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Study on hydride precipitation and the induced embrittlement behaviours in Zircaloy-4

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Study on Hydride Precipitation and the Induced Embrittlement Behaviours in Zircaloy-4

A Thesis submitted in fulfillment of the requirements for the award of the degree of

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by

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Declaration

I, Zhiyang Wang, declare that this thesis, submitted in fulfillment of the requirements for the award of Doctor of Philosophy, in the School of Mechanical, Materials and Mechatronic Engineering, Faculty of Engineering and Information Sciences, University of Wollongong, is wholly my own work unless otherwise referenced or acknowledged. The document has not been submitted for qualifications at any other academic institution.

Zhiyang Wang

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Abstract

The zirconium alloy, Zircaloys (Zr-4), has extensive applications in the nuclear industry as core structural components and fuel claddings in the nuclear reactors. The mechanical performance of these components can be strongly affected by the precipitation of brittle zirconium hydrides and the induced embrittlement. This work investigated the hydride precipitation behaviours in different Zr-4 materials with various thermo-mechanical states (i.e. the high-pressure torsion (HPT) processed disk, hot-rolled and annealed plate, and hot-extruded and annealed bar). The effect of hydride formation on the mechanical properties of Zr-4 materials was also studied.

A comparative study was conducted to clarify the effect of HPT processing on the hydride formation in Zr-4 materials. The Zr-4 materials before and after HPT processing were gaseously hydrided at 450 °C using different hydrogen pressures (10, 15 and 20 atm). Detailed quantitative characterisation of the microstructure of these hydrided samples showed that at the same hydriding conditions, more hydrides tended to form in the HPT samples compared with the counterparts without HPT processing. The enhanced potential for the hydride formation in the HPT samples was attributed to the generation of a large concentration of lattice defects by HPT, which could act as hydrogen traps, hydrogen fast diffusion channels and preferred hydride nucleation sites. Further, the gaseous hydriding-induced changes in the microstructure, texture and mechanical properties of Zr-4 processed by HPT were thoroughly assessed. Much δ-ZrH1.66 precipitation at 15 atm (volume fraction ~21%) incurred significant hardening of vacuum-annealed HPT samples, and pure ŪZrH2 obtained at 20 atm showed a
superior microhardness of 470 HV$_{0.3}$ and a low fracture toughness of 0.63 MPa m$^{1/2}$. The neutron diffraction measurements indicated that the Û-hydrides in HPT samples presented a weak (111) texture and followed the Û(111)/Û(0001) orientation relationship (OR) with the Û-Zr matrix.

Detailed microstructure and texture studies of the hydride precipitation in annealed Zr-4 materials were also performed by electron microscopy and neutron diffraction. Results showed that the precipitated Û-ZrH$_{1.66}$ generally followed the Û(111)/Û(0001) and Û[110]/Û[1120] OR with the Û-Zr matrix. Texture analyses of these hydried materials confirmed the result from the HPT samples that the Û-hydride precipitates displayed a weak texture, and further indicated that the hydride texture was determined by that of the Û-Zr matrix. This texture dependence essentially originated from the observed OR between Û-hydride and Û-Zr. The neutron diffraction line profile analysis and the high-resolution transmission electron microscopy observation revealed a significant amount of dislocations present in the Û-hydride with an estimated average density of one order of magnitude higher than that in the Û-Zr matrix, which contributed to the accommodation of the substantial misfit strains associated with the hydride precipitation in the Û-Zr matrix.

The hydride distribution in the bent and unbent Zr-4 plate samples subjected to gaseous hydriding was investigated by neutron tomography in conjunction with scanning electron microscopy and X-ray diffraction techniques. For the unbent plate sample hydried at a hydrogen pressure of 20 atm, thin hydride layers on the surface and concentrated hydrides at the edges/corner of the sample were observed. This localised hydride accumulation was presumably resulted from the preferential hydrogen
accumulation and saturation in these regions. For the bent plate hydrided at 10 atm, a thin hydride layer was present on the surface region with a significant compressive plastic deformation generated in the bending process. Besides, it was found that the hydride platelets in the hydrided bent plate tended to align parallel to the direction of the maximum tensile and compressive strain induced by the prior bending deformation. The electron backscatter diffraction (EBSD) observations on the hydrided bent sample showed that the primary OR between $\tilde{\gamma}$-hydride and $\tilde{\beta}$Zr matrix transited from $\tilde{\gamma}(111)/\tilde{\beta}(0001)$ in the tensile strain region to $\tilde{\gamma}(111)/(\tilde{\beta}(1010)$ in the compressive strain region of the bent sample.

Additionally, the influence of the hydride precipitation on the mechanical performance of hydrided Zr-4 plate materials containing different hydrogen contents were studied at room temperature. For the unnotched plate samples with the hydrogen contents ranging from 25–850 wt. ppm, the uniaxial tensile tests showed that the tensile ductility was severely degraded with increasing hydrogen content. Also, the degree of embrittlement and fracture mode were strongly related to the hydrogen content. When the hydrogen content reached a level of 850 wt. ppm, the plate exhibited negligible ductility, resulting in almost completely brittle fracture behaviour. For the hydrided notched plate, the tensile stress concentration associated with the notch tip facilitated the hydride accumulation at the region near the notch tip and the premature crack propagation through the hydride fracture during hydriding. The final brittle through-thickness failure for this notched sample was mainly ascribed to the formation of a continuous hydride network on the thickness section and the obtained very high hydrogen concentration (estimated to be 1965 wt. ppm).
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List of Publications during the PhD Course


List of Symbols and Abbreviations

1. Symbols

atm  standard atmosphere
barn  unit of neutron scattering cross-sections
HV\textsubscript{0.3}  unit of the Vickers microhardness (indentation load of 0.3 kg)
°C  Celsius degree
\textdegree  wavelength
Å  Angstrom
\text{min}^{-1}  per minute
[H]  hydrogen content
\dot{\sigma}_{0.2}  0.2\% offset yield strength
\dot{\sigma}_{\text{UTS}}  ultimate tensile strength
K_{IC}  fracture toughness
E  Young\'s modulus
H  hardness
P  indentation load
r  radius of the disk sample
h  thickness of the disk sample
N  number of revolutions in high-pressure torsion
\dot{\epsilon}  accumulated strain in high-pressure torsion
c  length of the radial cracks
\[ \zeta \] a constant related to the geometry of the indenter

\[ \hat{\epsilon} \] bending strain in the bent plate sample

\[ R_1 \] radius of curvature of the bent plate sample

\[ h \] thickness of the bent plate sample

\[ D \] average coherent domain size

\[ \langle \epsilon^2 \rangle^{1/2} \] mean lattice microstrain

\[ \rho \] average dislocation density

2. Abbreviations

RD rolling direction

TD transverse direction

ND normal direction

ED extrusion direction

TD\(\hat{\phi}\) tangential direction

RD\(\hat{\phi}\) radial direction

AD axial direction

HPT high-pressure torsion

DHC delayed hydride cracking

TSS terminal solid solubility

OR orientation relationship

ODF orientation distribution function

m.r.d. multiples of the random distribution
hcp  hexagonal close-packed
fcc  face-centred cubic
wt. ppm  weight parts per million
OM  optical microscopy
SEM  scanning electron microscopy
EBSD  electron backscatter diffraction
TEM  transmission electron microscopy
SAED  selected-area electron diffraction
HRTEM  high-resolution transmission electron microscopy
XRD  X-ray diffraction
JCPDS  Joint Committee on Powder Diffraction Standards
AS  Australian Standard
NIST  National Institute of Standards and Technology
3D  three-dimensional
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Chapter 1 Introduction

1.1 Background

Zirconium alloys, including the Zircaloy-4 (Zr-4) alloy, have been given the most distinctive position among all structural materials in nuclear applications, due to the combination of several attractive properties, such as good strength and ductility, excellent corrosion resistance and low neutron capture cross-section [1]. Zirconium alloys have been proven to be a suitable structural material in-reactor that could withstand the severe high temperature, pressure and intense irradiation conditions in the reactor operation environment and also maintain the high neutron economy. To date, various zirconium alloys have been developed and used extensively as fuel cladding materials as well as essential structural components within the cores of nuclear reactors (e.g. the application of cold worked Zr-4 as fuel cladding in the pressurised water reactors [2,3]).

