffraction exposures were being taken using
HEXRD. One of these samples had been loaded at high temperature prior to the experiment in order to produce creep strains at the notch. The purpose of this variation was to determine what, if any, mitigating effect on hydride embrittlement pre-existing creep strains might produce at PT flaws. Once the cycle to produce hydrides at the notched stress concentration was complete, the samples were subsequently overloaded (with respect to the hydride formation load) at room temperature. This is a more severe situation for overload failure than that performed by Kerr at al. [57] on hydrides grown in-situ, which were performed at 250°C. In that experiment no hydride fracture was observed, whereas in this experiment one of the explicit objectives was to fracture the notch-tip hydrides. A sample without hydrogen and the same notched, C-shaped geometry was also tested for comparison purposes. This latter sample was not subjected to any prior loading to induce creep strains.

3.3 Experimental Setup

The material tested was cold-worked Zr-2.5Nb pressure tube material. This material has a fine, two-phase microstructure with a grain size of ~0.35-0.5µm. The samples were cut from the wall of a production-grade pressure tube, as illustrated in Figure 3-5. All samples were cut from the same location of the same pressure tube, effectively eliminating any variation in properties due to differences in processing or trace elements. For samples containing hydrogen, the source pressure tube section was electrolytically hydrided, then subjected to an elevated temperature homogenization treatment to achieve the desired hydrogen concentration in solution (~60 wt-ppm) following the procedure detailed in [59]. C-shaped samples were provided by Kinectrics Inc. with nominal 3.2mm thickness, and containing a 0.75mm deep, 45° V-notch with a 15µm root radius obtained using a micro-broaching technique [60]. All samples had holes machined at
each end to allow the insertion of pins for loading during the experiment. For a dimensioned drawing, please refer to Appendix B. One sample was loaded at high temperature to produce creep strains at the notch prior to the experiment. In this case, the sample was loaded to the stress intensity to be used during the experiment to form notch-tip hydrides ($K_f \sim 8\text{MPa}\sqrt{\text{m}}$) at 300°C and held for 24 hours; the load was removed before cooling.

![Illustration showing the location of the test material on a section of pressure tube](image)

**Figure 3-5: Illustration showing the location of the test material on a section of pressure tube**

Samples were pin-loaded in tension, using grips affixed to a MTS load frame. When referring to the load applied to a sample with a sharp flaw at which a hydride can form, it is common in these types of studies [57, 58] to use the applied stress intensity ($K_I$), which is calculated as per ASTM-399 [61]. Although this is not strictly correct, as the stress intensity refers to an atomically sharp (ie. a fatigue crack) flaw, this is nonetheless a very useful approximation for normalizing the applied load with respect to the sample geometry. Often, loads will be referred to as a percentage of the applied stress intensity used during the hydride formation cycle ($K_f$).
When taking measurements, the X-ray beam and detector were stationary, and the sample stage was translated to allow the beam to strike different locations on the sample. Where heating was required, a halogen, clam-shell furnace was used. X-ray beam size was controlled by moveable slits; two beam sizes were used: 50 x 50µm, and 20 x 20µm. Diffraction measurements were taken in transmission geometry, and the resulting Debye-Scherrer diffraction rings were captured on a 40 x 40cm GE amorphous silicon detector. Well-defined diffraction rings were recorded due to the large number of grains sampled in each through-thickness measurement, even when using the smaller beam size. A basic schematic of this setup is shown in Figure 3-6. For a photograph of the real setup at the APS 1ID beamline, refer to Appendix C.

![Diagram showing the orientation of the sample with respect to the x-ray beam, translation axes, detector and applied load (not to scale)](image-url)

Figure 3-6: Simplified drawing showing the orientation of the sample with respect to the x-ray beam, translation axes, detector and applied load (not to scale)
Measurements at each location were integrated over ten, one second exposures in order to minimize the risk of saturation of the detector while increasing the signal-to-noise ratio. In order to obtain the necessary data to generate strain maps, measurements were taken at a number of locations around the notch, with both the 20 x 20µm and 50 x 50µm beam sizes. Each scan at the notch tip consisted of three consecutive grids of measurement locations: a set of exposures using the 20 x 20µm beam over an area of 300 x 200µm in 20µm steps, a set using the 50 x 50µm beam over an area of 500 x 500µm in 50µm steps, and a set using the 50 x 50µm beam over an area of 1.4 x 1.4mm in 0.2mm steps. The progression for a complete scan is shown in Figure 3-7. Due to changes in loading and/or thermal strains, the location of the notch had to be determined before each set of scans. This was done manually by observing the transmitted intensity of the X-ray beam as it was scanned in the x- and y-directions around the notch. The expected spatial accuracy for this technique was on the order of the beam size, or ±50µm.

A thermo-mechanical loading cycle was used to cause the precipitation of zirconium hydride at the notch stress concentration. This cycle was also applied to the sample without hydrogen. A clamshell type IR heater was used to heat the samples, with a thermocouple that was spot welded to the sample used to control the heater. A second thermocouple was also spot welded to the sample to verify the temperature. The details of this cycle are as follows:

- Heated to 350°C (25°C/min) and held for 30 minutes to dissolve all hydrides
- Cooled to 250°C (10°C/min), applied 100% load (k_f ~ 8MPaVm); two sets of exposures taken
- Cooled to 150°C (1°C/min)
• Turned off furnace and cooled to RT (~10°C/min); exposures taken at 100, 120, 130, 140% loads (relative to $k_i$)
Figure 3-7: (a) 20 x 20µm beam over an area of 300 x 200µm; (b) 50 x 50µm beam over an area of 500 x 500µm; (c) 50 x 50µm beam over an area of 1.4 x 1.4mm
3.4 Data Analysis

All analysis of the X-ray diffraction data was carried out using MATLAB scripts originally written by J. Almer (1-ID instrument scientist) at Argonne National Laboratory, which were then modified to meet the requirements of the experiment. The first step in interpreting the data was to sum the ten detector images taken at each measurement location, and then subtract the background from the images. The background was obtained by taking a ‘dark’ image with the beam blocked off, before each set of measurements. An example of a summed and corrected detector image is shown in Figure 3-8. One issue that is apparent when looking at the diffraction rings recorded by the detector is that the intensity is not continuous around their circumference; some weaker peaks appear nearly absent in certain orientations. The source of this phenomenon is the strong texture resulting from the fabrication of the Zr-2.5Nb pressure tubing.

Figure 3-8: An example of a summed and corrected detector image
In order to get an intensity distribution to which peaks could be fitted, the detector data was integrated over 20° slices centered on the angles 0°, 90°, 180°, and 270° and the diffraction angles converted to d-spacings. Macroscopically, these angles are either parallel or perpendicular to the loading direction. Data from equivalent angles was then averaged (ie. 0° & 180°). Peak fitting was carried out assuming a pseudo-Voigt shape for the fitted peaks. The α-zirconium (0 0 0 2) (basal planes) peak was fit singularly, while the α-zirconium {1 0 1 0} (prismatic planes) and δ-hydride {1 1 1} planes were fit as a pair because they overlap partially. No γ-hydride peaks were discernable in the diffraction data. The {1 1 1} plane was chosen for the δ-hydride because it proved the easiest to fit unambiguously. Information on expected d-spacings for α-zirconium and δ-hydride can be found in Appendix A. A lineout plot of normalized intensity coinciding with measured lattice spacings in the loading direction, along with labeled peaks of importance, can be seen in Figure 3-9. An example peak fit using the MATLAB peak fitting routine is shown in Figure 3-10.
Figure 3-9: Experimental plot of normalized intensity at angles aligned with the loading direction; peaks used for fitting are labeled

Figure 3-10: Example fit of the $\alpha$-zirconium $\{1010\}$ / $\delta$-hydride $\{111\}$ peak pair

Strains are calculated based on shifts in fitted peak-centre position with respect to a reference value. The reference value was the average of ten measurements ‘far’ (~1mm) from the notch
taken prior to loading (zero load) at room temperature. Reported zirconium strains are weighted averages based on the texture factor \((f)\), which is the fraction of poles for a given plane aligned with a specified macroscopic orientation (e.g., TD). Given the orthogonal relationship between the ‘c’ and ‘a’ directions in the HCP structure, the following relationships are true [62]:

\[
f_{(0002)} + f_{(10\overline{1}0)} + f_{(11\overline{2}0)} = 1
\]

\[
f_{(10\overline{1}0)} = f_{(11\overline{2}0)} = \frac{1 - f_{(0002)}}{2}
\]

For pressure tube material, typical texture factors [63] for the basal plane are: 0.352 (RD), 0.589 (TD), and 0.059 (AD). The actual texture of the material used in this experiment was not measured, so these were the values used. Average zirconium strains are then calculated for a given macroscopic direction as follows:

\[
\varepsilon_{AVE} = \varepsilon_{(0002)}f_{(0002)} + \varepsilon_{(10\overline{1}0)}(1 - f_{(0002)})
\]

This averaging is useful because it includes proportional contributions from the ‘c’ and ‘a’ directions, whose elastic responses would not be the same due to the anisotropy of the zirconium HCP crystal structure. For the FCC δ-zirconium phase, only the \(\{1 1 1\}\) reflection was considered for the elastic strain response; other peaks overlapped strongly with zirconium peaks, and the \(\{1 1 1\}\) was the only hydride peak for which an unambiguous fit was possible.

Uncertainty in the strain measurements is a combination of the uncertainty in peak position from peak fitting, and position-to-position variation within the sample. Peak intensity is what controls the uncertainty in determining the position of peak centres, with higher intensity resulting in higher confidence in the fit. Position-to-position uncertainty in strain measurement was due to grain-to-grain variation in interplanar spacing within the sampled volume. The
realized uncertainty, when accounting for both these contributions, was estimated to be 
±150µstrain for the Zr {0 0 2} peaks, and ±100µstrain for the Zr {1 0 1} and hydride {1 1 1} 
peaks. These values are for measurements near the notch tip, with uncertainty for the hydride 
phase increasing far from the notch due to decreasing peak intensity as a result of decreasing 
volume fraction of hydrides.

3.5 Results

Results from the strain measurements, which represent averages through-thickness, are 
presented in the form of two-dimensional strain maps. These strain maps were generated in 
MATLAB by using a cubic interpolation of the strain data points to create two-dimensional 
contours. On these plots, the notch tip is nominally located at the origin (0, 0). The loading 
applied to the samples is described as a percentage of the applied stress intensity used to form 
hydrides in this experiment (K_s~8MPa√m). All strains reported are parallel to the loading 
direction, which is the orientation of primary interest. As well, due to the strong texture of the 
pressure tube material, and the crystallographic relationship between the hydride phase and 
the surrounding zirconium [29], no {1 1 1} hydride peaks were discernable normal to the 
loading direction. ‘Holes’ in the strain maps for the hydride phase away from the notch are 
locations where hydride peaks could not be fitted due to very low peak intensity.

Line plots of strain versus distance from the notch are also presented for easier visualization of 
the strain response behaviour of the two phases (Zr and ZrH_x). These plots are presented in two 
ways: a ±50µm average (y-direction) along a line (x-direction) extending out from the notch tip, 
and also a straight extraction of the data points along that line (no averaging). The former
presents a more smoothed look at the data, with the averaging also acting to mitigate the effect of the uncertainty in locating the notch position exactly, whereas the latter is more indicative of the peak elastic strains present in the two phases. All samples in the proceeding subsections are labeled with their sample number (ie. SLS-09-050), as assigned when they were originally manufactured by Kinectrics Inc.

3.5.1 SLS-09-050: As-Received Hydrogen, No Pre-creep Cycle

Strain maps showing the average elastic strain in the α-Zr phase parallel to the loading direction for this sample can be seen in Figure 3-11. As expected for a stress concentration loaded in tension, the typical double-lobed strain shape was visible, with the strains increasing directly with load. Plots showing strain profiles from the notch tip are shown in Figure 3-12, with the type of profile (±50µm average or line extraction) indicated at the top. Again, these plots show the increase in elastic strain with higher load, as well as higher peak strains for the line extraction when compared with ±50µm averaging. There is some reduction in strain at values close to x=0, with peak strain seen at x~0.05mm.

Figure 3-11: Notch tip strain maps for sample SLS-09-050 showing average α-Zr elastic strains at (a) 100% load [K_i~8MPa√m], (b) 120% load [K_i~9.6MPa√m]
Figure 3-12: Sample SLS-09-050 strain profiles for (a) 100% load \([K_i \sim 8\text{MPa\text{	extdegree}m}]\), (b) 120% load \([K_i \sim 9.6\text{MPa\text{	extdegree}m}]\)

3.5.2 SLS-08-073: 60wt-ppm Hydrogen, No Pre-creep Cycle

Strain maps showing the average elastic strain in the \(\alpha\)-Zr phase parallel to the loading direction for this sample can be seen in Figure 3-13, and for the hydride phase in Figure 3-14. Plots showing strain profiles extending from the notch tip are shown in Figure 3-15, with the type of profile (±50\(\mu\)m average or line extraction) indicated at the top on maps of hydride intensity for the sample. When comparing the maps of zirconium strain to the equivalent sample without hydrogen (Section 3.5.1), it is clear that for the same load the strain in the zirconium phase strain is noticeably lower in the sample containing hydrides versus the one without hydrides. When looking at the line plots, if the peak strains at 100% load are considered, the difference in strain is \(\sim 1000\mu\text{strain} \).
The shift in position for the maximum strain away from the notch is observable between 120% and 130% loads. This is clear in the strain map for both phases, with the peak strain not only moving back from the notch in the hydride phase, but also separating into two distinct high strain regions. The shift in peak position in the line plots (based on the zirconium phase) appears to be ~70µm away from the notch tip. Before this shift occurs, the highest strain is in the hydride phase, whereas at 140% loading the zirconium experiences the highest strain. A SEM image of the hydride formed at the notch taken using backscatter electron imaging is shown in Figure 3-16. In this image a crack running through the hydride is clearly visible, and was measured to be ~80-90µm.
Figure 3-13: Notch tip strain maps for sample SLS-08-073 showing average α-Zr elastic strains at (a) 100% load \(K_i \approx 8\text{MPa}\sqrt{\text{m}}\), (b) 120% load \(K_i \approx 9.6\text{MPa}\sqrt{\text{m}}\), (c) 130% load \(K_i \approx 10.4\text{MPa}\sqrt{\text{m}}\), (d) 140% load \(K_i \approx 11.2\text{MPa}\sqrt{\text{m}}\)
Figure 3-14: Notch tip strain maps for sample SLS-08-073 showing average ZrHₓ elastic strains at (a) 100% load [Kᵢ~8MPa√m], (b) 120% load [Kᵢ~9.6MPa√m], (c) 130% load [Kᵢ~10.4MPa√m], (d) 140% load [Kᵢ~11.2MPa√m]
Figure 3.15: Sample SLS-08-073 strain profiles for (a) 100% load \([K_i \sim 8\text{MPa}\sqrt{\text{m}}]\), (b) 120% load \([K_i \sim 9.6\text{MPa}\sqrt{\text{m}}]\), (c) 130% load \([K_i \sim 10.4\text{MPa}\sqrt{\text{m}}]\), (d) 140% load \([K_i \sim 11.2\text{MPa}\sqrt{\text{m}}]\)
3.5.3 SLS-08-071: 60wt-ppm Hydrogen, Pre-crept

Strain maps showing the average elastic strain in the α-Zr phase parallel to the loading direction for this sample can be seen in Figure 3-17, and for the hydride phase in Figure 3-18. Plots showing strain profiles extending from the notch tip are shown in Figure 3-19, with the type of profile (±50µm average or line extraction) indicated at the top on maps of hydride intensity for the sample. The overall strain response of this pre-crept sample is similar to the previous sample (3.5.2), with two notable differences. First, the magnitude of the peak strain for the sample that had been pre-crept is lower than the sample that did not contain prior creep strains. Looking at the average plots at 100% load, it can be seen that the zirconium strain is
~500µstrain lower, and the hydride strain is ~400µstrain lower. It can also be observed from the line plots that the strain peak near the notch tip is broader in this sample than in the sample without prior creep strains.