An important consideration for the application of zirconium alloy components in the reactor systems is the degradation challenge of the material behaviours in the harsh operating environment. One of the principal mechanisms for the in-reactor degradation of the material properties is related to the hydrogen ingress in the zirconium alloy structural materials [1,4], which generally occurs through the corrosion reaction between the water coolant and the components at the reactor operating temperature. Zirconium alloys have a low terminal solid solubility of hydrogen (approximately 75 wt. ppm at 300 °C [5]) and once the solubility limit is exceeded, the excess hydrogen
Chapter 1

absorbed into the materials precipitates out in the form of the brittle zirconium hydrides. This hydride formation is a potential issue during the reactor shutdown, as the hydrogen solubility of the materials decreases significantly with decreasing the temperature. The cracking of the zirconium alloy components can occur by a slow cracking mechanism known as delayed hydride cracking (DHC), which is caused by the repeated precipitation, growth and fracture of hydrides formed at high tensile stress regions such as the tip of cracks and notches [6]. Also, the hydride precipitates may severely embrittle the zirconium matrix, resulting in the marked losses in tensile ductility, impact and fracture toughness [7-9]. The severity of the hydride-induced embrittlement depends not only on the amount of the hydride present, but also on its morphology and distribution, particularly the orientation of the precipitate with respect to the direction of the external stress [10]. As the hydride-induced embrittlement is a key life-limiting factor for the components made from zirconium alloys, the study of the hydride precipitation and its impact on the mechanical properties of zirconium alloys becomes very important. Although the embrittling effect of hydrides has been recognised, their precipitation behaviours in different zirconium alloys with various thermo-mechanical states are not fully understood. For example, the hydride formation in nanostructured zirconium alloys obtained by severe plastic deformation has not been clearly studied before this thesis work. Further investigations are needed to enhance the understanding on the hydride precipitation and the induced embrittlement behaviours in different zirconium alloys possessing diverse matrix microstructure and crystallographic texture.
1.2 Objectives of Current Research

The main objectives of this research work were to understand the hydride precipitation behaviours in different Zr-4 materials with various matrix microstructure and crystallographic texture, and to elucidate the influence of the hydride precipitation on the mechanical properties of Zr-4 materials. Detailed microstructure, texture and mechanical property analyses on the Zr-4 samples before and after gaseous hydriding were performed in order to improve our understanding on the hydriding processing–structure–property relationship of the materials. In addition, the effects of prior bending deformation on the hydride orientation and the hydride-matrix orientation relationship were investigated in the current work. The evaluation on the dislocation density in the hydride phase was also conducted to provide more fundamental knowledge about the behaviour of hydrides precipitated in Zr-4.
Chapter 2

Literature Review

This chapter introduces the basics of nuclear grade zirconium alloys, and provides a substantial amount of information relevant to the present topic which is considered to be essential for understanding the formation behaviour of hydrides and their induced embrittling effects in zirconium alloys.

2.1 General Introduction of Nuclear Grade Zirconium Alloys

Separate specifications and grades of zirconium alloys suitable for nuclear applications have been developed. The nuclear (or reactor) grade designates the zirconium alloys having low levels of naturally occurring hafnium (typically less than 0.01 wt.% [2]). This is because hafnium is a strong neutron absorber, possessing a particularly high cross-section of thermal neutrons (113 barn [11]) compared with that of zirconium (0.185 barn [1]). Thus, this element is required to be removed when producing nuclear grade zirconium alloys to ensure the high neutron economy.

2.1.1 Development and Applications

The development of nuclear grade zirconium alloys is essentially due to the nuclear industry, where zirconium alloys play the most important role among all structural materials for nuclear service. Design of zirconium alloys used in-reactor always considers the in-service requirements of mechanical and corrosion resistance properties, as well as the neutron economy (low neutron absorption cross-section). Only a few
alloying elements, such as tin (Sn), niobium (Nb) and oxygen (O), which have quite low neutron cross-sections, are added to a limited extent in zirconium alloys for nuclear applications [1].

According to the alloy compositions, the currently used reactor grade zirconium alloys can be classified into three series: (i) Zr-Sn system alloy (e.g. Zircalloys such as Zircaloy-2 and Zircaloy-4), (ii) Zr-Nb system alloy (typically Zr-2.5Nb, E110 and M5) and (iii) Zr-Sn-Nb system alloy (including Zirlo, MDA and N18) [12]. For comparison, the chemical compositions of common nuclear grade zirconium alloys and their typical applications are summarised in Table 2.1 [13-17]. Zircalloys have been widely used in both pressurised water and boiling water reactors, for example, as fuel cladding materials, pressure tubes (cold worked Zircaloy-2 in early CANDU reactors) and calandria tubes (Zircaloy-2, currently used in CANDU) [16]. For Zircaloy-4 (Zr-4), besides the extensive application as fuel cladding in the power reactors (Fig. 2.1a), this alloy was also selected to manufacture some of the major core components (such as the reflector vessel) for the OPAL research reactor in Australia (Fig. 2.1b). The dual phase Ŭ6 Zr-2.5Nb alloy is mainly used as pressure tubes in pressurised heavy water reactors (PHWR), while other niobium-containing alloys (e.g. Zirlo and M5 with ~1 wt.% Nb) are primarily used as fuel cladding in some Generation IV reactors for their adequate corrosion resistance and superior mechanical strength at the operating temperature.

2.1.2 Mechanical and Corrosion Performance

The composition of nuclear grade zirconium alloys was optimised mainly to
Table 2.1 Summarisation of the composition and applications of zirconium alloys in the nuclear industry [13-17].

<table>
<thead>
<tr>
<th>Alloys</th>
<th>Elemental composition (wt.%)</th>
<th>Typical Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Sn</td>
<td>Nb</td>
</tr>
<tr>
<td>Zicaloy-2 (USA, 1950)</td>
<td>1.2-1.7</td>
<td>δ</td>
</tr>
<tr>
<td>Zicaloy-4 (USA, 1950)</td>
<td>1.2-1.7</td>
<td>δ</td>
</tr>
<tr>
<td>Zr-2.5Nb</td>
<td>δ</td>
<td>2.4-2.8</td>
</tr>
<tr>
<td>Zirlo (Westinghouse, USA, 1990)</td>
<td>0.9-1.2</td>
<td>0.9-1.13</td>
</tr>
<tr>
<td>E110 (Russia, 1958)</td>
<td>δ</td>
<td>0.95-1.05</td>
</tr>
<tr>
<td>M5 (France, 1996)</td>
<td>δ</td>
<td>0.8-1.2</td>
</tr>
<tr>
<td>MDA (Mitsubishi, Japan, 1990)</td>
<td>0.8</td>
<td>0.5</td>
</tr>
<tr>
<td>Excel (Canada, 1970)</td>
<td>3.5</td>
<td>0.8</td>
</tr>
<tr>
<td>N18 (China)</td>
<td>1.0</td>
<td>0.3</td>
</tr>
<tr>
<td>N36 (China)</td>
<td>1.0</td>
<td>1.0</td>
</tr>
</tbody>
</table>

*Impurities, with Al <75 ppm, B and Cd <0.5 ppm, Co and Mg <20 ppm, and Hf <50-150 ppm [1].
improve their corrosion resistance and mechanical properties. Elementary Sn is a common addition in zirconium alloys, and was initially introduced into zirconium alloys to counter the poor corrosion performance of sponge zirconium caused by the trace impurity element of nitrogen [3]. It is presently known that the high Sn addition also has a negative impact on the in-reactor corrosion performance and a reasonable reduction in the Sn content generally improves the high-temperature corrosion resistance, e.g. for Zr-4 [18] and advanced alloys like Zirlo (see Table 2.1) [19]. The Nb addition in zirconium alloys contributes greatly to their low corrosion rate. For long exposures, Zr-Nb alloys (such as Zr-2.5Nb) have a better corrosion resistance compared with Zircaloys. In addition, the size and distribution of second phase particles (SPP) in zirconium alloys (e.g. the Zr(Cr,Fe)₂ SPP in Zr-4) play a crucial role in determining the