A shift in the location of the peak strain away from the notch is apparent in this sample between 120% and 130% load, which is the same behaviour observed in the sample without prior creep strain (3.5.2). The shift in location of the peak zirconium strain based on the line plots is ~70µm away from the notch. As with the sample not subjected to a pre-creep cycle (3.5.2), this shift in peak strain position is also associated with a drop in the hydride strain relative to the zirconium. A SEM image of the hydride formed at the notch taken using backscatter electron imaging is shown in Figure 3-20. In this image a crack running through the hydride is clearly visible, and was measured to be ~60-65µm.
Figure 3-17: Notch tip strain maps for sample SLS-08-071 showing average α-Zr elastic strains at (a) 100% load [$K_i \sim 8\text{MPa} \sqrt{\text{m}}$], (b) 120% load [$K_i \sim 9.6\text{MPa} \sqrt{\text{m}}$], (c) 130% load [$K_i \sim 10.4\text{MPa} \sqrt{\text{m}}$], (d) 140% load [$K_i \sim 11.2\text{MPa} \sqrt{\text{m}}$]
Figure 3-18: Notch tip strain maps for sample SLS-08-071 showing average ZrH$_x$ elastic strains at
(a) 100% load [K,$\sim$8MPa$\sqrt{m}$], (b) 120% load [K,$\sim$9.6MPa$\sqrt{m}$], (c) 130% load [K,$\sim$10.4MPa$\sqrt{m}$],
(d) 140% load [K,$\sim$11.2MPa$\sqrt{m}$]
Figure 3-19: Sample SLS-08-071 strain profiles for (a) 100% load [K\textasciitilde8MPaVm], (b) 120% load [K\textasciitilde9.6MPaVm], (c) 130% load [K\textasciitilde10.4MPaVm], (d) 140% load [K\textasciitilde11.2MPaVm]
3.6 Discussion

3.6.1 Resolving Hydride Fracture

Several indicators of hydride fracture are apparent from the results pertaining to the samples charged with hydrogen (3.5.2 & 3.5.3). In both samples there is a clear shift in the position of the peak strain, as observed in the line plots, when going from 120% and 130% load. It is clear from the metallography that the hydrides fractured, and this shift in the position of the peak strain is roughly equal to the observed crack length (within ~10-15µm). The shift in strain peak position from the HEXRD measurements and the crack length observed from metallography do not match up exactly, which is likely due to changing hydride morphology through-thickness.
Thus, the metallography exposing the hydride and associated crack size at a single sample depth is only representative of a small contribution to the HEXRD data, which averages through-thickness. The issue of variation in hydride morphology is examined in further detail in Chapter 6. The resolution in determining peak strain location is also limited by the incident X-ray beam size, the smallest of which used in the vicinity of the notch tip was 20 x 20µm.

Up to 120% load, in both hydride-forming samples, the strain in the hydride phase at the notch tip is higher than that of the zirconium. This consistent with previous studies indicating there is very little plasticity in the brittle hydride phase at room temperature [41]. It should be noted again, however, that only elastic strains are being directly measured using the HEXRD technique. Chapter 5 contains results from experiments attempting to look at the total strain response of both phases. As the zirconium undergoes plasticity, load is transferred to the brittle hydride phase. After loading to 130% there is a sudden shift in the relative strains between the two phases, with the hydride strain decreasing to a level at or below that of the zirconium. It is logical to conclude that this sudden drop in the hydride strain with increasing loading is associated with the fracture of the large, notch-tip hydrides. The zirconium strain peak after 130% load also becomes ‘narrower’, indicating that a flaw (ie. a crack) sharper than the 15µm root radius notch has been formed.

### 3.6.2 Effect of Prior Creep Strain

Of the two hydrogen-charged samples tested in this experiment, one had been subjected to a cycle intended to induce creep strains at the notch prior to the experiment (3.5.3), and one had
not (3.5.2). The purpose of this comparison was to see what effect (if any) prior creep has on hydride formation and subsequent overload fracture at room temperature. For equivalent loading, it can be seen in the strain maps that the pre-crept sample has lower peak zirconium strains than the sample without prior creep; at 120% load, this difference is ~1000µstrain. In the pre-crept sample, the strain is also more distributed, as seen by the broader strain peaks in the line plot. These effects are expected, as some blunting of the sharp notch would be expected due to the creep. The micrographs appear to show shorter notch-tip hydrides for the pre-crept sample, which is corroborated by the maps of hydride intensity near the notch.

The strain in the hydride phase at 120% load is only marginally lower for the pre-crept sample (~200µstrain). Hydride fracture for both samples in the room temperature overloads was detected somewhere between 120% and 130% load, as discussed previously (3.6.1). Given these observations, it is not possible to state definitively whether the inducing of prior creep strains had any effect in mitigating hydride embrittlement at room temperature. It is possible that the notch-tip hydride in the pre-crept sample cracked at a slightly lower load, but given that both samples cracked in the same 120%-130% range, this difference is not discernable from the current data.

3.6.3 Hydride Reference D-Spacing
One issue with this experiment that merits discussion is the validity of the d-spacing reference used when calculating strains. Strains reported here are relative to d-spacing measurements taken far from the notch at zero load. The relative nature of these strains makes it difficult to make direct quantitative comparison with similar experiments. However, it was important that
the reference d-spacing come from the same experimental setup, as different equipment and
calibration used to obtain hydride d-spacing in other X-ray experiments found in the literature
have an effect on the measured value. Unfortunately, using ‘far-field’ hydrides as a reference
obeys the influence of the initial strain state of the hydrides, which is expected to be
compressive due to the volume misfit strains generated in the hydride during precipitation [32,
64]. This effect is evident when looking at the line plots in the results (Section 3.5). After
fracture at 130% load, the zirconium strains tend to zero, whereas the hydride phase appears to
continue to experience a tensile strain of $\sim 3.2 \times 10^{-3}$. The sampled region near the notch likely
contains both cracked and intact hydrides, and in the ones that have fractured, the constraint of
the surrounding zirconium matrix would be partially removed; when using the d-spacing from
constrained hydrides as a reference, this relief of residual compressive strain would appear as
tensile strain in the unconstrained hydride phase.

Obtaining a stress-free reference lattice spacing would be ideal, but this is not straightforward,
since ‘far-field’ hydrides form within zirconium metal in relatively low volume fractions. An
attempt at measuring a stress-free d-spacing was made using a powder provided by Kinectrics,
Inc. This powder was made from ground up bits of hydride layers that had flaked off in their
hydriding apparatus. Measured d-spacings at different temperatures are shown in Table 3-1.

<table>
<thead>
<tr>
<th>δ-hydride {111}</th>
<th>Room Temp.</th>
<th>150°C</th>
<th>250°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>d-spacing (Å)</td>
<td>2.7629</td>
<td>2.7669</td>
<td>2.7712</td>
</tr>
</tbody>
</table>

The average thermal expansion coefficient calculated from these measurements is $13.3 \times 10^{-6} \text{K}^{-1}$,
which is not far off from the reported literature value of $14.2 \times 10^{-6} \text{K}^{-1}$[65]. When comparing this
measured room temperature d-spacing value to the average reference value used in the experiments reported here, it indicates that the hydride is initially experiencing a compressive residual strain of $\sim -5.7 \times 10^{-3}$. Applying this offset to the hydride strains obtained in the present results would indicate that the hydrides crack after very little tensile strain ($\sim 100-300 \mu \text{strain}$ from the line plots), and that the loading is expended primarily in overcoming the residual compressive stresses in the hydrides up until the point of fracture. Despite these potentially useful observations, the validity of the hydride powder for serving as a reference for the hydrides in the Zr-2.5Nb pressure tube material in this experiment is uncertain. Since the powder likely came from multiple samples with different hydrogen concentration, and possibly from different pressure tubes, the chemistry of the hydride powder is unknown. Chemistry effects can have a large influence on d-spacing, which is why the powder reference was not used when presenting the results.

### 3.6.4 Absence of Hydride Precipitation at 250°C

One of the goals of this experiment was to capture the precipitation of zirconium hydride at 250°C, and unfortunately, this was not achieved. In a similar experiment by Kerr et al. [57] using the same loading conditions, sample geometry and nominal hydrogen concentration (60wt-ppm), hydrides were observed to form in sets of exposures taken at 250°C. Consequently, the inability to discern any hydrides peaks in this experiment in what should have been the same conditions is unexpected. The Canadian Standards Associated provides the following expression [66] for the terminal solid solubility for precipitation (TSSP) of hydrogen in cold-worked Zr-2.5Nb alloys:
\[ TSSP = 4.1 \times 10^4 \exp \left( \frac{-28000}{RT} \right) \]

where 'R' is 8.314J/K·mole, T is the temperature in Kelvin and the result for TSSP is in ppm. At 250°C (523K) this results in an expected TSSP of ~65wt-ppm. This value is higher than the nominal 60wt-ppm hydrogen content of the samples; however the high stress at the notch tip drives the diffusion of hydrogen to this region, and if the local concentration exceeds the TSSP, then hydrides will form. This is clearly what occurred in the aforementioned experiment by Kerr, as hydride phase peaks were only detected in the vicinity of the notch tip at 250°C. The hydrogen content of the samples used in the experiments presented in this chapter was confirmed to be at least 60wt-ppm by differential scanning calorimetry (see Appendix D). It was initially thought that the hydride peaks may have been absent in the azimuthal angles corresponding to the loading direction due to texture effects, but further examination of the diffraction pattern found no hydride peaks present at any angle on the diffraction patterns. Hence, it would seem that the lack of observed hydride growth was due to an experimental problem, rather than an oversight in the post-processing of the data.

A likely cause of the problem could have been the clamshell type furnace used to heat the sample. It was noticed during the experiment that a couple of the halogen heating bulbs were burned out. Since these could not be readily replaced, and time was an issue, it was decided to push on with the experiment. A second thermocouple was attached to the sample away from the thermocouple used to control the furnace, on the opposite side of the notch. This second thermocouple indicated a temperature gradient across the sample of ~5-10°C. If this resulted in the actual temperature at the notch being somewhat higher than intended, this may have
suppressed hydride precipitation. This does not, however, alter the interpretation of the results reported here, which were measured at room temperature.

3.7 Conclusions

The results from the three samples tested using HEXRD resulted in several notable conclusions. First, it was observed that the hydride phase is stiffer than the zirconium matrix in which it was embedded at high load. Since the elastic stiffness of the hydride and the zirconium matrix is expected to be nearly the same, the observed differences in strain are due to plastic deformation of the zirconium while the deformation of the brittle hydride remains elastic. For the samples with no prior creep, the one containing a notch-tip hydride had lower notch-tip zirconium strain, indicating that the stiffer hydride was taking a larger proportion of the stress. The strain differential between the hydride phase and the zirconium increased up to the point of fracture in the hydrogen-charged samples. Hydride fracture could be resolved based on the sudden shift in load sharing between the two phases, and the shift in the location of the peak strain which corresponded to the crack size measured from post-test SEM micrographs. Lastly, it was found that a 24 hour pre-creep cycle reduced the peak notch-tip strain in the Zr upon loading, but no significant effect was discernable on the overload required to fracture the notch-tip hydride at room temperature.
Chapter 4

Finite Element Modeling

4.1 Background

Understanding the interaction of hydrides with stress fields, particularly at flaws, is critical to evaluating the susceptibility of zirconium reactor materials to fracture and failure due to delayed hydride cracking (DHC). This interaction can be complex, and is strongly influenced by misfit strains resulting from the transformation of HCP α-Zr to FCC δ-hydride; these strains result in a volume dilatation for the hydride phase of ~17% [32]. Exact details about how these transformational strains interact with the local stress field and how they are accommodated by the surrounding zirconium matrix are difficult to determine experimentally. Attempts to this end have been made [67], though the most promising work thus far has been with modeling. Models of hydrides embedded in a zirconium matrix have been constructed to understand precipitation/dissolution of hydrides, hydride growth and fracture.

4.1.1 Precipitation and Growth of Hydrides

Models to simulate the precipitation or dissolution of hydrides typically treat them as elastic inclusions in an elastic-plastic matrix. These models study the effect of external load, matrix properties (i.e. plasticity) and hydride shape on the accommodation energy for hydrides. Model predictions have found that when the hydride is embedded in an elastic-plastic matrix, the deviatoric stress influences the hydride accommodation energy for precipitation, which is not the case for a purely elastic matrix; this energy is also very dependent on hydride shape [68-71]. Work looking at the hysteresis for hydride precipitation and dissolution found that the energy of
dissolution was smaller under deviatoric stress states, as opposed to hydrostatic stress, but that this difference was sufficiently small that hydrogen concentration limits derived from unstressed material could be used with reasonable accuracy in regions of high tri-axial stress (ie. crack tips) [71].

High hydrostatic tensile stress at stress concentrations (ie. cracks, notches) is believed to drive the diffusion of hydrogen to these regions, which explains why hydrides form preferentially at these sites [72]. The difference in chemical potential due to hydrostatic pressure between the ‘far-field’ and the stressed crack tip can be expressed as:

\[ \mu(b) - \mu(a) = -\sigma_H V_H \]

Where \( \mu(b) \) and \( \mu(a) \) are the chemical potentials at the crack tip and ‘far-field’, respectively; \( \sigma_H \) is the hydrostatic pressure, and \( V_H \) is the partial hydrogen molar volume. This gradient in chemical potential is due to the work done by the hydrostatic stress field on the hydrogen in solution. Since the partial molar volume of hydrogen is nearly the same in the zirconium matrix as in the hydride, the difference in hydrostatic stress is the main contributor to the chemical potential gradient [15, 46].

A number of FE models have been generated that study the effects of hydride precipitation by calculating a local hydride volume fraction (ie. element hydride volume fraction) [70, 73, 74]. The hydride is not actually precipitated in these models; rather, the mechanical properties (ie. swelling) of the elements are altered to reflect the influence of increasing hydride volume fraction. Such approaches capture the reduction in stress due to hydride precipitation, but do not calculate hydride shape directly. Metzger et al. [74] developed a FE model that predicts...
hydride morphology from hydride volume fraction by using hydride solubility data. A comparison of a result from this model to observed hydride shape is shown in Figure 4-1. A substantial limitation of this model is the assumption of equilibrium conditions in the region surrounding the hydride, when hydride growth is a non-equilibrium process by definition.

Figure 4-1: (a) hydride shape calculated by Metzger et al. for a blunt notch; (b) observed hydride shape at a blunt notch [74]

4.1.2 Hydride Fracture

Analytical and FE methods have been used to analyze hydride fracture. Eshelby (analytical) approaches model the hydride as an elliptical inclusion within an elastic-plastic matrix, where the stress and strain in the hydride is assumed to be uniform [75]. The critical stress causing hydride fracture as calculated by this approach accounts for the effects of hydride volume expansion, as well as applied external stress and inhomogeneity in strain between the hydride and surrounding zirconium matrix. A key result from these models, which agrees with experimental observation, is that higher yield strength for the zirconium matrix increases the critical applied stress for hydride fracture [36, 76]; a stiffer matrix surrounding the hydride
increases the residual compressive stress due to the volume change during precipitation. Finite element methods have also been applied to this issue [34, 68], allowing for the modeling of more complex geometries. These models estimate the apparent fracture stress for hydrides subjected to residual compressive strains to be ~575MPa at room temperature.

A class of analytical approaches termed ‘process zone’ models [77] have been developed for the more complex case of hydrides located at a stress concentration. These models were originally developed to model plastic collapse [78] to describe, for example, crack bridging due to fibers in composite materials or crazing in polymers. The application of the process zone methodology to the problem of notch tip hydrides allows the calculation of a critical value of stress for hydride fracture and initiation of DHC. In these models a ‘fictitious’ crack (the process zone) at a flaw (notch) is subjected to two opposing sets of loading: the applied stress distribution due to the flaw, and a uniform restraining or cohesive stress (see Figure 4-2 [77]). These loading cases are superimposed on the ‘fictitious’ crack, and the location of the crack tip is determined by the location at which the stress intensity factors due to the two loading cases sum to zero. By setting the displacement of the process zone equal to a critical displacement (derived from experimental values), the process zone length and subsequently the threshold stress for DHC initiation (lowest peak flaw-tip stress at which DHC can occur) for the given geometry can be found.
Figure 4-2: Illustration of the process zone superposition approach. The stress in the process zone is modeled using the superposition of the stress due to the flaw ($\sigma(x)$) and a resisting cohesive stress ($p_c$) [77]

4.2 Introduction

The synchrotron X-ray diffraction results of Chapter 3 provided useful information about hydride strains in the vicinity of a stress concentration, though this approach came with significant limitations. Even the smallest beam size used (20 x 20$\mu$m) was large relative to the size of individual hydrides, obscuring precise details of hydride-matrix interactions. This method also permitted the measurement of only elastic strains, and the reported hydride strains were relative to ‘far-field’ hydrides, rather than absolute. The purpose of the work of this chapter is to overcome these limitations by applying a finite element modeling approach to the same geometry as the samples used in Chapter 3, under equivalent loading and thermal conditions. This setup allows validation of the model through the comparison of the elastic strain distribution from the experiments of Chapter 3. Once validated, the model can then be used to infer additional details that cannot be obtained from the synchrotron experiments, as well as predict the outcome for different geometries and loading conditions that were not tested.
4.3 Model Setup

4.3.1 Sample Geometry and Meshing

The geometries modeled in this chapter were notched (15µm radius), C-shaped samples identical to those tested in the HEXRD experiments of Chapter 3; drawings showing exact sample dimensions can be found in Appendix B. ABAQUS finite element (FE) software was used to generate the sample geometry and associated meshes, and to carry out all the FE calculations. Due to the symmetry of the samples, and to save computing time, only half of each sample was modeled, with symmetry conditions along the plane bisecting the notch. A full picture of the boundary conditions applied to the sample can be found in Appendix E. The loading was applied to the samples in the same manner as the HEXRD samples of Chapter 3. Due to the very high level of mesh refinement required in and around the notch to capture the behaviour of hydrides and the surrounding matrix, the samples were modeled in 2D so that the simulations could be run in a reasonable amount of time. The very large number of elements required, combined with the non-linearities introduced by using complex material parameters (plasticity, creep, etc.), made a full 3D model computationally prohibitive. Both plane stress and plane strain formulations were used for the models, as it would be expected that the through-thickness average strains obtained from the HEXRD measurements of Chapter 3 fall somewhere between these two states.

The sample geometry was meshed using six-node, quadratic, triangular elements. Triangular elements were used due to ease of meshing for the curved geometries in the models (eg. hydrides, notch-tip), and it was not expected that this resulted in any more or less accurate results than a mesh using quadrilateral elements would have provided; later re-meshing of one
of the hydride-containing samples with quadrilateral elements confirmed this to be the case. Using quadratic elements seemed prudent due the implementation of matrix plasticity, along with the presence of high stress gradients at the notch, as well as at the interfaces between the hydride and surrounding matrix. Mesh convergence was tested using different element sizes, and the final mesh contained elements sufficiently small that any further refinement had no significant effect on the results.

The large, notch-tip hydride in the sample was given a partial-ellipsoidal shape, and a length of 50µm, which was approximately the length of the hydrides observed in post-test metallography in Chapter 3. The location of the center of the ellipse, and thus the thickest portion of the hydride (5µm), was located 16µm away from the notch tip. The reasoning behind this is that it is believed hydrides tend to begin forming at the location with the highest hydrostatic tensile stress, and then proceed to grow both outward into the sample, as well as towards the notch face [74]. For the sample geometry and applied load at which the hydrides formed, it was found that the location of highest hydrostatic tensile stress occurred ~16µm away from the notch tip.

In addition to the large notch-tip hydride, one elliptical hydride (20µm x 2µm) and then a string of smaller hydrides (10µm x 1µm) were placed in a regular distribution (every 20µm) along the center of the sample up to 250µm away from the notch. These smaller hydrides ensured there would be a hydride ‘signal’ for a distance away from the notch comparable to that found in the HEXRD experiments of Chapter 3, allowing for direct comparison of the two results. There are additional reasons for the selection of this hydride distribution, which are discussed further in Section 4.6. The real hydride distribution that is to be modeled, along with the model geometry and resulting finite element mesh in the immediate notch-tip region, is shown in Figure 4-3.
In the HEXRD measurements of Chapter 3, it was found for both samples charged with hydrogen that the large notch-tip hydride had fractured in the measurements at 130% load ($K_I \approx 10.4\text{MPa}\sqrt{m}$). To be able to compare these measurements to the model, hydride fracture was simulated by disabling all boundary conditions constraining the notch-tip hydride; this assumes fracture occurs at 120% load, though in the real samples it occurred somewhere between 120% and 130% loads (not known exactly). Though this simple approach was certainly not sufficient to capture the complex stress state right at the crack tip, it was useful as a first approximation. The ‘averaging’ used to extract strain data from the FE model (see Section 4.4) also mitigated the influence of any unrealistic strains right at the crack tip.
4.3.2 Material Properties

The material properties applied to the FE model were intended to be as close as possible to those of the actual Zr-2.5Nb pressure tube material tested in Chapter 3. To the author’s knowledge, the implementation of material properties in this model for the problem of hydride precipitation at a stress concentration is more complex than anything published to date. Both the zirconium (Zr-2.5Nb) matrix and the hydride phase are modeled as a continuum; the specifics of grain-to-grain interactions, and any inhomogeneity in deformation at the grain level, is not considered in this study. All material properties were applied using a cylindrical coordinate system consistent with the macroscopic pressure tube directions (ie. AD, RD & TD).

For the zirconium matrix, the elastic constants are somewhat anisotropic, and the elastic stiffness tensor used was calculated by Mark Daymond [79] using the EPSC code based on previous modeling work on the deformation of Zr-2.5Nb [80], but using the texture of a typical pressure tube. The elastic stiffness tensor is implemented as an orthotropic material in ABAQUS, and is shown in Figure 4-4. The same elastic behaviour is applied to the hydride phase, as it has been found previously [57, 58] that strains are very close for the hydride and the zirconium matrix within the elastic regime; this approach is consistent with the modeling work discussed in Section 4.1, which all consider the hydride a purely elastic inclusion with Young’s modulus equal to that of the zirconium matrix. Though the elastic response of the hydride may not be exactly the same as the zirconium, particularly with respect to anisotropy, the assumption of the same elastic behaviour simplified the modeling process; as well, there is little information on what the ‘true’ elastic modulus would be for a hydride precipitated in zirconium.
Figure 4-4: Elastic stiffness tensor (values in GPa) for the zirconium matrix

Anisotropy of deformation for the Zr-2.5Nb PT material is much more pronounced in the plastic than in the elastic regime. In tension, the anisotropy is not very pronounced, and the baseline plastic curve (plastic strain vs. stress) entered into ABAQUS is based on the modeling work of Christodoulou et al. [63]. This study only contained data for the axial and transverse tube directions, so the radial direction was assigned the same plastic curve as the transverse direction (in tension); given the small amount of tensile anisotropy, and the expectation that the radial behaviour would be closer to the transverse behaviour rather than axial, this was deemed a reasonable assumption. In compression, the PT material exhibits much stronger anisotropic behaviour. The tensile plastic curves were scaled to approximate an experimental data set for the compressive behaviour of PT material in the three tube directions [81]. Stress-strain curves for different orientations resulting from simple uniaxial tests modeled with ABAQUS using room temperature properties are shown in Figure 4-5. A user subroutine (written in FORTRAN) is called at material points (integration points) to retrieve the stress tensor, and then calculate the hydrostatic stress; the subroutine then changes a field variable (i.e. 1 or 0) at that point, depending on whether the calculated hydrostatic stress is tensile or compressive. The field variable acts as a toggle to change between tensile or compressive plastic properties at a
material point. This implementation allows for tensile/compressive asymmetry in the plastic response, otherwise not available in ABAQUS.

![Figure 4-5: Room temperature stress-strain curves generated from FE uniaxial tension (T) and compression (C) tests](image)

**Figure 4-5: Room temperature stress-strain curves generated from FE uniaxial tension (T) and compression (C) tests**

4.3.3 Temperature Dependence

Attempts were made to introduce temperature dependence for the material properties, since the HEXRD experiments of Chapter 3 that were the aim of the FE simulations included thermal cycling to facilitate hydride precipitation. Two linear relationships were taken from the literature to scale the elastic constants with temperature: one for the shear modulus [82], and one for the Young’s modulus [83]. These relations are as follows:
\[ G(T) = G_0 - 0.0223(T - 273) \]
\[ E(T) = E_0 - 0.0574(T - 273) \]

where \( G_0 \) and \( E_0 \) are the moduli (in GPa) at room temperature, and \( T \) is the temperature in Kelvin. It was assumed that these relations applied to all directions equally (ie. isotropically), since no other information to the contrary was available. Temperature scaling was also applied to the plastic curves, based on the results of the study by Christodoulou et al. [63], who also performed tests at different temperatures. The ABAQUS implementation of this result was done by entering the values for the plastic curve at 300°C; all values between room temperature and this value are the calculated using a linear interpolation. The same scale factor was also applied to the compression values, since no additional experimental information was available.

### 4.3.4 Hydride Precipitation and Volume Dilatation

The change in phase from \( \alpha \)-Zr to \( \delta \)-ZrH\(_x\) results in a change in volume of \(~17\%\) [32]. The exact manner in which this volume change is accommodated is not entirely clear in the literature. It has been hypothesized that the macroscopic volume change upon hydride precipitation is accommodated preferentially in a direction normal to the hydride habit plane [29, 84]. This approach has been used in other modeling studies [85], and was applied to the hydride volume misfit strains for the FE simulations discussed in this chapter. Implementation of this behaviour in ABAQUS was accomplished by applying a swelling to the hydride region in a direction normal to the habit plane of the hydride. This swelling procedure occurs incrementally, while taking into account compliance with the surrounding zirconium matrix; thus, while the free volume expansion is 17\% normal to the hydride plane, the actual dimensional change was less due to constraint from the matrix. Since the hydride was modeled as an entirely elastic inclusion,
plastic deformation was disabled in the hydride region via a field variable ‘toggle’ using a user-defined FORTRAN subroutine at the beginning of the hydride precipitation process; this was much like that implemented to switch between sets of plastic properties (ie. tensile or compressive).

4.3.5 Creep

Some of the samples tested in Chapter 3 had undergone elevated temperature loading to induce creep strains at the notch prior to the HEXRD experiments. Creep has been implemented in this model in order to recreate these pre-existing creep strains, where applicable. The creep law used for this purpose was provided by Kinectrics Inc. [86] and is a proprietary property law; only outline details are given here. This creep equation is used to predict the total creep deformation of Zr-2.5Nb pressure tubes in-reactor, and has contributions from: primary thermal creep, secondary thermal creep, irradiation swelling and irradiation growth. Since the goal of this model was to predict the response of unirradiated material, the terms relating to irradiation were disregarded. The general form of the relations, for primary and secondary thermal creep respectively, is as follows:

\[
\varepsilon_{\text{eff,th,primary}} = \left[ p_4 \sigma_{\text{eff}}^4 \right] e^{-Q_1/T} (t + t_{\text{off}})^u
\]

\[
\varepsilon_{\text{eff,th,secondary}} = \left[ (K_1 \sigma_{\text{eff,th1}} + K_2 \sigma_{\text{eff,th2}}) e^{-Q_1/T} + K_3 \sigma_{\text{eff,th1}} e^{-Q_3/T} \right] \cdot t + \left[ s_4 \sigma_{\text{eff}}^4 \right] \left[ e^{-Q_1/T} \right] \cdot t
\]

Where the ‘\(\sigma\)’ terms denote Hill’s effective stresses (different subscripts denote the use of different sets of Hill parameters), ‘\(T\)’ is temperature, and the ‘\(Q\)’ terms are activations energies. The time is represented by ‘\(t\)’, where ‘\(t_{\text{off}}\)’ is a small offset to prevent an arithmetic exception (at \(t=0\), and ‘\(u\)’ is the time exponent. All other variables are coefficients used to fit the
experimental and in-reactor creep data. The creep laws were implemented in ABAQUS using a user defined creep subroutine written in FORTRAN. This subroutine passes two values back to the ABAQUS solver: the equivalent deviatoric creep strain increment ($\Delta \varepsilon^{ct}$), and the partial derivative of that creep strain increment with respect to the deviatoric (Hill) stress ($\partial \Delta \varepsilon^{ct} / \partial \sigma_{eff}$). An example showing the functioning of the creep behaviour is shown in Figure 4-6, for a ‘cube’ of material loaded in tension along the transverse PT direction to a stress of 400MPa for 1200h at 300°C.

![Creep Curve](image)

**Figure 4-6**: Model creep curve for a ‘cube’ of Zr-2.5Nb material subjected to a loading of 400MPa (TD) for 80h at 300°C

### 4.4 Post-Processing

In order to compare the results from the synchrotron experiments to those of the FE model, some additional post-processing was required. The data for the strain plots presented in this chapter comes from the synchrotron data points along a line extending from the center of the
notch into the sample. This is similar to the plots presented in Chapter 3, however in this case only data from a 20 x 20µm beam was used. Each HEXRD data point is actually an average of the strains over the area illuminated by the X-ray beam (20 x 20µm). In order to make an equitable comparison with the HEXRD results, strains were extracted from the FE model results in a similar manner to the way in which the X-ray beam generated strain data. A MATLAB script was created to average the strains at all nodes falling within rectangular regions of the same size as the X-ray beam, and at the same locations (distance from the notch). Since element size was not constant within these regions due to local mesh refinements, the strain value of each node was weighted with respect to the average area of all elements sharing that node. For a single strain data point, this can be described by:

$$\varepsilon = \frac{\sum \varepsilon_n V_n}{\sum V_n}$$

where the strain is a weighted average across all nodes ‘n’ within the 20 x 20µm region, and ‘\(\varepsilon_n\)’ and ‘\(V_n\)’ are the nodal strain and average element volume, respectively.

4.5 Results

All strains and stresses discussed in this section are parallel to the direction of load application, which is consistent with the presentation of results in Chapter 3. Loads are reported in the same manner as Chapter 3, with the applied stress intensity (\(K_I\)) at the notch tip calculated as per ASTM-399 [61]. Where a comparison to HEXRD results is made, the sample is listed by its sample number as assigned by Kinectrics, Inc. upon fabrication. Line plots of elastic strain along a line extending from the notch (ie. strain vs. distance from the notch) are presented for these samples, along with the equivalent FE model results for both plane stress and plane strain.
conditions. Two-dimensional strain maps from the FE model are presented showing total stress around the notch region for each load increment.

4.5.1 SLS-09-041: As-Received Hydrogen, No Pre-Creep Cycle

The results of the strain measurements on this sample were not presented in Chapter 3, since it was a very basic case of room temperature loading with no thermal cycling. The purpose of this sample was to provide a baseline for comparison with the FE model to ensure that the basic material properties, as well as the assumptions associated with 2D modeling, produced a reasonable result. Plots showing the change in elastic strain with distance from the notch tip along the center of the sample are shown in Figure 4-7 for the experimental HEXRD data, along with the model results. For the three loading cases shown, the experimental strain line lies between the plane strain and plane stress FE model results. The source of the drop in strain right at the notch tip in the experimental data is not entirely clear. At this location only part of the beam is in the sample, and of that portion of the beam that is in the sample, part is sampling low strain regions of the sample that are ahead of the notch (ie. around the notch ‘V’); this is likely a significant contributor to the observed drop in strain. A comparison of the experimental and FE model (plane stress) elastic strain maps at 100% load is shown in Figure 4-8.
Figure 4-7: Strain profiles for FE model results and HEXRD sample SLS-09-041 at (a) 100% load \([K_i \sim 8\text{MPa} \cdot \text{m}^{1/2}]\); (b) 120% load \([K_i \sim 9.6\text{MPa} \cdot \text{m}^{1/2}]\); (c) 130% load \([K_i \sim 10.4\text{MPa} \cdot \text{m}^{1/2}]\)
Figure 4-8: Elastic strain maps around the notch tip at 100% load \([K_i \sim 8\text{MPa} \cdot \text{m}]\) for: (a) HEXRD sample SLS-09-041; (b) plane stress FE model (mirrored) – same size area (same x/y length scales) as in (a), as well as using the same strain range for the contour map

4.5.2 SLS-09-049: As-Received Hydrogen, Pre-Crept

Like the previous sample (4.5.1: SLS-09-041), this sample was not discussed in Chapter 3 because it contained low (as-received) hydrogen, and underwent loading only at room temperature. This sample was also used for model tuning, except in this case the sample notch had been pre-crept by applying a loading of \(K_i \sim 8\text{MPa} \cdot \text{m}\) at 300°C for 24 hours. An equivalent pre-creep cycle was applied in the model, followed by room temperature loading. Line plots comparing the experimental and modeling results at the two room temperature loads tested are shown in Figure 4-9. It would appear from these results that the creep law implemented in the model is overestimating the amount of relaxation that occurs at the notch due to creep.

However, a zero-load HEXRD strain map was taken for this sample, and a line plot of the residual elastic strain at the notch is shown in Figure 4-10. This result indicates that the strain in the immediate vicinity of the notch was tensile, when modeling and basic deformation theory indicates that the residual strain should have been compressive. It was noticed that subtracting
these unexpected residual strains values from the loaded experimental curves resulted in better agreement with the model, as shown in Figure 4-11, with the experimental line being nearly coincident with the model plane stress case; this is discussed further in Section 4.6. Maps showing the stress at the notch before and after creep deformation are shown in Figure 4-12.

**Figure 4-9:** Strain profiles for FE model results and HEXRD sample SLS-09-049 at (a) 100% load \([K_i \sim 8 \text{MPa} \cdot \text{m}^{1/2}]\); (b) 120% load \([K_i \sim 9.6 \text{MPa} \cdot \text{m}^{1/2}]\)

**Figure 4-10:** Profile of residual elastic strain (no load) from HEXRD at the notch in sample SLS-09-049
Figure 4-11: Strain profiles for FE model results and HEXRD sample SLS-09-049 (offset by residual strain values) at (a) 100% load [$K_I \sim 8\text{MPa}\sqrt{m}$]; (b) 120% load [$K_I \sim 9.6\text{MPa}\sqrt{m}$]

Figure 4-12: Model stress distribution around the notch (300°C) at $K_I \sim 8\text{MPa}\sqrt{m}$ (a) prior to creep; (b) after creep
4.5.3 ‘Far-Field’ Hydride

The zirconium hydride strains reported in Chapter 3 are relative to ‘far-field’ hydrides formed away from the notch tip at zero load. In order to make an equitable comparison to these experimental results, a ‘far-field’ hydride reference was also required for the FE model. This was modeled as an elliptical hydride with a 10:1 aspect ratio precipitating (volume dilatation) in a rectangular region with symmetry boundary conditions; orientation of the hydride with respect to the PT material directions (RD, TD & AD) was the same as the notch-tip hydrides. Hydride occupied 1% of the area modeled, which was meant to represent a region of PT material with 1% hydride volume fraction. The mesh used for this setup can be found in Appendix E. The hydride was formed at 150°C and then cooled to room temperature. A strain map of the hydride and matrix material in its immediate vicinity is shown in Figure 4-13. Average elastic strains normal to the hydride plane were \(-5.35 \times 10^{-3}\) and \(-5.88 \times 10^{-3}\) for the plane stress and plane strain conditions, respectively. The mean of these two values \((-5.6 \times 10^{-3}\)) was used as a reference for the strain line plots for the hydride containing samples, meaning the model strain values were offset by this amount. This was done to provide an equivalent means of comparison with the experimental strain values, which used the d-spacing of ‘far-field’ hydrides as the reference value for calculating strains; ie. the reference for the HEXRD measurements was not strain-free due to the strains associated with hydride formation, so an attempt was made to incorporate these initial strains in ‘far-field’ hydrides into the modeling results in order to make a like-for-like comparison.