![Figure 2.1 Examples showing the typical applications of Zr-4: (a) Zr-4 tubes used as cladding materials in the nuclear power reactor [20]; and (b) a section view of reflector vessel and core components in the OPAL research reactor (Australia) manufactured using Zr-4 [21].](image)
corrosion performance of the materials. These insights have been utilized in the development of high corrosion resistant Zr-Sn-Nb alloys. For example, a series of new Zr-Sn-Nb alloys named HANA have been developed to improve the corrosion resistance of the fuel claddings in Korea [22,23]. Theses alloys containing relatively high Nb and low Sn contents (e.g. HANA-4 with the nominal composition of Zr\(_2\) 1.5Nb\(_2\) 0.4Sn\(_2\) 0.2Fe\(_2\) 0.1Cr) exhibit a superior corrosion resistance in the out-of-pile and in-pile conditions than Zr-4. The improved corrosion resistance of the HANA claddings is attributed to the optimised compositions as well as the fine distribution of the precipitate Zr(Nb,Fe,Cr)\(_2\) [22].

The typical mechanical properties of the commercially pure zirconium and some nuclear grade zirconium alloys under different thermo-mechanical conditions are shown in Table 2.2 [1]. Compared with unalloyed zirconium, zirconium alloys are much stronger and notably, Zircolloys have much better creep resistance. Zirconium alloys can be typically strengthened by three mechanisms: solid solution strengthening (e.g. the addition of soluble Sn and O in Zircolloys), precipitation hardening (such as the Zr\(_2\)(Fe,Ni) and Zr(Cr,Fe)\(_2\) intermetallic particles in Zircaloy-2) and work hardening. In general, the mechanical properties of zirconium alloys materials can be favourably tailored through the selection of proper thermo-mechanical fabrication routes. Note that the inherent anisotropic thermal and mechanical behaviours of the hexagonal close-packed (hcp) Zr phase, which is the major phase in nuclear grade zirconium alloys, lead to unequal thermal expansions along different crystallographic directions.
and formation of a significant crystallographic texture during thermo-mechanical working [1]. The presence of crystallographic texture of the fabricated zirconium alloys strongly influences the mechanical properties such as the yield strength, thermal and in-reactor creep strengths and is responsible for the mechanical anisotropy in the materials [1,24].

**Table 2.2** Typical mechanical properties of zirconium and 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>Elongation (%)</th>
<th>Fracture toughness</th>
<th>Creep strain rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure Zr</td>
<td>Room temperature</td>
<td>80</td>
<td>220</td>
<td>45</td>
<td>δ</td>
<td>At $\dot{\varepsilon} = 88 \text{MPa and}$ $310^\circ\text{C}: \sim 1 \times 10^{-4} \text{h}^{-1}$</td>
</tr>
<tr>
<td></td>
<td>300°C</td>
<td>45</td>
<td>120</td>
<td>55</td>
<td>δ</td>
<td></td>
</tr>
<tr>
<td>Zircaloy-2</td>
<td>Room temperature</td>
<td>275</td>
<td>435</td>
<td>20</td>
<td>δ</td>
<td>At $300^\circ\text{C,}$ $110\text{MPa:}$ $-2.4 \times 10^{-8} \text{h}^{-1}$, out-of-pile and $\sim 3.0 \times 10^{-7} \text{h}^{-1}$, in-pile</td>
</tr>
<tr>
<td>(Fully annealed)</td>
<td>343°C</td>
<td>103</td>
<td>200</td>
<td>δ</td>
<td>δ</td>
<td></td>
</tr>
<tr>
<td>Zircaloy-4</td>
<td>Room temperature</td>
<td>410</td>
<td>480</td>
<td>20</td>
<td>δ</td>
<td>δ</td>
</tr>
<tr>
<td>(Stress relieved)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zr-1Nb</td>
<td>Room temperature</td>
<td>205</td>
<td>272</td>
<td>28</td>
<td>δ</td>
<td>At $\dot{\varepsilon} = 88\text{MPa and}$ $350^\circ\text{C}: \sim 1 \times 10^{-4} \text{h}^{-1}$</td>
</tr>
<tr>
<td>(annealed)</td>
<td>380°C</td>
<td>127</td>
<td>145</td>
<td>33</td>
<td>δ</td>
<td></td>
</tr>
<tr>
<td>Zircaloy-2</td>
<td>Room temperature</td>
<td>420</td>
<td>580</td>
<td>18</td>
<td>$K_{JC} = 55-65 \text{MPa m}^{0.5}$</td>
<td>δ</td>
</tr>
<tr>
<td>(Cold worked)</td>
<td>300°C</td>
<td>270</td>
<td>330</td>
<td>12</td>
<td>$K_{JC} = 60-75 \text{MPa m}^{0.5}$ $K_{IH} = 10-17 \text{MPa m}^{0.5}$</td>
<td>δ</td>
</tr>
<tr>
<td>Zr-2.5Nb</td>
<td>Room temperature</td>
<td>600</td>
<td>650</td>
<td>12</td>
<td>$J_{2.2} = 120-160 \text{KJ m}^{-2} \text{dJ/d}a$ $= 120-360 \text{MPa}$ $K_{BI} = 6-9 \text{MPa m}^{0.5}$</td>
<td>δ</td>
</tr>
<tr>
<td>(Cold worked)</td>
<td>300°C</td>
<td>325</td>
<td>460</td>
<td>14</td>
<td></td>
<td>At $\dot{\varepsilon} = 150\text{MPa and}$ $350^\circ\text{C}: \sim 1 \times 10^{-4} \text{h}^{-1}$</td>
</tr>
</tbody>
</table>
2.2 Hydride Formation in Zirconium Alloys

During operation in light water reactors, corrosion occurs at the interface between the zirconium alloy cladding and the water coolant. As a result of this reaction (see equation 2.1), a zirconia layer on the metal and free hydrogen are produced.

\[
\text{Zr} + 2\text{H}_2\text{O} \rightarrow \text{ZrO}_2 + 4\text{H}
\]  

As schematically illustrated in Fig. 2.2, a portion of the produced hydrogen can be absorbed into the zirconium alloy by permeation through the barrier oxide and the subsequent diffusion into the bulk during corrosion. The absorbed hydrogen precipitates out as zirconium hydrides when its content is in excess of the terminal solid solubility (TSS).

\[\text{Zr} + \text{H}_2\text{O} = \text{ZrO}_2 + \text{H}_2\]

Figure 2.2 Schematic showing the hydrogen absorption and hydride precipitation during corrosion of the zirconium alloy claddings [25].
2.2.1 Hydride Phases

Three zirconium hydride phases, δ-hydride ($\text{ZrH}_{1.59-1.66}$ with a typical H/Zr ratio of ~1.66; face-centred cubic, fcc), ε-hydride ($\text{ZrH}_{1.74-2}$ with a typical H/Zr ratio of ~2; tetragonal) and γ-hydride (ZrH; tetragonal), can appear in zirconium alloys by varying the hydrogen concentration of material and the cooling rate during the hydride formation [10,26,27]. Table 2.3 lists the crystal properties of the typical hydride phases.