The average stress in the hydride in the direction perpendicular to the major axis of the ellipsoid was \(\sim 720\text{MPa}\), which is close to values obtained in a similar modeling study by Leitch et al. [68].
In that study, and for the same hydride aspect ratio, stresses normal to the hydride platelet ranged from 505.6-729.2MPa depending on the how the volume dilatation was accommodated. A significant difference with the Leitch model was that the matrix was treated as elastic-perfectly plastic with a yield stress of 500MPa, which constitutes a softer (and simpler) plastic response than that implemented in the FE model discussed in this chapter.

Figure 4-13: Model elastic strain map for a ‘far-field’ hydride at room temperature for the plane stress case – strains are normal to the plane of the hydride

4.5.4 SLS-08-073: 60wt-ppm Hydrogen, No Pre-Creep Cycle

For this sample, the same temperatures and loading conditions were applied to the model as were used in the HEXRD experiment (outlined in Chapter 3). The hydride formation temperature was chosen to be 150°C before the sample was cooled to room temperature and subsequently subjected to additional loading. This was done, rather than a gradual growth in hydride during cooling from 350°C, for ease of model implementation. A comparison of the
variation in strain in the zirconium matrix along the centerline of the notch extending into the sample is shown in Figure 4-14. The model appears to capture the general shape of the curves quite well, with the experimental curve falling between the model plane stress and plane strain cases for the zirconium phase. The magnitude of the peak strain at 100% load in the experimental data is 3.1x10^{-3}, which falls between the plane stress and plane strain values of 4.3 \times 10^{-3} and 2.7 \times 10^{-3}, respectively. There is a difference in the location of the peak strain between the models and experiment, with the experimental peak being \sim 20\mu m closer to the notch tip prior to fracture.

A similar series of plots is shown in Figure 4-15 for the hydride phase. Here, the models appear to be over-predicting the hydride strain, with the experimental line falling below both modeling lines before fracture. Reasons for this, as well as the non-zero plateau in hydride phase strain after fracture, are discussed in Section 4.6. Stresses at the notch-tip before and after hydride precipitation are shown in Figure 4-16, along with stresses due to additional loading, immediately before hydride fracture (120% load). Relaxation of the high tensile stress at the notch due to volume expansion of the hydride in the direction of that stress is apparent in the plots. Immediately before fracture, the model predicts that the stress in the hydride right at the notch face is \sim 700\text{MPa}.
Figure 4-14: Line plots along the centerline of the sample (SLS-08-073) comparing the zirconium strains from the experimental and modeling results for (a) 100% load \( [K_r \sim 8 \text{MPa} \mu \text{m}^{1/2}] \); (b) 120% load \( [K_r \sim 9.6 \text{MPa} \mu \text{m}^{1/2}] \); (c) 130% load \( [K_r \sim 10.4 \text{MPa} \mu \text{m}^{1/2}] \) (50µm hydride ‘fractured’)
Figure 4-15: Line plots along the centerline of the sample (SLS-08-073) comparing the hydride strains from the experimental and modeling results for (a) 100% load $[K_i\sim 8 \text{MPa} \text{m}^{1/2}]$; (b) 120% load $[K_i\sim 9.6 \text{MPa} \text{m}^{1/2}]$; (c) 130% load $[K_i\sim 10.4 \text{MPa} \text{m}^{1/2}]$ (50µm hydride ‘fractured’).
Figure 4-16: Model stress distribution (SLS-08-073) for (a) 100% load [K~8MPa·m] before hydride precipitation; (b) after hydride precipitation; (c) after subsequent load increase to 120% load [K~9.6MPa·m]
4.5.5 SLS-08-071: 60wt-ppm Hydrogen, Pre-Crept

For this sample, the same temperatures and loading conditions were applied to the model as were used in the HEXRD experiment (outlined in Chapter 3). A pre-creep cycle equivalent to that which the experimental sample was subjected was also applied to the model (see Section 4.3.5). The hydride was formed at 150°C before the sample was cooled to room temperature and subsequently subjected to additional loading. A comparison of the variation in strain in the zirconium matrix along the centerline of the notch extending into the sample is shown in Figure 4-17. The model does well in capturing the behaviour of the matrix up until the region right at the notch tip, where a drop in strain is predicted at 100% load, and there is only a small decrease in the experimental result; up until this point the experimental data falls between the model plane stress and plane strain lines. The value of the peak experimental strain at 100% load at 100% load is $3.2 \times 10^{-3}$, falling between the plane stress and plane strain values of $4.0 \times 10^{-3}$ and $2.9 \times 10^{-3}$, respectively. At 120% load, the experiment shows a decrease in strain toward the notch tip more consistent with the model, but as in the previous sample (4.5.4: SLS-08-073) the position of the peak strain predicted by the model is different. The experimental peak strain is $\sim 20 \mu$m closer to the notch top.

A similar plot is shown in Figure 4-18 for the hydride phase. For the hydride strains, the magnitudes predicted by the model are close to the experiment, but whereas the model predicts a peak in strain near the notch, the experiment shows a steady decrement; the peak strain for the hydride phase is lower in the experimental data than for both model cases, consistent with the un-crept sample. After fracture, there is no high strain peak in the experimental hydride data, but this is likely because there was insufficient hydride intensity
beyond ~0.15mm using the 20 x 20µm for successful peak fitting. Stresses at the notch-tip before and after hydride precipitation are shown in Figure 4-19, along with stresses due to additional loading (120% load) immediately before hydride fracture. Immediately before fracture, the model predicts that the stress in the hydride right at the notch face is ~650MPa.

Figure 4-17: Line plots along the centerline of the sample (SLS-08-071) comparing the zirconium strains from the experimental and modeling results for (a) 100% load \([K\sim8\text{MPa}\cdot\text{m}^{1/2}]\); (b) 120% load \([K\sim9.6\text{MPa}\cdot\text{m}^{1/2}]\); (c) 130% load \([K\sim10.4\text{MPa}\cdot\text{m}^{1/2}]\) (50µm hydride ‘fractured’)
Figure 4-18: Line plots along the centerline of the sample (SLS-08-071) comparing the hydride strains from the experimental and modeling results for (a) 100% load \([K_i \sim 8\text{MPa}\sqrt{\text{m}}]\); (b) 120% load \([K_i \sim 9.6\text{MPa}\sqrt{\text{m}}]\); (c) 130% load \([K_i \sim 10.4\text{MPa}\sqrt{\text{m}}]\) (50µm hydride ‘fractured’)
Figure 4-19: Stress distribution (SLS-08-073) for (a) 100% load [$K_i \approx 8 \text{MPaVm}$] before hydride precipitation; (b) after hydride precipitation; (c) after subsequent load increase to 120% load [$K_i \approx 9.6 \text{MPaVm}$]
4.6 Discussion

4.6.1 Validity of Misfit Strains and ‘Far-Field’ Hydride Reference

The 17% volume dilatation necessary for the transformation from HCP \( \alpha \)-Zr to FCC \( \delta \)-ZrH\(_x\) was accommodated normal to the habit plane of the macroscopic hydride, as mentioned previously (Section 4.3.4). Though there is support for this approach, and it has been used in other modeling studies, the situation is not entirely straightforward. The macroscopic hydrides being modeled are actually composed of a tightly stacked series of smaller hydride platelets, whose orientation does not necessarily correspond to the macroscopic hydride habit plane. Since the calculated volume dilatation based on crystallographic considerations actually applies to these sub-platelets [29], lumping all the volume change into a single direction may not be entirely realistic; however, this choice was strongly influenced by modeling difficulties.

Several studies modeling hydride precipitation involving a volume dilatation both normal to and within the macroscopic hydride habit plane showed a strong dependence of strains on hydride aspect ratio. The source of this dependence was from Poisson effects in the hydride. Since the hydrides have such an oblate shape, even a small strain within the hydride plane caused significant dimensional changes normal to the plane. The amount of strain due to this Poisson expansion normal to the plane depended strongly on the aspect ratio of the hydride region, with the hydride strain appearing to be tensile for ‘flatter’ hydride shapes even though the stress in the hydride was compressive. In order to eliminate this strong sensitivity to aspect ratio, the decision was made to impose all the volume change in the direction normal to the hydride habit plane. Given that the impact of this type of effect (if any) in real, non-homogeneous hydrides is unknown, this seemed to be the most unambiguous approach. The calculated average hydride
strain for a ‘far-field’ hydride (4.5.3) using this assumption was -5.6mstrain. This value matches up very well with the HEXRD hydride powder measurement of ~-5.7mstrain found in Chapter 3, which provided additional confidence that this was a reasonable approach.

The model hydride that was grown ‘far-field’ to generate a reference strain with which to offset the notch-tip hydride strain results, was assigned the same orientation with respect to the material (RD, TD, & AD) as the notch-tip hydrides. Given that the locations for the reference hydride strains in the HEXRD samples were in tension, mainly in the transverse direction, the assumption that the ‘far-field’ hydrides precipitated mostly in this orientation is not unreasonable. However, since the stress state for the immediate notch-tip region and measurements ‘far-field’ are not the same, the actual orientations of the hydrides in these regions may be somewhat different.

4.6.2 Hydride Shape and Distribution
Hydrides precipitated in pressure tube material are often described as having a ‘cornflake’ shape. These geometries are somewhat irregular, with sharp edges (stress concentrators), which do not lend themselves well to finite element modeling; for this reason, the shape of the hydrides was approximated as an ellipse. Modeling work has also been done showing that, in the ideal case of a hydride precipitating in a homogenous elastic-plastic medium, a smooth (spheroidal) shape is more energetically favourable than a plate-like (cuboidal) shape [68]. The large notch-tip hydride was also semi-elliptical, and its size was chosen to correspond to the metallographic observations performed on the real samples.
The most limiting aspect of the present modeling approach was the selection of how hydrides were distributed near the notch tip. In a real sample, the location and size of hydride precipitates is governed by a complex interaction between diffusion to high areas of tensile hydrostatic stress, and the reduction of that stress through the nucleation and growth of hydrides. The resulting distribution is complex and three-dimensional. In the current model, this distribution is represented as a one-dimensional distribution of hydrides in a two-dimensional plane. Attempts were made to place hydrides in locations of peak hydrostatic stress, which included some iterating to try to capture where sympathetically nucleating hydrides would appear due to the shift in stresses induced by the precipitation of a parent hydride. The real process, however, involves nucleation and subsequent hydride growth, rather than a sudden change across the whole volume finally occupied by hydride; this means the manual positioning of hydrides within the model is not entirely realistic, even in the sense of the one-dimensional distribution used.

The string of hydrides far from the notch are meant to provide a hydride signal over a distance equivalent to that measured in the HEXRD experiments. These experiments showed gradually decreasing hydride intensity with increasing distance from the notch. This case proved difficult to implement for a two-dimensional model, since there was a minimum hydride spacing that could be used (the beam size), below which the hydride region is essentially being undersampled; since the actual measurement is through-thickness, the in-plane hydride distribution can be much more sparse (and likely was) and still provide a consistent signal. One way to approach this would have been to gradually reduce the hydride size over the measured region rather than keeping it constant; however, this resulted in tiny hydrides that were difficult
to mesh, with little change in the end result. This approach is also not grounded in reality, since a change in hydride spacing is more likely responsible for the decrease in intensity, rather than a gradual reduction in mean hydride size. The best solution for getting a realistic hydride distribution would be a full 3D model with coupled stress and diffusion, simulating incremental hydride growth. Such a model would constitute a significant investment of time and computational resources, however, and was beyond the scope of the modeling work performed in this thesis.

4.6.3 Model Comparison with Hydride-Free Samples
Two samples from the HEXRD experiments were tested purely for the purpose of assessing of the model and material parameters used, and did not contain hydrides. These were tested at room temperature, and were useful for validating the basic model setup and material parameter inputs. The first of these samples (Section 4.5.1) showed very good agreement with the model predictions, with the experimental results falling between the model plane stress and plane strain conditions for all three load levels tested. The second sample tested (Section 4.5.2) had been subjected to a pre-creep cycle prior to the HEXRD loading, and these results deviated from the model predictions. It would appear as though the creep law, as implemented in the model, was over-predicting the amount of creep strain at the notch. The creep law used in the model was derived using data from experiments and in-reactor deformation on large sections of pressure tube under uniaxial or biaxial stress. Since the stress state at the sample notches tested in this experiment is more triaxial, and higher in magnitude than the data used to derive the creep laws (<550MPa hoop stress for the creep law with >650MPa near the sample notch tip), it is not clear how applicable the creep law is to the scenario modeled in this chapter.
An interesting observation was that the residual strain very close to the notch tip in the pre-crept sample was slightly tensile, where one would reasonably expect the residual stress to be compressive close to the notch tip. Whether this is due to experimental error, such as inadvertent loading in compression during pre-creeping (very unlikely), or is a real effect, is not entirely clear. It could be there was some process occurring at the microstructural level in the region of high stress and creep strain that was causing a local alteration in the d-spacing of the material, which resulted in apparent tensile strains based on the shift in X-ray peak position even though the stress was actually compressive. More experiments would be required to verify the validity of this observation, and to find a satisfactory explanation for such behaviour. However, it was found that when these unexpected residual tensile strains were subtracted from the other HEXRD data sets associated with creep tests, the experimental curves approached the plane stress model curves. Following this logic, if the expected residual compressive strain was used as the reference for offsetting the results from the loaded experimental data, rather than zero strain, one would expect the curve to shift even further downward; the resulting experimental curves would likely fall between the plane stress and plane strain modeling conditions.

4.6.4 Model Comparison with Hydrided Samples
Two samples that were the subject of HEXRD strain mapping experiments in Chapter 3 were modeled. The first sample modeled (Section 4.5.4) was not subjected to loading prior to the experiment to induce creep strains. This sample showed good agreement between the models and experiments in terms of the shape of the curves. Locations of the peak strain for the model
predictions did not coincide exactly with the experimental results. The reason for this discrepancy is almost certainly the selection of hydride distribution in the model not accurately reflecting the real hydride structure. The magnitude of the strains for the zirconium matrix matched up well with the experiment, in that the experimental curve fell between the plane stress and plane strain lines. However, the predicted hydride strains were noticeably higher for the model. The likely cause for these higher strains was again the choice of hydride distribution, and more specifically the hydride spacing. As previously mentioned (4.6.2), the model hydride spacing was likely smaller than in the real sample, which resulted in greater interaction between the stress fields (due to precipitation) of the hydrides. Since hydride precipitation results in tensile stresses immediately adjacent to the hydride (see ‘far-field’ hydride results in 4.5.3), closer hydride spacing results in higher (positive) hydride strain.

The second sample modeled (4.5.5) was subjected to a pre-creep cycle prior to the HEXRD strain mapping experiments. As with the sample that was not crept, the shape and magnitude of the curves for the zirconium matrix appears to be correct, with a slight difference in peak strain location. One notable difference is the strain very close to the notch tip at 100% load, which shows a significant drop for the model, and very little change for the experiment; the likely reason for this discrepancy is the over prediction of creep strains near the notch-tip in the model (see 4.5.2). For the hydride phase, the experimental strain values are much closer to the model predictions than for the sample without prior creep. This change in agreement with the model from the previous sample (no pre-creep) could be partly due to the over prediction of creep strains in the matrix, as well as to a similar reason to that used to explain the difference between the experimental and modeling results for the sample without creep, ie. hydride
volume fraction. Experimental hydride intensity maps are shown in Figure 4-20. Though in the pre-crept sample the decay in hydride intensity is steeper, such that strain measurements were not obtainable with the 20 x 20μm beam beyond 0.15mm from the notch tip, it is also true that the peak hydride intensity close to the notch for this sample is noticeably higher than the non-crept sample. Higher hydride intensity means a denser distribution of hydrides in that location, which could explain the higher strains for this sample due to stronger hydride-hydride stress field interactions.