There is some discrepancy about the composition of these hydride phases in the literature, but the above compositions are typical of the ranges cited [16,27]. In general, the δ-hydride is formed upon slow cooling (i.e. furnace cooling) at relatively high hydrogen concentrations of the material, while the appearance of γ-hydride is favoured by fast cooling and low hydrogen concentrations. The δ- and ε-hydrides are both stable phases, as typically revealed in the equilibrium phase diagram of the Zr–H system (Fig. 2.3) [28]. Relative to δ-hydride, ε-hydride is less commonly observed in hydrided zirconium alloys as this phase precipitates at rather high hydrogen contents (in excess of ~6000 wt. ppm according to Daum et al.’s results [27]). The γ-hydride phase is mostly regarded as metastable, although there is still some controversy on the stability of this phase [29,30]. It is notable that the reported stable δ-phase and metastable γ-phase essentially only differ in the degree of ordering of the hydrogen atoms, which mainly occupy the tetrahedral sites in the crystals [31]. In the fcc δ-phase, four hydrogen atoms randomly occupy the eight available tetragonal (0.25, 0.25, 0.25) sites, whereas the fct γ-phase has been identified with an ordered tetragonal structure, where the hydrogen
atoms occupy the tetragonal sites on alternating (110) planes. Apart from the above mentioned three hydrides, a new metastable hydride phase ($\zeta$-Zr$_2$H) was identified recently [32] in hydried Zr-4 obtained by gaseous hydriding with fast cooling. This $\zeta$-hydride phase, with lattice parameters of $a = 0.33$ nm and $c = 1.029$ nm, has a hexagonal lattice that belongs to the trigonal crystal system with a $P3m1$ space group.

Table 2.3 Crystallographic properties of typical $\delta$, $\gamma$ and $\epsilon$ hydrides in zirconium alloys [27].

<table>
<thead>
<tr>
<th>Hydride phase</th>
<th>JCPDS Card No.</th>
<th>Crystal structure and space group</th>
<th>Lattice parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\delta$-ZrH$_2$</td>
<td>34-0690</td>
<td>tetragonal, $P4_2/n$</td>
<td>$a = 0.4596$ nm, $c = 0.4969$ nm</td>
</tr>
<tr>
<td>$\zeta$-Zr$_2$H</td>
<td>17-0314</td>
<td>tetragonal, $I4/mmm$</td>
<td>$a = 0.3520$ nm, $c = 0.4450$ nm</td>
</tr>
</tbody>
</table>

Figure 2.3 Equilibrium phase diagram of the zirconium $\delta$ hydrogen system [28].
2.2.2 Hydride Nucleation and Growth

The hydride formation in zirconium alloys is accompanied by dilatational misfit strains due to the significant volume expansion of hydrides (17.2% for $\tilde{\text{U}}$-hydride and 12.3% for $\gamma$-hydride) relative to the $\tilde{\text{U}}$Zr matrix [33]. The hydride tends to nucleate at some preferred sites so as to effectively accommodate the strains associated with the hydride precipitation [34]. The preferential sites for hydride nucleation are primarily the grain boundary or inter-phase boundary, specific habit planes, intermetallic particles and dislocations in the zirconium matrix [35-38]. Notably, the hydride nucleation in the zirconium grains does not necessarily require the presence of dislocations but the preferential precipitation will occur on them when present [35]. Fig. 2.4 shows an example of the hydride nucleation at intermetallic particles in Zircaloy-2, and it was observed that some dislocation loops were generated around the precipitated hydride needles resulting from the accommodation of the dilatational strain involved in the $\text{Zr} \rightarrow \text{hydride}$ transformation [37]. For the hydride formation in the dual phase $\tilde{\text{U}}\beta$ Zr-2.5Nb alloy, the electron backscatter diffraction (EBSD) measurements revealed that, even though there are a considerable number of $\tilde{\text{U}}\tilde{\text{U}}$ grain boundaries present in this two phase material, the hydrides were predominately formed along the $\tilde{\text{U}}\beta$ interface [38]. Also, the hydrides along the $\tilde{\text{U}}\beta$ interface were observed to grow only into the adjacent $\tilde{\text{U}}$Zr grains but not into the $\beta$-Zr phase, as shown in Fig. 2.5. Mani Krishna et al. considered that this is a consequence of a higher affinity of hydrogen to Zr than to Nb which is present in a significant amount in the $\beta$-Zr phase [38]. The grain boundary
Figure 2.4 Hydride nucleation at intermetallic particles in Zircaloy-2, with dislocation loops around the hydride needles [37].

Figure 2.5 EBSD micrograph showing the distribution of hydrides in the Zr-2.5Nb alloy charged with 300 wt. ppm hydrogen [38].

Structure and energy of zirconium alloys are the crucial factors in determining the precipitation sites of hydrides (i.e. intergranular or intragranular). The preferred grain
boundaries for the Ú-hydride precipitation in Ú-Zr alloys are those lying on the basal plane of one bounding Ú-Zr grain and having a high Gibbs free energy [39,40], while coincident site lattice (CSL) boundaries and the boundaries surrounded by elastically harder Ú-Zr grains generally arrest the formation of hydrides [41].

The hydride habit planes and the orientation relationship (OR) between the hydride and the zirconium matrix have been determined in numerous investigations. Various lattice planes of the hcp structure ÚZr matrix have been suggested as probable habit planes for hydrides including the Ú-hydride with a fcc structure and the Ò-hydride with a tetragonal structure, like the prismatic plane \{10\bar{1}0\} [35], twining planes of \{10\bar{1}2\}, \{1\bar{1}21\} and \{1\bar{1}22\} [39], \{10\bar{1}7\} plane [36], pyramidal plane \{10\bar{1}1\} [42] and the most frequently reported basal plane (0001) [43]. The diverse hydride habit planes observed might be attributed to the different alloy compositions, hydrogen concentrations and hydriding treatment condition (e.g. solution temperature and cooling rate) used in the different experiments. However, the exact factors influencing the habit planes of hydrides in zirconium alloys are still not well known. Of all the Ú-hydride habit planes reported, it is commonly accepted that the primary habit plane is the basal plane of the Ú-Zr matrix, as derived from the statistic EBSD observations [42,43]. In addition, the Ú-hydride mainly follows the Ú(111)∥Ú(0001) OR with the Ú-Zr matrix for various zirconium alloys including Zircaloys and Zr-2.5Nb [38,39,43]. Further, it should be pointed out that the applied stress during hydriding may change the preferential hydride-matrix OR in zirconium alloys. Some investigations have confirmed that hoop
stress could induce the dominant OR between $\tilde{\text{U}}$-hydride and $\tilde{\text{U}}\text{Zr}$ transit from $\tilde{\text{U}}(111)//\tilde{\text{U}}(0001)$ to $\tilde{\text{U}}(111)//\tilde{\text{U}}(10\bar{1}0)$ in textured zirconium alloy tubes [44,45].

2.2.3 Hydride Morphology and Orientation

The hydride precipitates in zirconium alloys have a characteristic acicular or platelet morphology, which can be easily observed by optical or scanning electron microscopy [39,46]. The transmission electron microscopy (TEM) examinations revealed that the "macroscopic" hydride platelets observed in the optical microscope (Fig. 2.6a) are actually composed of stacks of smaller, microscopic hydride platelets (Fig. 2.6b) sharing a common habit plane [47]. Perovic et al. [47,48] proposed that the hydride stacks are developed by repeated nucleation and growth of platelets, which eventually grow and coalesce into macroscopic hydride platelets. They suggested that the repeated nucleation of these stacks is facilitated by an auto-catalytic nucleation process, where the strain field produced by a larger parent hydride platelet helps the nucleation of a smaller daughter hydride platelet. Besides, it is worthwhile to note that the matrix microstructure of zirconium alloys appears to have an impact on the morphology of the hydrides precipitated. The macroscopic hydrides composed of many smaller hydride platelets tend to form in the fine-grained $\tilde{\text{U}}\tilde{\text{b}}$ zirconium alloys (average grain size $<1 \mu$m), such as the cold worked and stress relieved Zr-2.5Nb pressure tube material, while in the larger grain sized single phase zirconium alloys like Zircaloys, the formed macroscopic hydrides normally comprise fewer hydride platelets [16,49].
Figure 2.6 Micrographs of the same hydrided Zr-2.5Nb material with 190 wt. ppm hydrogen: (a) optical micrograph showing macroscopic hydride platelets and (b) TEM micrograph showing stacks of hydride platelets [47].

It is well known that the hydride platelets observed by optical metallography are generally oriented parallel to a particular direction in the material. For example, in the rolled zirconium alloy sheet and plate materials, the hydride platelets formed under the hydriding conditions without stress tend to align parallel to the rolling direction [39,50,51], as representatively shown in Fig. 2.7. Normally, the apparent orientation of hydride platelets in zirconium alloys is believed to be dependent on the fabrication history, crystallographic texture and stress state (both applied and residual) of the material [36,52,53]. Based on the limited information available in the literature regarding the effect of the deformation strain before hydriding on the resultant hydride orientation, the hydride platelets are preferentially oriented along the direction of the prior deformation strain in the absence of an external stress field [54,55]. Kearns and
Woods showed [56] that the hydride orientation is also closely related to the basal pole texture in unstressed samples, and it is currently understood that this correlation originates from the preferred nature of hydride habit planes. When hydrided zirconium alloys are subjected to thermal cycling under stress, the hydride platelets tend to precipitate perpendicular to a tensile stress direction or parallel to a compressive stress axis, as illustrated in Fig. 2.8 [52]. This phenomenon is known as the stress reorientation of hydrides. In the hydrided zirconium alloy cladding tube materials, the hydrides with two different orientations could be observed on the circumferential and radial plane of the tubes, i.e. the circumferential hydride and radial hydride [57], as depicted in Figs. 2.9a and b, respectively. For the commercial zirconium alloy tubes with strong radial

![Figure 2.7 Optical micrographs showing typical hydride orientation in different hot-rolled plate materials: (a) Zr-1Nb and (b) Zr-2Nb charged with 598 and 462 wt. ppm hydrogen, respectively [50].](image)
alignments of the basal poles, only circumferential hydrides form under the unstressed hydriding conditions [58]. The radial hydrides are usually obtained by reheating the

![Image](image_url)

**Figure 2.8** Hydride orientation in a Zircaloy-2 sample with a bending stress applied on the material during thermal cycling [52].

![Image](image_url)

**Figure 2.9** Micrographs showing orientation of hydrides in Zr-4 cladding tube containing ~230 wt. ppm hydrogen: (a) as-hydried and (b) after 8 cycles of thermal treatment under a hoop stress of 160 MPa [57].
hydrided samples with circumferential hydrides to certain temperature and then cooling them under hoop (tensile) stress to initiate the reorientation process. After repeated thermal cycling, the full reorientation (i.e. 100% radial hydrides) could be present (Fig. 2.9b). It is necessary to point out that the stress reorientation of hydrides will not occur if the applied stress is lower than a critical value (threshold stress). This threshold stress is dependent on the material strength, microstructure and texture, and the solution temperature of the thermal treatment [10,58,59]. Northwood and Kosasih [10] reported that the threshold stress increases with increasing the material strength, but decreases with increasing the solution temperature. Zheng et al. [59] showed that the hydride reorientation threshold stress of the tube with basal poles concentrated in the radial direction is significantly higher than that of the tube with the majority of basal poles in the circumferential direction. For the recrystallised Zr-4 materials, the typical threshold stress reported for the hydride reorientation in the temperature range of 300 to 500 °C is between 70 and 95 MPa [51,57,60].

2.2.4 Hydride Distribution

The uniformly distributed hydrides in zirconium alloys shown in Fig. 2.6a are normally observed experimentally after homogenization annealing treatment. In contrast, the distribution of hydrides formed in the zirconium alloy fuel cladding during reactor operation is generally inhomogeneous. For instance, a hydride rim (concentrated hydride layer) is typically formed near the outer surface of the zirconium alloy fuel
cladding at high burnup, as shown in Fig. 2.10. The explanation for the formation of such a rim is that the hydrogen tends to migrate to the cooler region (i.e. the outer skin of the cladding tube), leading to the favourable hydrogen saturation and the resultant accumulation of hydrides near the outer surface [4]. Also, the spallation of the surface oxide layer adherent to the cladding that can occur in the high burnup fuel enhances the local thermal conductivity, resulting in a cold spot where hydride blisters can form [61].

The hydride blisters are the fully-localised hydrides accumulated at the outer surface of the cladding, and they are often lens shaped and composed of a very high concentration of hydrides or of a solid hydride [62,63]. In addition to the inhomogeneous hydride distributions (hydride rims and blisters) induced by temperature gradients, the local accumulation of hydrides was also observed at stress concentrations such as the crack

![Image](image.jpg)

**Figure 2.10** Cross section optical micrograph of high-burnup Zr-4 cladding in pressurised water reactors, showing a rim of hydride precipitates present near the outer surface [4].
tip [64]. The reason for this may be attributed to the fact that hydrogen tends to concentrate in the regions of high stress concentrations causing the preferential hydride precipitation in these areas.

2.3 Hydride Embrittlement in Zirconium Alloys

The precipitation of the brittle hydride phase in zirconium alloys may affect the mechanical behaviour of the materials, leading to the mechanical strengthening (e.g. the elevation of the strength and hardness at room temperature) and the loss of the ductility. It should be stated that the main effect of hydride/hydrogen is causing the embrittlement of the host matrix, while the influence on strength is generally not important even for very high hydrogen contents up to ~1200 wt. ppm [8,65]. Two forms of hydride embrittlement have been recognised for zirconium alloys, i.e. the gross embrittlement induced by the precipitation of certain quantity of hydrides that are uniformly distributed in the matrix, and the localised embrittlement due to delayed hydride cracking (DHC) and/or blister formation [66]. As one of the most important reasons for the failure of the zirconium alloy components, hydride-induced embrittlement has attracted considerable attention. It is important to review the literature regarding the mechanical behaviour (especially the tensile ductility) of hydrided zirconium alloys and the fracture mechanisms in the presence of hydrides. The relevant factors influencing the gross hydride embrittlement of zirconium alloys will be the main focus of this review.
2.3.1 Gross Embrittlement

The occurrence of hydride-induced gross embrittlement in zirconium alloys could significantly degrade the macroscopic mechanical properties, resulting in the overall reduction in the tensile ductility, impact and fracture toughness of the materials. Investigations have shown that the extent of this embrittlement is strongly dependent on many factors, including the hydrogen content, matrix microstructures, stress state, and the hydride morphology, distribution and orientation relative to the loading direction [7,8,67-69]. An important issue of the gross embrittlement in zirconium alloys is the occurrence of an abrupt ductile-to-brittle transition at room temperature when the hydrogen content increases to a critical value. Based on the uniaxial tensile tests at room temperature on hydrided Zr-4 samples with different heat-treated states, Bai et al. [8,70] found that the heat treatment shifts this transition (to zero elongation or reduction of area) considerably from about 1050 wt. ppm hydrogen for the stress-relieved state to 760 wt. ppm for the recrystallised state, as illustrated in Fig. 2.11. Under the room-temperature uniaxial tension condition, Arsene et al. [71] also observed that the ductile-to-brittle transition takes place at a lower hydrogen concentration in the case of the recrystallised Zircaloy than that in the case of the stress-relieved Zircaloy. However, they reported a different hydrogen content range at the transition which is between 800 and 1200 wt. ppm for the recrystallised material, and between 1500 and 2500 wt. ppm for the stress-relieved material. In a study of the effect of hydrogen content on the tensile properties of Zr-4 sheets, Lin et al. [72] found that the ductile-to-brittle transition
at 20 °C occurs in the 400 to 800 wt. ppm hydrogen content range, which is a lower threshold content than that reported by Arsene et al. [71]. These differences may be ascribed to the fact that the effect of hydrides on tensile properties is very sensitive to the tensile sample geometry and the matrix microstructures that can be modified by the prior thermo-mechanical treatment [8]. In general, the embrittlement of hydrided zirconium alloys is easily observed when the sample thickness is reduced or when the matrix has coarse grains [73]. Huang and Huang [74] conducted the tensile tests on notched samples of hydrided Zr-4. They reported a room-temperature ductile-to-brittle transition at very low hydrogen concentrations ranging from 30 to 140 wt. ppm, indicating that the notched samples exhibit a higher sensitivity to hydride embrittlement when compared to the unnotched samples. According to the works of Simpson [75] and Puls [76], the enhanced brittle fracture behaviour in the presence of notches is probably

**Figure 2.11** Influence of hydrogen content on the tensile ductility of Zr-4 at 20 °C [70].
because of the fact that the plastic strain required to fracture hydrides was greatly lowered under a triaxial state of stress imposed on the notched samples compared with that in a uniaxial stress state for unnotched samples. In an investigation of the influence of multiaxial state of stress on the hydride embrittlement in Zircaloy-2 sheets, Fan and Koss [67] noted that the ductility of hydrided samples decreases with increasing both hydrogen content (≤615 wt. ppm) and stress biaxiality at room temperature. They suggested that the link-up of damage (i.e. voids formed due to the strain-induced fracture of hydrides) is initiated at a much lower critical void density in equibiaxial tension than in uniaxial tension, leading to the acceleration of the crack propagation during straining and the resultant reduction in macroscopic ductility.