Figure 4-20: Hydride intensity maps for (a) SLS-08-073: No pre-creep; (b) SLS-08-071: Pre-crept

Very close to the notch tip (up to ~5µm away), the model predicts a difference in stress (parallel to the loading direction) between the crept and non-crept samples of only ~50MPa (amplitudes of ~700MPa non-crept / ~650MPa pre-crept). This seems to reaffirm the observation in Chapter 3 that the prior creep strains induced in the sample have only a small effect when it comes to reducing the peak strain experienced by the hydride upon overloading. Indeed, the experimental result suggested that the load interval size (120% to 130% overload) was too large to capture any difference in the fracture load required for the samples, and the model reinforces this assertion as well.
4.6.5 Additional Influences on Hydride Strain

The precipitation of hydride in zirconium is a complex process, and there are other possible influences on final hydride strain which are not accounted for in the modeling approach used in this chapter. Creep, though used to simulate pre-creep cycles in the model, could also contribute to relaxation of the strains in the hydride due to precipitation. However, given that no hydride was detected in scans at 250°C, this would mean that any creep would have to have happened between this temperature and room temperature as the sample was cooling (1°C/min to 150°C, then ~10°C/min to room temperature). Given the high peak stresses associated with hydride precipitation, it is possible some creep could have occurred to relieve the strain in the precipitating hydrides even at lower temperatures. However, this could not be sufficiently quantified for inclusion in the model, and there is also the question as to how applicable the creep law derived for macro pressure tube deformation would be to the high stress magnitude and triaxiality around the interface between hydride and the surrounding zirconium.

One other possible influence on the final strain of precipitated hydrides is a difference in thermal expansion between the hydride phase and the surrounding zirconium. These thermal expansions have been reported in literature as $\alpha_{\text{Hydride}} = 14.2 \times 10^{-6} / ^\circ\text{C}$ and $\alpha_{\alpha-Zr} = 6 \times 10^{-6} / ^\circ\text{C}$ [65], meaning that the hydrides contract faster than the surrounding zirconium upon cooling. Attempts to implement this difference in thermal expansion revealed the same correlation of strains with aspect ratio that was a problem when determining how to accommodate the volume change of precipitating hydrides (see 4.6.1). These modeling attempts did however show the influence of this difference in thermal expansion was small (<200μstrain), and since it
was not known at exactly what temperatures hydrides started and stopped precipitating, the addition of thermal misfit to the model was not deemed worthwhile. The small magnitude of the strains, coupled with their sensitivity to assumptions of geometry, made their inclusion a distraction from trying to compare more important aspects of the model to the experiments.

4.7 Conclusions

Overall, the finite element approach employed in this chapter did well in predicting the equivalent results obtained from HEXRD strain mapping experiments, particularly given that the real 3D distribution of hydrides was approximated using a 1D distribution in a 2D model. Ultimately, the biggest problem with the modeling approach was the assumption of a hydride distribution. The basic material properties were shown to yield model results very close to the experiments, though the creep law implemented in the model appeared to over predict the amount of creep occurring in the region in immediate proximity to the sample notch tip. In the samples with hydrides, the model did well in predicting the overall shape of the experimental curves, as well as the magnitude of the strains in both hydride and zirconium phases. Stress maps showed clearly how the precipitation of hydride reduces the peak stress at a stress concentration.
Chapter 5

Strain Mapping Using In-Situ SEM Imaging and Digital Image Correlation

5.1 Background

One method of extracting information about the strains developing at the microstructural level of a material is digital image correlation (DIC). This procedure was first proposed for measuring strains as early as 1983 [87] but has been the subject of renewed interest in recent years due to the falling cost and increased power of computing, as well as improvements in the resolution of images (i.e. CCD resolution) that can be easily obtained, allowing fine details to be captured with good local contrast. In a DIC routine, the basic principle is the comparison of two digital images: one image from before deformation has occurred, and one in the material’s deformed state. A simple representation of this is shown in Figure 5-1 [88].

Figure 5-1: Illustration of the fundamental principle of digital image correlation (DIC) [88]
5.1.1 DIC Methodology

Through the application of a correlation algorithm the displacements, and subsequently the strains, occurring within the imaged region can be determined. The great appeal of this method for the experimentalist is its inherent simplicity. Since DIC is a purely computational routine it can, in theory, be used with images extracted with almost any microscopy technique; DIC has been successfully implemented [89] using optical microscopy, scanning electron microscopy (SEM), transmission electron microscopy (TEM), scanning tunnelling microscopy (STM) and atomic force microscopy (AFM). The strain maps discussed in the experiments of this chapter are two-dimensional; however, using images from a stereomicroscope setup or images that inherently contain topographic information such as from an AFM, three-dimensional strain maps can be created as well [90]. Thus, DIC can produce strain maps at virtually any length scale for which an imaging technique exists, as long as the images are amenable for image correlation.

The first step in most digital image correlation routines is the subdivision of the image into discrete rectangular subsets known as ‘facets’, which can then be located and compared from one image to the next. The image correlation algorithm, which is essentially the core of the DIC software, compares a given facet before and after deformation by comparing their grayscale distributions [88]. A schematic for visualizing this basic procedure is shown in Figure 5-2 [91].
Figure 5-2: Basic procedure utilized by most image correlation algorithms [91]

Each facet must contain enough features such that the correlation between the deformed and undeformed images is unambiguous. A feature in this context is a region of high contrast that clearly stands out from the ‘background’, ie. the dark spots in Figure 5-2. Through this
procedure, the relative displacements of all facets are determined, creating a displacement map for the entire image. Different strategies are employed to carry out the comparison of facets. A number of image correlation algorithms have been developed to cross-correlate grayscale pixel intensity variations from the facets, employing a number of mathematical and computational strategies; these include simple least squares approaches, Fourier transforms or Bayesian probability methods. Some series of displacements and rotations is typically applied to a facet from the undeformed image so that it correlates with the deformed image. Typically, the quality of the fit between facets as a result of these transformations is given by a correlation coefficient, which is iterated until it is minimized below some threshold error value [88, 92]. An illustration to visualize this is shown in Figure 5-3 [93]. If the correlation coefficient cannot be minimized below the prescribed value, then the correlation will fail for that facet.

Figure 5-3: Illustration of the minimization of the correlation coefficient between facets [93]

An important point to emphasize is that displacement maps are found first, and these are subsequently converted to strain maps. This is because strains calculated from the displacements map provide much better results than strains directly calculated from facet
displacement gradients, as they are less sensitive to noise [94] in the image. W.G. Knauss et al. [95] have illustrated this by showing how the correlation coefficient varies strongly with respect to $u$ but is not very sensitive to $du/dx$, implying more accurate results for displacements than for gradients of displacements. It is also important to recognize that the data contained in images is discrete, in that it is a digital compilation of pixels and not a continuous signal. Since these discrete points do not always move in integer values of pixel spacing, some interpolation (ie. cubic spline) is typically applied by the DIC software to allow for the determination of subpixel displacements [95, 96].

### 5.1.2 General DIC Limitations

In order to evaluate the utility of DIC, it is important to understand its limitations and potential problems that may arise, so that they can be avoided or compensated for. There are several restrictions on the images and the imaging conditions that must be imposed in order for the algorithms to correctly cross-correlate two images to determine relative displacements. The basic imaging conditions should remain as constant as possible from one image to the next. Changes in focus between subsequent images can have a particularly deleterious effect, since this can cause a failure to correlate facets due to apparent changes in the size of features. This can be particularly problematic when using optical microscopy with its low depth of field, which can cause features to move out of focus simply due to Poisson contraction during straining of a specimen; in order to avoid this, constant refocusing between images would be required. Most algorithms can compensate for ‘noise’ in the greyscale distribution from one image to the next, but significant variation due to changes in imaging conditions (ie. illumination in optical microscopy or probe current on a SEM) could cause the correlation to fail.
When natural contrast is not sufficient to achieve a good distribution of features, a pattern must be applied to the surface, which can introduce other limitations to the usefulness of DIC. Often DIC investigations are performed to determine how microstructural features affect the strain field under certain stress conditions, and these features may become obscured if material is deposited on the surface to form a pattern for DIC. Pattern degradation is also a potential problem, and care must be taken such that the applied material remains strongly adhered to the material throughout the entire deformation process; if this is not true, then the change in the pattern will not be representative of the deformations occurring in the underlying material.

Finding an optimum facet size can prove problematic, and often requires some trial and error to determine. The fundamental problem here is that one typically wants the displacement map to be as dense as possible to get the highest possible spatial resolution for strains, however if the facet is made too small it will not contain enough features to be correlated unambiguously before and after straining and the procedure will fail. Increasing the facet size will result in increasingly better correlation between images, however this has limitations. Increasing facet size will decrease displacement resolution and could lead to potentially misleading strain results. This is because when facets become too large, the fundamental assumptions about displacement typically applied to facets by correlation algorithms (ie. usually assumed to be constant within the facet) become invalid. Somewhere between these two extremes an optimum balance can be found. Along with this there is also the issue of overlap, whereby one can allow adjacent facets to overlap to some degree to increase spatial resolution of displacements without further decreasing facet size; unfortunately, this too has its limitations.

In addition to the aforementioned problems with larger facet sizes, features with better contrast
and displacements closer to integer values of pixel spacing tend to have more weight in the
displacement calculation for facets [91], which can lead to some bias; too much overlap and
neighbouring facets will also share this bias, since they contain the same features, leading to
skewed results in the displacement map.

Large changes in the specimen surface during straining could also result in the software being
unable to correlate the images. Specifically, the emergence of new features of high contrast
such as shear bands or cracks could cause facets from the undeformed and deformed images to
look so different they cannot be correctly correlated. This effect can be reduced by taking
multiple images throughout the loading process, and performing image correlation on these
images sequentially. Displacements found from these intermediate images can be added by
vector addition to find the total displacement of the facet for the entire deformation process.
Care must be taken when finding displacements in this manner, as any errors in the
intermediate steps will propagate through the calculations possibly resulting in significant errors
in the final strain map.

5.1.3 SEM Specific Limitations

Depending on the type of imaging used for DIC, different potential challenges present
themselves. Since the work of this chapter makes use of SEM imaging, the possible problems
specific to this technique warrant further discussion. One important consideration when
performing scanning electron microscopy is which imaging mode should be used: secondary
electron imaging (SEI) or backscattered electron imaging (BEI). Using secondary electrons for
imaging provides contrast based on variations in the topography of the specimen surface.
Backscattered electrons are much more sensitive to the atomic mass of the material being imaged, and can give good contrast based on compositional variations within the material. Thus, for a material with different phases or precipitates present at the length scale of interest, BEI might be the optimal imaging mode for DIC. It was also found that adjusting the brightness and contrast on the SEM such that the grayscale intensity variation histogram for the SEM images is evenly distributed results in the best correlation [97]. It has been shown that to produce the best SEM images for DIC, low probe currents, high accelerating voltages and minimal working distances are typically used [93].

Certain nuances specific to electron optics can also result in distortion of SEM images leading to DIC failure or incorrect strain map results. SEM imaging can be affected by spatial and drift (temporally varying) distortion. This issue is particularly troublesome in non-conducting specimens, as specimen charging is one of the primary causes for these effects. It is therefore very beneficial if distortion correction [97] is available on the SEM imaging system. One must also be cognizant of stray magnetic fields which could affect the electron beam during specimen imaging. This can be particularly troublesome when attempting to image samples during in-situ loading, as the magnetic fields generated by any motor used to impose loading could potentially cause distortion in the SEM images.

It is important that the resolution of SEM micrographs is sufficient such that features that are used to track deformations are sufficiently large in terms of number of pixels such that they can be recognized from one image to the next. Essentially, what this means is that features must be oversampled such that they remain recognizable even with subpixel translations. Quinta Da
Fonseca et al. found that the minimum feature size required is 3 x 3 pixels [91]; in practice, larger sizes are advisable. A representation of how features can become distorted due to resolution effects in SEM imaging is illustrated in Figure 5-4 [98]. This figure shows how identical objects may appear different depending on their location on the image if the resolution is insufficient to accurately capture their geometry.

![Figure 5-4: Illustration of how features can become distorted due to resolution limitations in SEM imaging [98]](image)

5.1.4 DIC Deformation Studies Using SEM Imaging

Numerous examples of using SEM imaging with DIC techniques to study deformation at very small length scales exist in literature. For example, Lagattu et al. [93] attained a spatial resolution of ~1µm for displacements when studying a Ti-6Al-4V titanium alloy, highlighting the potential use of such techniques for studying deformation processes at the microstructural level. Li et al. [97] demonstrated that micro-scale thermal strain measurement in aluminum at
temperatures up to 125°C with a standard deviation of ~150μstrain is possible with the judicious application of distortion correction procedures. Kang et al. [88] used incremental image referencing to study aluminum alloy sheet material subjected to large deformation, which was able to account for the emergence of strain bands and allow measurement of the strain inhomogeneity caused by these features. Jin et al. [99] studied the ductile fracture behaviour of Al 6061-T651 alloy using pre-cracked CT samples, and showed that the in-situ SEM method was able to capture the high strain gradients produced in the region around the crack tip during loading.

5.2 Introduction

In the experiments of Chapter 3, the strain distribution at a stress concentration in Zr-2.5Nb pressure tube (PT) material was measured using high-energy X-ray diffraction (HEXRD). These measurements showed clearly the differences in strain upon loading between the zirconium hydride phase and the surrounding zirconium metal. One limitation of this technique, however, was that only elastic strains could be directly measured. Measurements were also through-thickness, providing an average of all the hydrides illuminated by the incident X-ray beam, and thus obscuring the details of the strain interaction between the zirconium and individual hydrides. Though the modeling technique of Chapter 4 could potentially provide information on plastic strains, it is still only a model that contains idealizations about hydride shape and distribution intended to represent the ‘average’ behaviour of the HEXRD measurements. The next logical step would be to find a technique to measure the full strain evolution between specific hydrides and the zirconium, including plastic strains. This is what is attempted in this
chapter, using an in-situ loading technique within a SEM, and analyzing the resulting images using DIC software.

5.3 Experimental Setup

All samples discussed in this chapter were machined from sections of Zr-2.5Nb pressure tube (PT) material; all material came from the same pressure tube. The material was charged with hydrogen using an electrolytic hydriding procedure (see Appendix D), followed by a homogenization heat treatment to reach the desired hydrogen concentration [59]. Two target hydrogen concentrations were used in this experiment: 60wt-ppm and 100wt-ppm. Compact tensile (CT) samples were cut from the sections of PT material using electric discharge machining (EDM); this machining technique was used because it would minimize residual stresses imparted to the samples, and it is very precise. An illustration showing how the material was removed from the sections of PT can be found in Figure 5-5, along with how the sample is oriented with respect to the macroscopic tube directions (axial, radial, and transverse directions). For a real photograph showing a pressure tube section with removed sample material, refer to Appendix C. A notch with a root radius of ~40µm was EDM cut into the samples. For a drawing showing the exact sample dimensions, refer to Appendix B.
The samples from the hydrogen-charged material were subjected to thermal cycling while under load in order to grow large hydrides at the stress concentrating notches; this procedure is referred to as thermal ratcheting [100]. During this process the sample is cycled between temperatures, with the temperature at the high end being sufficient to dissolve some, but not all, of the hydride and freeing up hydrogen into solution; freed hydrogen can subsequently diffuse to the stressed notch at the low end of the temperature cycle, where hydrides re-precipitate. In this way, the hydrides at the notch increase in size with each temperature cycle.

Details of the thermal cycle used are as follows:

1. Heated at 1°C/min to a maximum temperature of 350°C and held for 1 hour in order to dissolve all hydride.

2. Cooled at 1°C/min to 185°C and held for 3 hours in order to allow diffusion of hydrogen to the notch and growth of hydride.
3. Cooled at 1°C/min to 60°C (not held) to maximize hydride precipitation.

4. Heated at 1°C/min to 300°C and held for 1 hour to return some (but not all) hydrogen back to solution.

5. Repeat from Step 2.

During the temperature cycling the load applied to the samples was kept constant by means of a computer-controlled stepper motor that compensated for the thermal expansion/contraction of the components within the oven. The load (75lbs) was chosen to produce a nominal stress intensity (K) of ~8MPa√m at the notch, assuming a sharp crack as per ASTM E399 [61]; this is equivalent to the load used to promote the precipitation of hydride in the experiments of Chapter 3. This load was reduced slightly in some samples to reduce the likelihood of premature hydride fracture. The number of thermal cycles used was ~5-6, which was found to produce sufficiently large hydrides, without the risk of premature fracture (seen in some early attempts to grow hydrides). A listing of the hydrogen-charged samples discussed in this chapter indicating the loads and number of thermal cycles they were subjected to, along with their hydrogen concentrations, is shown in Table 5-1.