Previous studies have clearly established that the cracking of hydride precipitates is the cause of hydride embrittlement of zirconium alloys [10,67,73,75]. The dependence of the degree of embrittlement on hydride features (e.g. the orientation, morphology and distribution) has been well documented in the literature. Due to their common thin platelet shape, the embrittling effect of hydrides is orientation dependent and most severe when the hydride platelets are oriented normal to a tensile stress axis [8]. Hong and Lee [69] reported that for hydrided Zr-4 tubes with 220 wt. ppm hydrogen, the room-temperature tensile ductility decreases to zero under hoop tension when a sufficient quantity of radial hydrides (with their normal parallel to the stress) are present. Their results also showed that at the same level of hydrogen content, the Zr-4 tubes containing a majority of circumferential hydrides maintain a high ductility. Bai et al. [8]
compared the tensile behaviours of stress-relieved Zr-4 sheets containing different orientations of hydrides. This study revealed that, in the very adverse conditions (i.e. the hydrides oriented perpendicular to the tensile stress axis), the tensile ductility of Zr-4 samples at room temperature can be markedly decreased by as little as 70 wt. ppm of hydrogen. The fractographic examination showed that the fracture surface was characterised by small cleavage facets in coincidence with hydrides, implying that the fracture in this case was basically brittle. Conversely, for the samples with most hydrides aligned in the stress direction and containing 230 wt. ppm of hydrogen, very little reduction in the ductility was observed. The strong detrimental effect of hydride platelets oriented perpendicular to the tensile stress axis is because the hydrides of such alignment provide an easy crack propagation path under a tensile stress. Some theoretical and experimental results [10,68,72] indicated that the embrittling effect of hydrides can be considerably reduced if the morphology is changed from platelet-like to globular. Besides, the microstructural observations [8,65] confirmed that the variation of the fracture micromechanisms in hydried zirconium alloys at the ductile-to-brittle transition is related to the changes in the distribution and size of hydrides with increasing the hydrogen content. At low hydrogen contents below the threshold value of the brittle-to-ductile transition, the hydrides are commonly discretely distributed in the matrix. During the tensile cracking of these samples, the voids are preferentially nucleated at the cracked hydrides, and the subsequent growth and coalesce of voids (i.e. the crack propagation) are mainly achieved by the plastic deformation and tearing of the
ductile matrix, leading to the final ductile rupture. With the significant increase of hydrogen content in zirconium alloys, the hydride size and the continuity of the hydride network generally increase while the inter-spacing between hydride platelets decreases. For the samples with high hydrogen content above the critical level at the transition, the hydride precipitates normally form a continuous hydride network along the matrix grain boundaries. In this case, the fracture after tensile testing at room temperature is totally brittle with extensive cleavage facets appeared on the fracture surface, as illustrated in Fig. 2.12 [8]. The fracture paths are found to strictly follow the continuous hydride network present, suggesting that the complete brittle fracture behaviour results from the formation of a continuous hydride network. Some studies have shown that intergranular hydrides or large hydrides break more easily under applied load [65,76]. Based on these results and the observations of the predominant precipitation of intergranular hydride

![Fracture surface of a stress-relieved Zr-4 sample with high hydrogen content (above the threshold value of the brittle-to-ductile transition) tested at 20 °C](image)

**Figure 2.12** Fracture surface of a stress-relieved Zr-4 sample with high hydrogen content (above the threshold value of the brittle-to-ductile transition) tested at 20 °C [8].
platelets with the increased thickness at high hydrogen contents, Grange et al. [65] interpreted the brittle-to-ductile transition as a transition in the hydride morphology (thin or thick) and site of precipitation (intra- or intergranular). In contrast, some researches [73, 74, 77] pointed out that the inter-hydride spacing is a crucial parameter controlling the failure mechanisms of hydried zirconium alloys, whereas the influence of hydride size (thickness and length) on the failure is not significant. The experimental observation of Coleman and Hardie [73] indicated that the hydried zirconium alloys with smaller inter-hydride spacing (below ~160 μm) are more susceptible to the brittle fracture, which supported the consistent theoretical result of Chan [68]. This is because the closely spaced hydrides facilitate the crack propagation between the adjacent hydride platelets during fracture. Further, Arsene et al. [71] assumed that the ductile-to-brittle transition occurs when a critical inter-hydride spacing is reached, but this threshold spacing was not reported in their work.

The hydride embrittlement of zirconium alloys at elevated temperatures (100°–350 °C) has also been studied [8, 71, 74]. It is generally accepted that the hydride embrittlement was reduced with increasing temperature. Huang and Huang [74] reported that the brittle-to-ductile transition initially observed at room temperature disappears as the temperature increases to 100 °C. They attributed this disappearance to the improved ductility of the zirconium matrix with increasing temperature, as well as the partial dissolution of hydrides at high temperatures which is clearly noticeable for the samples tested in their experiments with low hydride contents (corresponding
hydrogen contents ≤ 340 wt. ppm). Under the uniaxial tension at 350 °C, Bai et al. [8] found that the tensile ductility of recrystallised and stress-relieved Zr-4 samples containing high hydrogen contents up to 1100 wt. ppm exhibits only a slight decrease. They assumed that the smooth bent regions observed on the fracture surface (Fig. 2.13) are the indication of the plastic deformation in hydrides. Based on this insufficient evidence, the authors believed that the low sensitivity to hydride embrittlement at 350 °C is mainly due to the improved plasticity of hydrides at this temperature. In fact, the plastic deformation capacity of zirconium hydrides at elevated temperatures is controversial. Evans and Parry [78] observed that the hydrides can be plastically deformed to considerable strains together with the zirconium matrix at 150 °C and above. Arsene et al. [79] also reported that some hydride precipitates in zirconium alloys with a favourable crystallographic orientation relative to matrix grains can

![Fracture surface of a recrystallised Zr-4 sample with 1100 wt. ppm hydrogen tested at 350 °C](image)

**Figure 2.13** Fracture surface of a recrystallised Zr-4 sample with 1100 wt. ppm hydrogen tested at 350 °C [8].
undergo plastic deformation at 300 °C. However, some other investigations showed that the plasticity of hydrides is not improved at high temperatures. Previous study [73] showed that many cracks are generated in hydrides in zirconium when deformed at 170 °C. The tensile experiments on bulk ū-hydrides (ZrH$_{1.66}$) showed that no measureable ductility is observed for the tested samples over the temperature range of 20 to 500 °C [80]. Notably, in a study on the tensile behaviours of hydrided Zircaloys at 300 °C, Arsene et al. [71] also found that the hydride embrittlement is not distinct for high hydrogen contents (up to ~2000 wt. ppm), in consistence with the finding of Bai et al. [8]. Nevertheless, at a higher hydrogen content of 3000 wt. ppm, a drastic reduction in the tensile ductility and completely brittle fracture for recrystallised Zircaloys were observed at this high temperature. Although no reasonable interpretation on this phenomenon was given in the report of Arsene et al., it is speculated that a possible cause for the reappearance of brittle fracture for highly hydrided Zircaloys at 300 °C is the precipitation of the brittle ū-hydrides when the overall or local hydrogen content becomes very high [8].

2.3.2 Localised Embrittlement: Delayed Hydride Cracking

In addition to gross embrittlement, zirconium alloys are susceptible to a localised embrittlement process called delayed hydride cracking (DHC) which occurs at a stress concentration in the material as reviewed in references [10,81,82]. DHC is caused by the preferential hydrogen diffusion to tensile stress concentrations (such as crack tips or
other sharp flaws) and the subsequent precipitation and growth of brittle hydrides when the local hydrogen solid solubility is exceeded [83]. The hydride platelets of a critical size will fracture under concentrated stress, and the crack then propagates forwards in a very small region along the length of platelets and arrests in the ductile matrix. The repetition of this hydride precipitation, growth and fracture process, results in the slow, discontinuous crack propagation (i.e. DHC), which is responsible for the potential of the eventual failure of the material. The initiation of DHC is favoured by cooling from high to low temperature, as the hydrogen solubility in zirconium alloys decreases and the hydride precipitation takes place. However, cooling is not essential for DHC which can occur on heating or under isothermal conditions [16].

2.4 General Summary of Previous Work

Considerable work has been reported on the hydride formation and hydride embrittlement in zirconium alloys in several aspects such as the crystallographic and microstructural features of the hydride precipitation, the effect of hydride precipitation (morphology, amount, orientation and distribution) on the mechanical properties of the alloys, and the mechanisms of delayed hydride cracking (DHC). Although substantial research efforts have been devoted, some significant fundamental issues related to the hydride precipitation and the induced embrittlement behaviours in zirconium alloys still remain to be resolved. The majority of previous work on hydride formation in zirconium alloys concentrates on the materials in the annealed/recrystallised state, and
the hydride precipitation phenomenon and associated embrittlement in severally deformed zirconium alloy materials are seldom investigated and thus not well understood. Also, the factors that influence the hydride precipitation morphology, distribution and the hydride-induced embrittlement are not fully clarified. Some crystallographic and microstructural characteristics of hydrides including the orientation relationship of δ-hydride with α-Zr matrix and the dislocation distribution in hydrides are still controversial. Besides, the origin and characteristics of the hydride bulk texture are not completely clear due to the lack of specific studies on the macroscopic texture of hydrides precipitated in various zirconium alloys with distinct textures. Further studies that would contribute to solve these issues are still worthwhile to improve our understanding on hydride formation and the induced embrittlement behaviours in zirconium alloys.
Chapter 3

Experimental Instruments and Methodology

This chapter provides a description of the experimental instruments and methodology applied for the sample preparation and characterisation in the current thesis work.

3.1 Hydrided Sample Preparation

The gaseous hydrogen charging method was applied to introduce hydrogen into the Zircaloy-4 (Zr-4) samples. Compared with the electrolytic hydrogen charging approach, this method allows the introduction of high concentrations of hydrogen into Zr-4 samples in a relatively short charging time [7]. During gaseous hydriding, the samples were exposed to the atmosphere of high pressure hydrogen and soaked at a high temperature for certain period. Fig. 3.1 shows the two facilities used for the current hydrogen charging experiments. The first equipment is a commercial Sieverts furnace (Advanced Materials Corporation, USA) with a small chamber size of $10 \text{ mm} \times 30 \text{ mm}$ (Fig. 3.1a). Most of hydrided samples analysed in this work were prepared using this Sieverts apparatus, except that some large-sized samples for the tensile testing were hydrided in a self-developed pressure vessel at ANSTO with a chamber volume of 100 cm$^3$ (Fig. 3.1b). This vessel was manufactured with 316 stainless steel due to its low affinity to hydrogen, and a tube was welded on the vessel to facilitate the evacuation of the air from the vessel and the hydrogen intake into the system [7].
Figure 3.1 Two kinds of facilities used for the gaseous hydrogen charging: (a) a Sieverts furnace (Advanced Materials Corporation, USA); (b) a self-developed pressure vessel at ANSTO [7].

3.2 Characterisation Methodology

3.2.1 X-ray and Neutron Diffraction

X-ray diffraction (XRD) experiments were performed with a GBC MMA X-ray diffractometer using monochromatic Cu Kα radiation (wavelength \( \lambda = 1.5418 \) Å) to identify the phase constitution of the samples before and after hydriding. The method of the phase identification using XRD is based on Bragg’s law [84]:

\[
n\lambda = 2d_{hkl} \sin \theta_{hkl}
\]  

(3.1)

where \( hkl \) are the Miller indices of crystallographic planes of a crystalline phase, \( d \) is the interplanar spacing of specific \( hkl \) lattice planes, \( \theta \) is the angle between the incident beam and the scattering lattice planes, and \( n \) the order of reflection. When a monochromatic X-ray beam is incident upon a polycrystalline sample, the reflection
Chapter 3

platforms in all those crystallites which are in the reflection orientation satisfying Bragg’s law (equation 3.1). In the current XRD measurements, the X-ray tube voltage and loading current was set as 35 kV and 28.6 mA, respectively. A continuous-scan mode was employed with a scanning speed of 1° min⁻¹. The volume fractions of the formed hydrides in the hydrided samples were estimated using the integrated intensities of \( \tilde{\mathbf{u}}(111) \) and \( \tilde{\mathbf{U}}(0002) \) peaks from the identified \( \tilde{\mathbf{u}} \)-hydride and \( \tilde{\mathbf{U}} \)-Zr phases. The basic principle of the XRD phase quantification analysis is that the volume fraction of a crystalline phase is proportional to the integral intensity of the recorded diffraction peaks at set reflection angles and the various angular orientations of the sample [84]. Details of this estimation approach are given in Appendix B.

Neutron diffraction experiments on the virgin and hydrided Zr-4 samples were conducted using the high intensity powder diffractometer (Wombat) at the OPAL reactor of ANSTO [85]. The incident wavelength (\( \varphi \)) was adjusted to 2.4 Å using a focusing Ge (115) monochromator at a takeoff angle of 90°. The wavelength calibration was also carried out using a coarse-grained NIST standard LaB₆ powder sample, and a relatively precise \( \varphi \)-value of 2.414 Å was determined. The bulk texture measurements were implemented on the Wombat instrument, with the samples mounted on an Eulerian cradle, as shown in Fig. 3.2.
Figure 3.2 Photograph of an Eulerian cradle installed on the high intensity powder diffractometer (Wombat) at the OPAL reactor for the texture measurement.

The texture of a polycrystalline material is defined by the orientation of its crystallites in relation to the sample coordinate system \([86]\). It is described mathematically as a fraction of a volume, \(dV_g\), with the crystallite orientation \(g\) of the total investigated sample volume \(V\):

\[
 f(g) \, dg = \left( \frac{1}{V} \right) \, dV_g
\]

(3.2)

where the orientation \(g\) of a crystallite in a polycrystalline sample is described by specification of the rotation which transforms the sample coordinate system \(K_A\) into the crystal coordinate system \(K_B\) \([87]\), as shown in Fig. 3.3 \([88]\); and \(f(g)\) is the orientation distribution function (ODF). The classical texture analysis using the polycrystal diffraction methods is based on the determination of the pole density distribution functions (also called pole figures), which are the direction distribution functions of
Figure 3.3 Definition of the orientation $g$ of an individual crystallite in a polycrystalline sample. $K_A$ is the sample coordinate system, $K_B$ is the crystal coordinate system [88].