Table 5-1: List of properties for hydrogen-charged samples discussed in this chapter

<table>
<thead>
<tr>
<th>Sample</th>
<th>#1</th>
<th>#2</th>
<th>#3</th>
<th>#4</th>
<th>#5</th>
</tr>
</thead>
<tbody>
<tr>
<td>[H] (wt-ppm)</td>
<td>60</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>60</td>
</tr>
<tr>
<td>Growth Load (lbs)</td>
<td>75</td>
<td>75</td>
<td>70</td>
<td>70</td>
<td>70</td>
</tr>
<tr>
<td># Cycles</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>6</td>
</tr>
</tbody>
</table>

Surface preparation to give the best DIC result was a lengthy process of trial and error. It was decided early on that using the material microstructure to provide the required contrast variation across the sample surface for DIC would be the ideal approach. Given the fine grain
size (~0.2µm) of the cold-worked, two-phase Zr-2.5Nb PT microstructure, a high spatial resolution for the strain maps could be achieved. This method also allowed the direct comparison of calculated surface strains to microstructural features of interest, ie. hydrides and the surrounding zirconium; depositing another material on the surface to provide image contrast would have obscured the details of the hydride/zirconium interaction. After several unsuccessful attempts, a procedure was devised to etch the surface enough to provide sufficient contrast for DIC, but not so much that surface features of the interest were obliterated.

![Figure 5-6: Failed attempts to optimize the surface due to: (a) over-etching destroying microstructural features; (b) under-etching providing insufficient contrast for DIC](image)

The optimal balance was achieved by grinding the sample surface to 1200grit sandpaper followed by several rounds of attack polishing using 0.6µm colloidal silica with a solution of 5%HF / 5%HNO₃ / 5%H₂O₂ / 85% H₂O. This produced a surface that was slightly over-etched, providing good contrast, but not so much so that the hydrides were obscured. The hydride phase was difficult to discern using secondary electron imaging (SEI), so backscatter electron images (BEI) were taken before DIC testing was commenced in order to locate the hydrides for later comparison with strain maps (generated from SEI images). An example of the optimized
surface condition and a backscatter image showing the location of hydrides at the notch tip is shown in Figure 5-7.

Figure 5-7: SEM micrographs showing: (a) optimized surface preparation with α/β Zr-2.5Nb microstructure visible around the notch tip; (b) BEI image revealing the locations of hydrides

Once the samples had been prepared, they were tested as soon as possible to minimize the effects of surface oxidation. Samples were loaded using a small loading stage designed to fit inside the SEM chamber. The SEM used for the experiments was initially a JEOL JSM-840 at Queen’s University, and later a Philips XL30 FEG at Kinectrics, Inc.; the rationale behind this change in equipment is explained in the discussion Section 5.6. In order to pin-load the CT samples, special grips had to be fabricated to fit on the loading stage (see Appendix B for drawings). For a picture of a sample in the loading stage, please refer to Appendix C. Samples were loaded incrementally under load control until a notch-tip hydride fractured. At each increment, control of the loading stage was paused, and several minutes were allowed to pass so that any relaxation could occur and the load could stabilize; relaxation was not significant at the loads used, and the resulting drop never exceeded 2% of the peak load. Images were taken after refocusing the SEM on the sample surface, which would move between increments due to
Poisson contraction; though the SEM had a large depth of field, this ensured the best image quality.

5.4 Data Analysis

Analysis of the strained images was performed using the commercial DIC software package ISTRA 4D. All images were correlated with respect to a reference image taken at zero load prior to starting the test. Sequential referencing of images was unnecessary, as changes in the sample surface during deformation were not significant enough to cause problems when correlating to the undeformed image. The size of the facets used to carry out the correlation differed from sample-to-sample, but were chosen to be as small as possible and still correlate successfully; this lower limit on facet size is limited by the quality of the images and the surface preparation. Strains reported are parallel to the loading direction (normal to the notch).

Though strain in any direction can be calculated with this method, the chosen direction is consistent with the results of Chapter 3, while also being very close to the direction of the maximum principal strain near the notch.

The calculated displacement results were filtered using an adaptive spline polynomial algorithm. Without filtering, the strain is wholly calculated based on the distortion of the individual facets, which in these experiments produced very noisy results. Filtering the data with the algorithm makes the strains more dependent on the gradient of the deformation; the 7 x 7 filter size used in this experiment resulted in the calculated strain values depending almost entirely on the deformation gradient [101]. The effect of increased filtering is shown in Figure 5-8 for a loaded, notched CT sample without hydrides. While filtering does smooth the results, and proved to be
necessary in the experiment in order to make any useful observations, it does reduce the spatial resolution. Error in the strain measurements was estimated by correlating two consecutive images at zero load. Based on this, the uncertainty on a single strain data point as presented was estimated to be ±300µstrain.

Figure 5-8: Strain maps showing the effect of displacement filtering: (a) no filtering; (b) 3 x 3 filter; (c) 5 x 5 filter; (d) 7 x 7 filter

5.5 Results

The results presented in this section are for the five notched CT samples detailed in Table 5-1. These samples all contained pre-grown, notch-tip hydrides. For each sample images are presented showing the region upon which image correlation was performed, followed by a plot.
showing the size of the facets into which the image was subdivided. Also shown for each
sample is a BEI image showing the location of the hydrides, followed by an image from the end
of the test showing the crack formed at the notch-tip. Strain maps are presented for the last
loading step before hydride cracking was observed; this provided the best opportunity for
observing differences in the strain response of the hydride and surrounding zirconium. Note
that any ‘holes’ that appear on the strain map correspond to facets that did not successfully
correlate. To better relate the calculated strains to the microstructure, a version of the strain
maps is also presented with an image of the hydrides superimposed. For each sample, one
representative measurement is also shown for the strains across a line spanning both the
hydride and surrounding zirconium in a location close to the notch face.

5.5.1 Sample #1

Images showing the area correlated, facet size, hydride locations and final crack location are
shown in Figure 5-9. Particles appearing on the surface of this sample are silicon carbide that
‘stuck’ to the surface after the final stage of grinding (1200grit sandpaper). These particles had
no discernable impact on the DIC procedure, and did not obscure any features of interest on the
surface. The final crack location can be seen to correspond to a large, notch-tip hydride. Notch-
tip hydride fracture occurred at 124% load (K_i~10.1MPaVm), and strain maps at 120% load
(K_i~9.8MPaVm) are shown in Figure 5-10. Note how in regions where there is hydride, there
appears to be lower strain than the surrounding zirconium. This is most apparent in the region
around the hydride that is to fracture (indicated in Figure 5-10). In this region, in the immediate
vicinity of the notch face, the strain difference between the visible hydride region and the
surrounding matrix is \(\sim 4-4.5\) strain. The strain distribution at one location is shown in Figure 5-11.

Figure 5-9: Images for sample #1 showing (a) DIC region; (b) DIC facet size; (c) hydride positions (BEI); (d) final crack position
Figure 5-10: DIC results for sample #1 showing: (a) strains at 120% load; (b) strains at 120% load with hydride (BEI) overlay and with region of interest (fracture location) indicated
5.5.2 Sample #2

Images showing the area correlated, facet size, hydride locations and final crack location are shown in Figure 5-12. The final crack location can be seen to correspond to a large, notch-tip hydride. Notch-tip hydride fracture occurred at 125% load ($K_I \approx 10.2\text{MPa}\sqrt{\text{m}}$), and strain maps at 120% load ($K_I \approx 9.8\text{MPa}\sqrt{\text{m}}$) are shown in Figure 5-13. Unfortunately, there appeared to be a small pre-existing crack or flaw near the surface at this location (visible in Figure 5-12). Although right at the notch tip most of the strain appears concentrated at this flaw, further away from the notch face a strain differential is again visible between the hydride and surrounding zirconium, though it is smaller than in sample #1 at $\sim 3-4\text{mstrain}$. The strain distribution at one location is shown in Figure 5-14.
Figure 5-12: Images for sample #2 showing (a) DIC region; (b) DIC facet size; (c) hydride positions (BEI); (d) final crack position
Figure 5-13: DIC results for sample #2 showing: (a) strains at 120% load; (b) strains at 120% load with hydride (BEI) overlay and with region of interest (fracture location) indicated
Figure 5-14: Plot for sample #2 showing the strain distribution along a line spanning the hydride (centered at ~8µm) near the notch-tip; facet size across sampled area shown above.

5.5.3 Sample #3

Images showing the area correlated, facet size, hydride locations and final crack location are shown in Figure 5-15. The final crack location can be seen to correspond to a large, notch-tip hydride. Notch-tip hydride fracture occurred at 141% load \((K_I \sim 10.8\text{MPa} \text{Vm})\), and strain maps at 136% load \((K_I \sim 10.4\text{MPa} \text{Vm})\) are shown in Figure 5-16. A distinct strain differential between the hydride region at which the crack later occurred and the surrounding zirconium is visible. Measurements around this location indicate a difference of ~4-4.5mstrain. The strain distribution at one location is shown in Figure 5-17.
Figure 5-15: Images for sample #3 showing (a) DIC region; (b) DIC facet size; (c) hydride positions (BEI); (d) final crack position
Figure 5-16: DIC results for sample #3 showing: (a) strains at 136% load; (b) strains at 136% load with hydride (BEI) overlay and with region of interest (fracture location) indicated
Figure 5-17: Plot for sample #3 showing the strain distribution along a line spanning the hydride (centered at ~10µm) near the notch-tip; facet size across sampled area shown above

5.5.4 Sample #4

Images showing the area correlated, facet size, hydride locations and final crack location are shown in Figure 5-18. The final crack location can be seen to correspond to a large, notch-tip hydride. Notch-tip hydride fracture occurred at 145% ($K_I \sim 11.0\text{MPa} \sqrt{\text{m}}$) load, and strain maps at 136% ($K_I \sim 10.4\text{MPa} \sqrt{\text{m}}$) load are shown in Figure 5-19. A strain differential between the hydride region and the zirconium around the notch is visible, however this was noticeably lower than in the other samples at only ~1-2mstrain; all the calculated strains were also lower than what would be expected based on the behaviour of the other tested samples. The strain distribution at one location is shown in Figure 5-20.
Figure 5-18: Images for sample #4 showing (a) DIC region; (b) DIC facet size; (c) hydride positions (BEI); (d) final crack position
Figure 5-19: DIC results for sample #4 showing: (a) strains at 136% load; (b) strains at 136% load with hydride (BEI) overlay and with region of interest (fracture location) indicated
Figure 5-20: Plot for sample #4 showing the strain distribution along a line spanning the hydride (centered at ~10µm) near the notch-tip; facet size across sampled area shown above

5.5.5 Sample #5

Images showing the area correlated, facet size, hydride locations and final crack location are shown in Figure 5-21. The final crack location can be seen to correspond to a large, notch-tip hydride. Notch-tip hydride fracture occurred at 166% (KI~12.7MPa√m) load, and strain maps at 161% (KI~12.3MPa√m) load are shown in Figure 5-22. In this sample, a strain differential is visible between what appears to be the largest hydride at the notch tip and the surrounding material of ~4-4.5mstrain; however, this was not the hydride that was observed to fracture at the end of the test. The strain distribution at one location is shown in Figure 5-23. Note that a number of facets did not correlate, and these were all collinear; this was likely a problem with the electron beam raster, but did not affect the results in the region of interest.
Figure 5-21: Images for sample #5 showing (a) DIC region; (b) DIC facet size; (c) hydride positions (BEI); (d) final crack position
Figure 5-22: DIC results for sample #5 showing: (a) strains at 161% load; (b) strains at 161% load with hydride (BEI) overlay and with region of interest (fracture location) indicated
5.5.6 Sample #5: Post-Fracture

Strain maps were also generated for the samples after fractured had occurred. Most of the samples showed the typical ‘double-lobed’ strain distribution expected at a sharp crack, though correlation of the facets in the immediate vicinity of the crack tip was often poor due to large deformation. The strain distribution after cracking is shown in Figure 5-24 for sample #5. This was one of the better quality post-fracture strain maps, and also has a more unique situation in that a small hydride fractured immediately adjacent to a much larger one. There appears to be a noticeable drop in strain visible across one of the high strain ‘lobes’ where it crosses the larger hydride.
Figure 5-24: Strain map showing the strain distribution in sample #5 after fracture of a notch-tip hydride

5.5.7 Expected Strain Distribution without the Presence of Hydrides

Several tests were conducted on samples without hydrides present, however these were all on a different SEM than the one from which the other results in this section were derived. These results were lower resolution and suffered from problems with image stability which lead to them being deemed unreliable. Thus, in order to present the (idealized) result one would expect for strains in a baseline CT sample without notch-tip hydrides present, a simple, 3D finite element model was constructed using ABAQUS. This model used the same Zr-2.5Nb material
properties that were discussed in the modeling work of Chapter 4, applied to the CT sample geometry with the same nominal dimensions as the test samples of this chapter. Quadratic, wedge-shaped elements were used to mesh the model; the mesh used can be found in Appendix E. Results from the finite element simulation are shown in Figure 5-25 under an applied loading to $K_I \sim 10.3\text{MPa}\sqrt{\text{m}}$, for strains normal to the notch direction.

Figure 5-25: FE model showing expected strain distribution in a hydride-free sample at a load equivalent to $K_I \sim 10.3\text{MPa}\sqrt{\text{m}}$

There is a single high-strain region at the root of the notch, with strain decreasing with distance from the stress concentration, as would be expected. The strains in the vicinity of the notch-tip are of the same order as those observed in the experiments. The peak strain at the notch tip in this model was 17.4mstrain, which agrees well with peak values from the DIC experiments; for example, the peak strain recorded for sample #1 ($K_I \sim 9.8\text{MPa}\sqrt{\text{m}}$) was $\sim 16\text{mstrain}$, and in sample #5 ($K_I \sim 12.3\text{MPa}\sqrt{\text{m}}$) was $\sim 18\text{mstrain}$.
5.6 Discussion

5.6.1 Image Stability and Pseudo-Strains

Image quality and stability proved to be a recurring problem throughout the course of these experiments. Initial in-situ loading experiments were performed on a JEOL JSM-840 SEM at Queen’s University. When attempting to perform DIC on the images captured during these experiments, image distortions in the form of bands running across the image resulted in calculated strains larger than those that were the target of the measurements. These image distortions could not be discerned by eye, yet resulted in significant strain when subjected to DIC. Pseudo-strains due to these imaging artifacts made it difficult or impossible to interpret the DIC results. A survey of literature found that this problem was not unique, and was encountered by Lagattu et al. [93] in similar in-situ SEM loading experiments. A comparison showing the similarity of their problem to the one encountered in this experiment is shown in Figure 5-26. In their paper, they report that this problem was resolved through the minimization of electromagnetic disturbances until the calculated pseudo-strains were deemed acceptably low. Attempts were likewise made to reduce disturbance sources in this experiment, to no avail; even DIC performed on subsequent images under no load without the loading stage in the chamber still had the issue.
Figure 5-26: Comparison of strain distortions from (a) Lagattu et al. [93]; (b) initial experiments on the JEOL JSM-840 SEM

The solution to this problem came about through collaboration with Kinectrics, Inc. Access to their Philips XL30 FEG SEM allowed for high quality images that proved much more stable and amenable to the DIC process. Occasional fluctuations in strain of up to ±500µstrain were still apparent under zero loading, but this is close to the level of ‘noise’ achieved by other researchers [93], and substantially lower than the target notch-tip strains for the experiment.

5.6.2 Uncertainty in Image Correlation Strain Values

Quantifying the uncertainty associated with the strain data points generated from DIC performed on the SEM images was difficult to do precisely. The estimate of ±300µstrain stated in Section 5.4 was based on repeated measurements taken at zero load and represents the random error associated with the strain measurements. This level of uncertainty was derived from strain maps that had been filtered, which acts to reduce the scatter in the strain values at the expense of spatial resolution. Though sufficient to see differences in strain between hydride regions and the surrounding zirconium, an exact value of realized spatial resolution could not be obtained from the software; in future work this situation could be resolved by writing custom
DIC software, where the details of the correlation algorithm and the effects of data filtering would be more transparent than in a commercial software package.

The resolution of the SEM micrographs was sufficiently high that the distortion of features due to resolution effects as described in Section 5.1.3 was not expected to be significant, though the distribution of features could be expected to have some effect on the accuracy of the correlation; facets containing more features may have been correlated more accurately than those that were more sparsely populated. However, a minimum ‘correlation accuracy’ of 0.1 pixels was specified, below which the correlation of a facet would fail. Beyond this the position-to-position influence of this effect could not be precisely quantified, again because of the closed nature of the software. It should be noted, however, that this effect would have contributed to the stated uncertainty (±300µstrain), since strain values came from different locations on the sample surface at zero load. Systematic errors may have also been present that could have shifted the calculated strain values away from their true values. For example, though the SEM was carefully refocused between loading steps, there still may have been slight differences in focus that would introduce pseudo-strains into the entire strain map.

5.6.3 Hydride and Zirconium Matrix Strain Differential

Qualitatively, there is an observed strain differential between some regions containing hydride and the surrounding zirconium material in most of the samples tested. Where this is indicated, it is clear that there are two high strain regions separated by the hydride, with the strains in the hydride being lower than in the zirconium matrix immediately surrounding it. This observation would seem to reinforce the commonly-held belief that at room temperature, the zirconium
matrix yields plastically, while the loading of the hydride is almost entirely elastic up to the point of brittle fracture. In all cases except for sample #5, the hydride region with the largest visible strain differential compared to the surrounding Zr-matrix was where the sample cracked at the end of test. In sample #5, there are two visible notch-tip hydrides, with the visible strain differential appearing to be associated with the one which is much larger; in the end, however, it was the smaller hydride which fractured. The explanation for this lies in the unpredictable nature of hydride fracture, and brittle fracture in general, which is highly dependent on the presence and distribution of flaws in the material. However, after the smaller hydride in sample #5 fractured, there was a noticeable drop in strain within the high strain region generated at the notch tip where it crossed the larger hydride.

Extracting exact, quantitative information from the 2D strain maps regarding strain differences between the hydride phase and the surrounding zirconium at high stress locations is not straightforward. Unlike in diffraction methods, where strains can be uniquely attributed to one phase or another based on shifts in peak positions, the situation for DIC is not so clear. The use of some data smoothing in this experiment, which proved necessary to interpret the results, only confounds the issue further. This is the reason for the general ranges of strains which are presented in the results section, which were arrived at by several measurements around the hydride region and meant to give a general sense of the strain difference. In general, with the exception of sample 4, the strain differential between the hydride region and surrounding Zr-matrix fell into the range of 3.5-4.5mstrain, so some consistency was achieved. Sample 4, however, was anomalous not only in the observed strain differential but also in the magnitude of the strains observed at the notch, which were significantly lower than would be expected for
the applied load; it is possible that the grips applying the load could have been slightly misaligned, resulting in a slight bending moment compressing the face of the sample being imaged by the SEM.

There could be several possible reasons for the observed sample-to-sample variation in the measured strain differential between the hydride and the zirconium before fracture. The first, and perhaps the most obvious, is that not all the strain maps were taken at the same load. The purpose of these experiments was to see if any difference could be observed between the hydride and the surrounding zirconium. Strain maps shown in this chapter are the closest imaged loading state to hydride fracture, since this would be expected to give highest strains, and most pronounced strain differential; however, as mentioned, hydride fracture is unpredictable, and none of the samples saw hydride fracture at exactly the same load. Notch-tip hydride morphology was also different from sample-to-sample, with different sizes and distributions of hydrides. In addition, only the hydride distribution at one depth is being observed by this method, whereas it is expected that the entire hydride distribution through-thickness controls the onset of cracking. An attempt to look at the through-thickness distribution of hydrides is discussed in Chapter 6.

Trying to separate the influences of the different contributing factors to the observed load sharing and hydride fracture behaviour would require further testing. Originally twelve samples were to be tested in these experiments, but this was reduced to five due to attrition stemming from problems with the thermal ratcheting apparatus used to grow the notch trip hydrides, and
early SEM imaging difficulties. A larger sample size would have been helpful in increasing confidence in the observed results.

5.6.4 Comparison with Synchrotron X-Ray Strain Measurement

In this chapter two-dimensional strain maps were generated around notched stress concentrations in Zr-2.5Nb PT material, much like what was done in Chapter 3 using high energy X-ray diffraction (HEXRD); however, there are distinct differences between what is being represented by these measurement techniques. One would expect the stress state around the notch to vary through-thickness, with the stress state close to plane stress near the surface and closer to plane strain near the centre. Strain maps using the DIC method are strictly surface measurements, and thus represent only a single stress state (plane stress), whereas the HEXRD measurements represent an average through thickness. Strain measurements from HEXRD represent elastic strains in the material, whereas the DIC method gives the total strain including plastic contributions; however, the strains of each phase (hydride or zirconium) can be directly determined using HEXRD, whereas the situation is not so unambiguous with DIC. Thus, neither technique can be considered ideal, which is the reason why both methods of strain mapping were attempted.

One interesting observation that relates to the HEXRD results is the peak strains calculated for the hydride phase in the last measurement before fracture. The two samples in the DIC experiments that were the least ambiguous were sample #1 and #3. In both these samples there was a clear strain differential around the hydride that later went on to fracture, and there was no additional uncertainty added by surface defects (sample #2) or anomalous strains.
resulting from possible misalignment of the grips (sample #4). The strain in the large hydride around the notch face for these samples is ~6mstrain, which is very consistent with the peak elastic hydride strains observed before fracture in Chapter 3. Since it is expected that there would have been little plastic deformation in the hydride phase at room temperature, this level of agreement is very encouraging.

5.7 Conclusions

The results of this chapter showed the potential for SEM imaging combined with DIC to produce high spatial resolution strain maps around a notched stress concentration. Differentiation between strains in large notch-tip hydrides and the surrounding zirconium matrix was found to be possible using this method. The magnitude of the zirconium strains were of the same order as those predicted by FE modeling, and the hydride strains were shown to have a very good level of agreement with the results of Chapter 3. This technique was not without its problems, however, and proved to be very sensitive to sample preparation and imaging conditions. Future work would be required to optimize imaging parameters, and test more samples to increase confidence in the repeatability of this strain characterization technique.
Chapter 6

Investigation of Hydride Morphology Using Neutron Tomography

6.1 Background

Tomography is a technique used to reconstruct the internal structure of an object based on measurements of radiation transmitted through, reflected by, or emitted from that object. Development of this tool began in the early 1960s [102] and advanced rapidly due to its utility in medical applications. In most tomography applications, measurements of an object are made by taking radiographs, where the contrast is provided by the attenuation of the radiation by internal features of the object. Each measurement represents a projection of the internal features along the plane of the detector used to record the radiation. A single projection does not contain sufficient information about the morphology of the features through-thickness; for this reason, multiple projections are taken at angles distributed around the object of interest to acquire additional information. The shape and distribution of features (attenuation coefficients) within the object in a plane normal to the projection planes is reconstructed by computer algorithms from the angular projections around the object [103].

In order to perform a tomographic reconstruction all that is required is measurements that show differences in attenuation by internal structures of an object at enough angular locations to provide sufficient information to reconstruct them unambiguously. Since the measurements used for tomographic reconstruction in this chapter were generated using neutron radiography, this is all that will be discussed here. In the experiments of this chapter, 2D neutron radiography images taken at different angular orientations were used to obtain the required attenuation
data. Unlike in X-ray imaging, where attenuation is due largely to electron cloud interactions, the attenuation of neutrons is due to interactions with atomic nuclei and is governed by quantum mechanics. As a result of this, X-ray attenuation tends to increase with increasing atomic number (density), whereas neutron attenuation varies non-uniformly across the periodic table [104]. This makes light elements very difficult to discern amongst heavier elements using X-rays, whereas neutrons have a very strong (scattering) interaction with, for example, hydrogen. The basic relationship for the attenuation of a neutron beam passing through a material can be described by [105]:

$$\phi = \phi_0 e^{-\Sigma_i t}$$

where $\Sigma_i$ is the total macroscopic cross-section, $t$ is the thickness of the object, and $\phi$ and $\phi_0$ are the transmitted and initial intensities, respectively. The total macroscopic cross-section (units of cm$^{-1}$) represents the total probability of interaction, by either scattering or absorption, for a neutron passing through a volume of material. The probability of interaction also changes with incident neutron energy [106]. Absorption tends to increase with increasing neutron wavelength (decreasing energy). Neutron energy can have a large effect on scattering as well, particularly in crystalline materials where changes in neutron energy (wavelength) can change whether the Bragg diffraction condition is met for different sets of crystallographic planes [107]. This property has been successfully used to enhance the contrast of different materials or phases within a body by using energy-selective neutron radiography [108, 109].

The sensitivity of neutron tomography (NT) to the presence of hydrogen has made it an extremely useful tool for numerous applications ranging from the determination hydrogen distribution in titanium alloy compressor blades [110] to the inspection of rubber ‘O-rings’
within metal valve bodies [111] (see Figure 6-1). The NT experiments described in this chapter were performed at the ANTARES beamline of the FRM-II research reactor operated by Technische Universität München (TUM). The reactor at this facility operates at a nominal power of 20MW, and a cold neutron spectrum peaked at ~5meV, with a flux of \( \sim 9.1 \times 10^{13} \text{ cm}^{-2} \text{s}^{-1} \), is produced by a liquid D_2 moderator at ~25K [112]. An adjustable diaphragm collimator setup at the ANTARES beamline allows L/D ratios of 400 and 800 and delivers expected neutron fluxes \( 9.3 \times 10^7 \) and \( 2.3 \times 10^7 \text{ cm}^2 \text{s}^{-1} \), respectively [113].

Figure 6-1: 3D tomographic reconstruction of a rubber ‘O-ring’ that was inside a one inch thick stainless-steel valve [111]

6.2 Introduction

The purpose of the experiments described here was to make use of NT to determine the morphology of notch-tip hydrides in Zr-2.5Nb pressure tube material. Though these experiments do not involve the measurement of strains, they do have implications for the previous chapters (3, 4 & 5). In all of experiments or modeling work discussed previously, one
A piece of information that was missing is the three-dimensional, through-thickness variation in hydride distribution and morphology. It has been shown that local hydrogen concentration in zirconium can be roughly determined using neutron radiography [114]. This is due to the very strong scattering interaction for neutrons with hydrogen, and the hope for these experiments was that the very high proportion of hydrogen in zirconium hydride (ZrH$_x$, $x$$\sim$1.5-1.6) would produce high contrast for the tomographic reconstruction of notch-tip hydrides.

### 6.3 Experimental Setup

Samples examined in this chapter were C-shaped, and machined from the wall of Zr-2.5Nb pressure tubing; the material and geometry of the samples is identical to that described in Chapter 3, and a dimensioned drawing can be found in Appendix B. Each of the samples examined using NT were previously used in synchrotron X-ray diffraction experiments by Kerr [57, 58]. The first sample, which will be referred to as ‘Sample 1’, was used in an experiment designed to observe the in-situ precipitation of hydride at the notch, and the resulting strain distribution [57]; the resulting notch-tip hydride was \(~100\mu\text{m}\) long and unfractured. The second sample, or ‘Sample 2’, was used in an experiment designed to observe the overload fracture behaviour of a pre-grown hydride [58]; the notch tip hydride in this sample was \(~100\mu\text{m}\) long and was fractured during that experiment. SEM micrographs showing the notch-tip (near surface) hydride distributions for the samples are shown in Figure 6-2.
Figure 6-2: SEM images (BSE) showing near-surface notch-tip hydride distributions for: (a) Sample 1; (b) Sample 2

Neutron radiographs were taken at different angular positions around the sample by attaching it to a rotating sample stage that was programmed to rotate the sample between exposures; this is illustrated in Figure 6-3, along with an example of a radiograph from Sample 1. For each sample 800 radiographs were taken, spread evenly over 180° (0.225°/exposure) with a 70 second exposure time for each image. After each set of rotated radiographs on a sample, 10 ‘dark’ images were taken (neutron beam blocked off), as well as 25 ‘open beam’ images (no sample) for detector calibration. The neutron detector used was a $^{6}\text{LiF}+\text{ZnS(Ag+Cu+Au)}$ scintillator screen [113]. In order to maximize spatial resolution such that the hydride region could be resolved, the thinnest available (10µm) scintillator was used; however, using a thinner scintillator also had the drawback of poorer counting statistics, and therefore ‘noisier’ images. Light generated by the scintillator was reflected from a 45° mirror, through a focusing lens, and onto a cooled CCD with a resolution of 2048x2048 pixels; the mirror’s purpose in this arrangement was simply to allow the CCD to sit outside of the neutron beam. Using this arrangement, the calculated pixel size for the images was 15.8µm.
Three different conditions for the notch-tip hydrides were examined using NT in this experiment. In the first set of NT scans, Sample 1 was examined in its initial state with the notch tip hydrides intact. Once these scans were completed, the sample was overloaded in tension to 150% of the load used to form the notch-tip hydrides, resulting in fracture; this load was maintained throughout the subsequent radiography to keep the crack(s) open and potentially more visible. In order to apply the required tensile load to the sample, a tensile loading apparatus was designed and constructed that incorporated a load cell and allowed application of the load by hand (using a wrench). An illustration of the load apparatus is shown in Figure 6-4, along with an optical micrograph taken after the experiment confirming that the applied load was sufficient to fracture the notch-tip hydrides. The shaft supporting the load, and through which neutrons would have to pass in some of the radiographs, was made out of aluminum (very high neutron permeability) to reduce imaging artifacts due to its presence. For
a picture of the real setup at the ANTARES beamline, see Appendix C. Sample 2, which already contained cracked notch-tip hydrides, was examined in the last set of radiographs. In an attempt to make the crack more visible, a gadolinium-based ‘dye’ (very strong neutron absorber) was applied to the sample in a vacuum chamber prior to the experiment.

![Diagram of tensioning apparatus](image)

**Figure 6-4:** (a) tensioning apparatus used to load Sample 1; (b) 500x optical micrograph showing the resulting notch-tip crack in Sample 1

### 6.4 Data Analysis

Reconstruction of two-dimensional slices through the samples from the set of radiographs taken at angular positions around them was carried out using software written by the beam scientists at FRM-II [115]. The software automatically normalized the radiographs with respect to the open beam and dark images (averaged) to eliminate inhomogeneities from the neutron beam, scintillator, or CCD. A filter was also employed to automatically remove bright spots from the
images, which were due to gamma rays striking the CCD. Since the axis of rotation of the sample was not necessarily centered in the radiographs, all the images were shifted and rotated by the software; in order to perform this operation, the first (0°) and last (180°) images had to be manually aligned, and the software interpolated and applied the necessary transformation parameters to all the intermediate images. Once these initial corrections were made, the software reconstructed the 2D slices through the sample volume. An example showing a reconstructed slice through Sample 1 is shown in Figure 6-5.

![Reconstructed cross-sectional slice from Sample 1](image)

**Figure 6-5: Reconstructed cross-sectional slice from Sample 1**

The reconstruction software produced a ‘stack’ of images representing cross-sections through the sample. In order to transform these image sets into 3D representations of the samples, the open source image processing software FIJI (based on ImageJ) was used. Since the objective was to see a very small high-contrast region near the notch of the sample (hydrides), significant adjustments had to be made to the colour levels and brightness / contrast of the images to distinguish this region from its surroundings.
6.5 Results

Results from the three samples examined are presented in the form of images taken from the assembly of the 2D tomographic slices into a 3D sample volume. First, a 3D image will be presented showing the reconstructed sample volume in the region around the notch tip. A second image will be presented that is cropped and adjusted to reveal the 3D contrast (hydride) distribution along the notch tip. The last image to be presented is a hydride cross-section, nominally bisecting the notch, through the plane which was found to contain the strongest contrast distribution. An illustration showing the approximate location of this section on the samples is shown in Figure 6-6. A second version of this cross-section is also presented using a ‘thermal’ filter, which makes the highest intensity regions along the notch more clearly defined; ‘dots’ appearing in this image are high contrast points (voxels) outside of the plane being examined. In all the reconstructions and planar slices through them, high scattering volumes (ie. hydrides) appear darker.

Figure 6-6: Illustration showing the approximate location of the section plane (A-A) through the sample used for the hydride region cross-section results
6.5.1 Sample 1: Intact Hydrides

The first sample examined had relatively large (~100µm), unfractured hydrides at the notch tip. A 3D representation of the volume reconstructed from the cross-sectional, tomographic slices around the notched region of the sample is shown in Figure 6-7, along with a closer view of the notch-tip region with further contrast adjustment to allow observation of the hydrides. In Figure 6-8, 2D representations are shown for a ‘slice’ bisecting the notch region showing the hydride distribution. The distribution of hydride along the notch appears to be fairly continuous along its length, however the size and distribution of the hydride region is not constant through-thickness; hydride concentration appears to be denser at some thickness locations than in others.

Figure 6-7: Sample 1 (experiment 1), 3D representation of: (a) reconstructed sample volume around the notch region; (b) closer view along the notch tip with contrast further enhanced
6.5.2 Sample 1: Fractured Hydrides

The sample examined in 0 was loaded to 150% of the hydride formation load (K~12MPa√m) in order to fracture the notch-tip hydrides. A 3D representation of the volume reconstructed from the cross-sectional, tomographic slices around the notched region of the sample is shown in Figure 6-9, along with a closer view of the notch-tip region with further contrast adjustment to allow observation of the hydrides. In Figure 6-10, 2D representations are shown for a ‘slice’ bisecting the notch region showing the hydride distribution. Of the three sets of tomographic reconstructions, this was the most difficult in terms of removing noise from the notch region to observe clearly where the hydride was clustered. Like the first reconstruction on this sample (before the hydrides were fractured, 0), the hydride distribution and morphology appears to vary through-thickness, though the contrast is weaker; however, unlike in the previous sample, the hydride region is clearly discontinuous along the notch. The crack running through the hydrides along the notch could not be discerned.
6.5.3 Sample 2: Pre-Cracked Hydrides

The hydrides in this sample were cracked prior to travelling to the research facility to perform the experiment. In an attempt to increase the local contrast for neutron imaging, a gadolinium ‘dye’ was forced into the notch-tip crack. A 3D representation of the volume reconstructed from the cross-sectional, tomographic slices around the notched region of the sample is shown in Figure 6-11, along with a closer view of the notch-tip region with further contrast adjustment.
to allow observation of the hydrides. In Figure 6-12, 2D representations are shown for a ‘slice’ bisecting the notch region showing the hydride distribution. In this sample, the hydride intensity appears to be very high and continuous on one side of the notch, but drops significantly towards the other side, indicating substantial non-uniformity in hydride distribution through-thickness.

Figure 6-11 Sample 2, 3D representation of: (a) reconstructed sample volume around the notch region; (b) closer view along the notch tip with contrast further enhanced

Figure 6-12: Sample 2, 2D slice through the plane bisecting the notch tip (top); also presented with a ‘thermal’ filter applied (bottom)
6.6 Discussion

6.6.1 Selection of Neutron Imaging and Limitations

Tomography itself is a purely computational procedure for reconstructing cross-sections through a sample from radiographs at angles distributed around the sample. The type of radiation used to generate these images determines what one is able to see, and at what resolution. Synchrotron light sources produce X-ray beams with very high brilliance, allowing for very high spatial resolution. X-ray attenuation scales with density, however, and the difference in this property between zirconium (α-Zr) and zirconium hydride (δ-ZrHₓ) is ~13% [116]. Early tests on samples with notch tip hydrides using lab-based X-rays in an Xradia Micro XCT tomography machine found that there was not sufficient contrast to discern the hydrides. Scaling up these experiments to tomography using synchrotron X-rays may yield better results due to better spatial resolution and counting statistics, but it was decided that the cold neutron source at FRM-II would provide a better opportunity to see something useful. Zirconium is a material with a fairly low neutron interaction cross-section, whereas hydrogen interacts with neutrons very strongly (very high scattering cross-section), particularly at low energies; for 0.0253eV neutrons, the microscopic cross-section of hydrogen is ~5x greater than zirconium [117]. The hope was that this difference, combined with the very high hydrogen concentration in the hydride phase, would provide good contrast for mapping the hydride distribution at a notch tip.

Based on the results of this chapter (6.5) it can be concluded that the contrast generated using neutron imaging was sufficient to identify the presence of hydride at the notch tips of the Zr-2.5Nb samples. However, major limitations were encountered that prevented the
determination of detailed, quantitative, morphological information for the notch-tip hydrides. The most obvious problem was resolution. Hydrides at the notch tip were expected to be ~100µm long, and only a few microns in thickness. Compare this to the calculated pixel size of 15.8µm, and you have a hydride that appears (at best) in the tomographic reconstruction as ~6 pixels long by ~1 pixel in thickness; even the single pixel in the thickness direction likely encompasses more than one hydride. This is the reason the resulting images from the notch tip in this experiment appear so ‘blocky’, or pixelated. General information about the presence and location of hydrides could be determined from this data, but certainly not detailed topology.

Another problem with the images generated in this experiment was noise. In order to maximize spatial resolution, the thinnest scintillator available at the ANTARES beamline was used. The scintillator works by the absorption of a neutron by Li-6, which subsequently produces an alpha particle whose interaction with ZnS-Ag particles produces visible light [105]. A thinner scintillator means a shorter potential path for the alpha particles, and thus a smaller spot size for the light emitted for a given ray path through the sample to the detector. Unfortunately, a thinner scintillator means less light is produced, and thus longer exposure times are required. The longer the exposure is, the more time there is for stray gamma rays to reach the CCD where they saturate the pixel locations that they strike. In this experiment, the required exposure times resulted in a level of noise that was not removed entirely by the gamma spot removal algorithm of the reconstruction software. The regions of high hydride concentration could still be identified above this noise, but smaller hydrides that may be in the vicinity of the large notch tip hydrides cannot be unambiguously identified.
6.6.2 Useful Observations on Hydride Distribution

Despite problems with resolution and noise in this experiment, some useful observations could still be made. In the first experiment (0) a high contrast zone extending into the sample to roughly the same depth one would expect for the notch to tip hydrides (~100µm) was clearly identifiable above the noise. This hydride zone was continuous along the notch and about the same size, though there was variability in intensity and distribution. For modeling purposes, this would seem to indicate that assuming a constant size and profile for hydrides through-thickness is not such a bad assumption.

The results of the second experiment (6.5.2) were significantly noisier. When looking at the 2D slices it would seem as though the hydride is more sparsely distributed and the hydride regions at the notch are less intense. It is possible that the aluminum threaded rod supporting the loading of the sample, though having very low contrast due to its high neutron permeability, could have caused a reduction in the quality of the reconstruction. A better design for the tensioning device would have been one where the shaft supporting the load is in the field of view throughout the entire rotation, so that it is reconstructed along with the sample rather than potentially causing artifacts. As well, due to the size of the tensioning device, the sample had to be moved further back from the detector to allow for full rotation; this likely resulted in a slight reduction in spatial resolution. However, a very possible physical cause for the observed inhomogeneity of hydride distribution is the presence of the crack.

The 2D slice through the sample was positioned such that the most intense distribution of hydrides at the notch was visible; for the second experiment, the determination of this plane
was more difficult. In this sample, the hydride region is essentially bisected by a large crack, which was propped open by the applied tensile load. Due to this separation, it is very possible that hydrides that were previously contributing contrast to a single pixel, for example, are now split between two or more pixels. The manner in which the crack propagated through the sample could also mean hydrides that were previously coplanar are no longer so, meaning that a single slice through the sample fails to capture all their contributions to hydride intensity at the notch. These effects could explain why the hydrides appear more sparsely distributed, and less intense.

The final sample examined, which had a pre-existing crack treated with a gadolinium dye penetrant, had a high contrast region clearly discernable from the background that was again roughly the same length one would expect for the hydrides; this reinforces the observations from the first sample. Interestingly, this region seemed much higher contrast towards one side of the sample. Unfortunately, it is not possible to say whether this is a real difference in hydride distribution, or simply a difference in how well the gadolinium solution was absorbed. The purpose of the dye was to increase the visibility of the crack to see how it had propagated through the sample, though in the end the resolution was insufficient to make any such distinctions. Since there was no load applied to this sample to open the crack, as in the second experiment (6.5.2), a straightforward comparison of the results is not possible.

6.7 Conclusions

The primary objective of these experiments, which was to gain detailed information about the through-thickness variation in notch-tip hydride topology in C-shaped Zr-2.5Nb PT samples, was
unsuccessful due to the current limitations in neutron imaging technology. The realized spatial resolution was not sufficient to make out any meaningful detail in hydride morphology, or even enough to view single hydrides. However, the technique provided enough contrast to discern regions of high hydride concentration, and showed some variation of the hydride distribution along the notch through-thickness. It can be concluded based on these observations that using neutron tomography for this application is, in principle, a sound approach. As improvements in scintillator and digital imaging technology are developed that push the achievable spatial resolution in neutron imaging, this could become a viable technique for the non-destructive evaluation of hydride distributions at stress concentrations. The samples have now been sent for synchrotron tomographic imaging. Following that, it will be feasible to break the samples open to obtain microscopic views of hydride distribution for comparison with the tomography results.
Chapter 7

Closing Remarks

7.1 General Discussion

Though all the studies discussed in this thesis employed different methodologies, they were all focused on gaining additional insight into the problem of hydride formation at flaws in Zr-2.5Nb pressure tubes. The different techniques are complementary and provide fundamental knowledge about the changes that occur at a flaw due to hydride formation, and how those changes affect the susceptibility of the material to cracking. The HEXRD measurements of Chapter 3 provided average through-thickness strain maps with a spatial resolution equivalent to the smallest beam size used (20 x 20µm area through the sample thickness of 3mm). Chapter 4 presented a model to gain greater insight into hydride behaviour at a stress concentration, and the data from Chapter 3 was used to test its validity. The DIC strain mapping method of Chapter 5 provided better spatial resolution than the X-ray method, though only surface strains could be observed and it was more difficult to differentiate between matrix zirconium and hydride strains. For Chapter 6, the aim was to use neutron tomography to gain greater insight into the through-thickness hydride distribution at a stress concentration in order to improve models for hydride embrittlement, such as in Chapter 4, with a 2D spatial resolution comparable to Chapter 3’s HEXRD results.

Hydride embrittlement and subsequent cracking at a flaw is the first step in the delayed hydride cracking failure mechanism which has caused the failure of pressure tubes in the past and remains an ongoing concern. Current service guidelines for pressure tubes in-reactor are overly
conservative [118] due in part to uncertainty in the strain field at stress concentrations where hydrides are present. All the work undertaken in this thesis is intended to provide fundamental knowledge in this area with the hope that it could lead to more precise service guidelines. In particular, many of the limits in these guidelines are derived from process zone models used to predict the onset of DHC. Information about the strain state of the hydride under different conditions is an input into these models, and the more accurate this information is, the more reliable the model can be considered.

7.2 Conclusion

Several approaches were undertaken to characterize the effect of hydrides precipitated at a flaw in Zr-2.5Nb pressure tube material. Taken as a whole, they provide new insight into hydride formation and strain field interactions at stress concentrations. The hope is that experimental and modeling data generated by these studies will eventually lead to more accurate service guidelines, and assist pressure tube manufacturers and reactor operators in avoiding conditions that favour embrittlement due to hydrides.

7.3 Future Work

The work presented in this thesis is far from exhaustive when it comes to the problem hydride embrittlement at flaws in pressure tubes. Possible future work that would improve the understanding of this phenomenon could include:
• More carefully controlled in-situ precipitation experiments using synchrotron X-rays to map strains. This was attempted in the experiments discussed in Chapter 3, but was unsuccessful in capturing precipitation as it occurred.

• Synchrotron X-ray strain mapping experiments similar to those of Chapter 3, but with smaller load increments to try to capture more accurately when hydride fracture occurs, and possibly better resolve any possible influence that creep may have. However, this may not be practical given the statistical nature of hydride fracture, and the much greater amount of beam time that would be required to do more frequent sets of exposures.

• More work needs to be done on obtaining a stress-free hydride lattice parameter for hydrides of known composition. The powder result obtained in Chapter 3 seemed reasonable, but uncertainty in the chemistry of the powder cast doubt on its validity. How to obtain a sufficiently large sample of hydride powder with a controlled composition remains an ongoing problem.

• Experiments to get a better understanding of the effects of creep at a sharp stress concentration. If it can be proven that sharp flaws become blunted by creep during reactor operation, this might be used to improve service guidelines (ie. less conservative).

• The expansion of the modeling work of Chapter 4 to three dimensions, and the inclusion of coupled stress/diffusion behaviour for hydride precipitation would be a considerable improvement towards more accurate modeling of the hydride embrittlement process.

• Better tomography results for hydrides. The samples mapped in the experiments discussed in Chapter 6 have since been sent for examination by synchrotron X-ray
tomography (results pending). High energy X-rays would provide better spatial
resolution than the experiments using neutrons (Chapter 6), however it remains to be
seen whether hydrides would have sufficient contrast with this approach. It may be
that the hydrides are simply too small to map accurately with the current level of
advancement in tomography techniques.

- Work should be done on irradiated material. Irradiation can have a marked effect on
  material properties from hydrogen diffusion to yield strength. Any of the experiments
  performed in this thesis, or mentioned above, could be performed on irradiated
  material. This would likely give a better indication of the behaviour of actual pressure
tubes that have been operating in-reactor for some time. Of course, working with
irradiated material can be hazardous, and must be approached carefully, which makes
conducting such experiments difficult.
References


67. Goldthorpe, S., Analysis of hydride effects in Zr-2.5Nb micro pressure tubes, in Department of Mechanical and Materials Engineering. 2010, Queen's University: Kingston.


Appendix A

Reference Lattice Spacing

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Figure A-1: Reference d-spacing information for the α-Zr phase, δ-hydride and γ-hydride phases

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¹ Kerr, A., Mechanical Characterization of Zirconium Hydrides with High Energy X-Ray Diffraction, in Department of Mechanical and Materials Engineering. 2009, Queen's University: Kingston.
Appendix B

Engineering Drawings

Figure B-1: Engineering drawing for C-shaped samples provided by Kinectrics Inc.
Figure B-2: Engineering drawing for CT samples

Sample: Crack || to axial direction
Contact: Greg Allen (allen@me.queensu.ca)
Material: 1 x Zr-2.5Nb (Zr alloy) Tube section
Quantity: 12
Note: Tap 2 holes and EDM starter notch in blanked samples provided.
Figure B-3: Pin loaded grips used for SEM in-situ experiment

Job: SEM Stage Grips
Drawn By: Greg Allen
Scale: 2:1
Material: 4330 or 4340 Steel
Quantity: 2
Dimensions: inches
Tolerances: +/- 0.005 unless specified
Finish: Milled, deburred
Appendix C

Experimental Pictures

Figure C-1: Setup of the 1ID beamline at the Advanced Photon Source at Argonne National Lab
Figure C-2: Photo showing how the CT samples were removed from PT sections

Figure C-3: CT sample in the small loading stage (not in SEM chamber)
Figure C-4: Setup of the ANTARES beamline at FRM-II
Appendix D

Items Relating to Hydrogen Concentration

Table D-1: Minimum required hydride layer thickness needed to achieve the desired hydrogen concentration (top) during electrolytic hydriding, along with required homogenization times (bottom)

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</table>

Formula: $T_{\text{hydride}}$ (μm) = 7.232 x 10^{-2} x [H]_{Zr} x T_{Zr}(mm)

$[H]_{Zr}$ = hydrogen level required

$T_{Zr}$ = thickness of plate.

<table>
<thead>
<tr>
<th>Hydrogen Concentration Required (ppm)</th>
<th>Homogenization Temperature (°C)</th>
<th>Diffusivity D** (cm²/s)</th>
<th>Homogenization Time = 1.5L²/D (hours)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>246</td>
<td>2.29 x 10^7</td>
<td>72.7</td>
</tr>
<tr>
<td>50</td>
<td>280</td>
<td>4.32 x 10^7</td>
<td>38.6</td>
</tr>
<tr>
<td>70</td>
<td>305</td>
<td>6.57 x 10^7</td>
<td>25.4</td>
</tr>
<tr>
<td>90</td>
<td>325</td>
<td>8.97 x 10^7</td>
<td>18.6</td>
</tr>
<tr>
<td>120</td>
<td>350</td>
<td>1.28 x 10^8</td>
<td>13.0</td>
</tr>
</tbody>
</table>

---

Figure D-1: DSC results for SLS-08-071 (care of Kinectrics Inc.)

Figure D-2: DSC results for SLS-08-073 (care of Kinectrics Inc.)
Appendix E

Modeling Related Items

Table E-1: Plastic behaviour used in the FE models

Baseline plastic curve:

<table>
<thead>
<tr>
<th>σ (MPa)</th>
<th>ε_p</th>
</tr>
</thead>
<tbody>
<tr>
<td>650</td>
<td>0</td>
</tr>
<tr>
<td>663.9341</td>
<td>0.000399374</td>
</tr>
<tr>
<td>802.803</td>
<td>0.015601574</td>
</tr>
<tr>
<td>847.1352</td>
<td>0.031001574</td>
</tr>
<tr>
<td>877.5907</td>
<td>0.055501574</td>
</tr>
<tr>
<td>949.5333</td>
<td>0.192201574</td>
</tr>
</tbody>
</table>

T = 293K

<table>
<thead>
<tr>
<th>Load</th>
<th>Pot.</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>T</td>
<td>R11</td>
<td>1</td>
</tr>
<tr>
<td>T</td>
<td>R22</td>
<td>0.909091</td>
</tr>
<tr>
<td>T</td>
<td>R33</td>
<td>0.909091</td>
</tr>
<tr>
<td>C</td>
<td>R11</td>
<td>0.821429</td>
</tr>
<tr>
<td>C</td>
<td>R22</td>
<td>1.22619</td>
</tr>
<tr>
<td>C</td>
<td>R33</td>
<td>0.952381</td>
</tr>
</tbody>
</table>

T = 573K

<table>
<thead>
<tr>
<th>Load</th>
<th>Pot.</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>T</td>
<td>R11</td>
<td>0.681309</td>
</tr>
<tr>
<td>T</td>
<td>R22</td>
<td>0.687074</td>
</tr>
<tr>
<td>T</td>
<td>R33</td>
<td>0.687074</td>
</tr>
<tr>
<td>C</td>
<td>R11</td>
<td>0.559647</td>
</tr>
<tr>
<td>C</td>
<td>R22</td>
<td>0.926732</td>
</tr>
<tr>
<td>C</td>
<td>R33</td>
<td>0.719792</td>
</tr>
</tbody>
</table>

T= Tension, C=Compression
Figure E-1: Load and boundary conditions for the C-shaped samples modeled in Chapter 4
Figure E-2: (a) boundary conditions for the ‘far-field’ hydride in Chapter 4, along with (b) finite element mesh.
Figure E-3: Isometric view of 3D finite element meshed discussed in Chapter 5 (top), along with a closer view at the notch tip (bottom)