A particular crystal direction given by [88,89]:

$$P_h(y) = \frac{dV_{hly}/V}{d\Omega} \quad \text{with} \quad h \perp (hkl), \quad y = \{\mathbf{\tilde{U} \mathbf{b}}\}$$  \hspace{1cm} (3.3)

where $h$ is a particular crystal direction (often represented by a direction perpendicular to a low-index crystal lattice plane $(hkl)$), $y$ is a particular sample direction (often specified by spherical polar coordinates $\{\mathbf{\tilde{U} b}\}$), and $d\Omega = \sin\mathbf{\tilde{U}} \cdot d\mathbf{\tilde{U} b}$ is a solid angular element around $y$. The defined pole figures (equation 3.3) has a degree of freedom about the direction $h$; this means that the pole figure is an integral two-dimensional projection of the three-dimensional (3D) ODF [86,89]. Hence the relation between the pole figure and the ODF can be written as:

$$P_h(y) = P_{(hkl)}(\mathbf{\tilde{U} b}) = (1/2 \pi) \int f(g) d\Omega$$  \hspace{1cm} (3.4)

where $\Omega$ is the rotation angle around $h$ with $h\|y$. The above equation is commonly called the basic equation of the texture analysis. Based on this equation, the ODF $f(g)$ can be calculated from several pole figures with different $(hkl)$ by solving the integral equation. This procedure, known as the pole figure inversion or ODF analysis is the
basis of the quantitative texture analysis [87,89].

The pole figure can be represented on the pole sphere as shown in Fig. 3.4a or in some projection to the equatorial plane, e.g. the stereographic projection as illustrated in Fig. 3.4b [88]. The resulting pole figures can be used for a graphical representation of the texture. Experimentally, two measuring techniques based on neutron, synchrotron or X-ray diffraction are being applied for pole figure measurements using an Eulerian cradle, i.e. the reflection and transmission geometry (Fig. 3.5) [90]. The Eulerian cradle allows the rotation of the sample through three angles {\( \gamma, \varphi, \phi \)}. In order to perform the measurements on different pole figure directions, the sample has to be rotated around

**Figure 3.4** Definition of the \((hkl)\) pole figure: (a) the direction \( h \perp (hkl) \) on the pole sphere and its stereographic projection into the equatorial plane; (b) pole density distribution in stereographic projection [88]. The axes of the chosen sample coordinate system coincide with the rolling direction (RD) and transverse direction (TD) in the case of the sheet and plate samples.
two axes, tilting (\( \phi \) in reflection and \( \chi \) in transmission) and rotation (\( \phi \) in reflection and \( \chi \) in transmission). The pole figure coordinates \( \{ \alpha, \beta \} \) can be determined based on their correlations with the Bragg angle \( \theta_{hkl} \) and the angles of the Eulerian cradle \( \{ \chi, \phi, \omega \} \), which are given by [88]:

\[
\begin{align*}
\chi &= \theta_{hkl} = \text{constant} \\
\phi &= \bar{U} \\
\beta &= \bar{b} \\
\end{align*}
\]

reflection geometry \hspace{0.5cm} (3.5)

\[
\begin{align*}
\chi &= \theta_{hkl} - \bar{U} \\
\phi &= \bar{b} \\
\omega &= \text{constant} = 0^\circ \\
\end{align*}
\]

transmission geometry \hspace{0.5cm} (3.6)

The reflection geometry is used in the present pole figure measurements using neutron diffraction on Wombat. A cylindrical position sensitive \(^3\text{He}\) area detector (as indicated in Fig. 3.2), which allows the simultaneous acquisition of 120° in diffraction angle \( 2\theta \), was applied to record the diffraction images from the sample. For each measurement the

**Figure 3.5** Diffraction geometry in pole figure measurements: (a) in reflection and (b) in transmission [90].
sample was tilted ($G = 0\bar{1} 90^\circ$) and rotated ($\bar{U} = 0\bar{1} 360^\circ$) in equal-distance steps, typically on a $15^\circ \times 5^\circ$ grid in a 3D orientation sphere. The detector covers $15^\circ$ in $G$ and the detector image may be further partitioned (usually split into three sections with each of $5^\circ$) to give finer angular resolution in the obtained pole figures ($5^\circ \times 5^\circ$). The $\gamma$ angle was fixed at $27.6^\circ$ because the diffraction peaks of the tested sample around the angle of $2\theta = 55.2^\circ$ (i.e. $2\gamma$) are most interesting. Therefore we selected this $\gamma$ angle to achieve almost full pole figure coverage. The diffraction patterns extracted from the acquired diffraction images were analysed to determine the diffracted peak integral intensity and pole figure coordinates {\(\vec{\gamma} \vec{b}\)} using the software package 2DiffCalc [91]. The obtained pole figure data were then used to calculate the texture of the hydride and/or the $\bar{U}Zr$ matrix in the measured samples adopting the MTEX algorithm [92]. The line broadening analysis on some representative diffraction patterns of the hydrided samples was performed to evaluate the average dislocation densities in the hydride and the $\bar{U}Zr$ matrix phase.

### 3.2.2 Microscopy

#### 3.2.2.1 Optical Microscopy

The microstructure of some hydrided Zr-4 samples was examined and photographed using a Leica DMRM optical microscope under polarised light. When illuminated with polarised light, each grain of the anisotropic $\bar{U}Zr$ phase in the hydrided sample exhibits a different light intensity and colour in the recorded micrograph, which
depends on its crystal orientation relative to the light beam [93]. This polarised light illumination improves the phase contrast between the hydride and ÚZr phases and produces more distinguishable detail of the microstructural features than the bright-filed illumination.

3.2.2.2 Scanning Electron Microscopy

The metallographic and fractographic observations in this work were carried out primarily using a JEOL JSM-6490LA scanning electron microscopy (SEM), operating at 20 kV. In some cases, the microstructural characterisation was performed with a Zeiss Ultra Plus field emission gun SEM at 30 kV. An Oxford/HKL system was mounted on this field emission SEM and was employed for the present electron backscatter diffraction (EBSD) measurements. Details of the EBSD sample preparation appear in Appendix A. EBSD is a powerful characterisation tool in materials science, which allows crystallographic information in terms of individual grain orientations, microtexture, point-to-point orientation correlations, and phase constitutions to be acquired from small volumes of material. EBSD maps are formed by moving a focused electron beam point by point across a grid of positions on the surface of a bulk sample in an SEM [94]. As schematically illustrated in Fig. 3.6 [95], an EBSD pattern (termed Kikuchi pattern) is generated at each scanning point on a phosphor screen by backscatter diffraction of a beam of electrons from a volume of crystal material [96]. The generated Kikuchi pattern on the phosphor screen is then recorded by a photon
sensitive imaging detector, typically a sensitive charge coupled device (CCD) camera. The sample is generally highly tilted (usually 70°) toward the detector, to improve the quality of the patterns acquired [94]. The phase identification with the EBSD system is performed by the indexing of the recorded patterns. For the microtexture determination using EBSD, it may be mentioned that the direct calculation of ODF is possible because full grain orientations are obtained directly in this technique rather than calculated from crystal direction distributions (i.e. the measured pole figures) as in the case of macrotexture measurements using neutron or X-ray diffraction [97].

![Schematic showing the experimental set-up for EBSD observations](image)

**Figure 3.6** Schematic showing the experimental set-up for EBSD observations [95].

3.2.2.3 Transmission Electron Microscopy

The detailed microstructural characteristics of the hydrided sample, such as the hydride substructure and the dislocation distribution in hydrides, were examined by transmission electron microscopy. The observations were made on a high-resolution JEOL JEM-3000F transmission electron microscope operating at 300 kV.
3.2.3 Neutron Tomography

Neutron tomography experiments on some selected hydried Zr-4 samples were performed with the cold neutron beamline ICON at the Swiss spallation neutron source (SINQ) of the Paul Scherrer Institut (PSI) [98], using the micro-tomography setup. As neutrons could be effectively attenuated by some specific elements such as cadmium, gadolinium and hydrogen which possess high neutron scattering and absorption cross-sections, neutron tomography is a suitable technique for investigating the materials containing these elements [99]. This characterisation method was applied in the current work aiming to reveal the spatial distribution features of hydrides in the samples.

3.2.4 Mechanical Properties Tests

Microhardness measurements on hydried and unhydried Zr-4 samples were performed using a LECO M-400-H1 Vickers hardness tester at an indentation load of 0.3 kg and dwelling time of 12 s. Nanoindentation tests were conducted on a bulk hydride sample occasionally obtained in the hydriding experiments using a Hysitron TI 900 TriboIndenter equipped with a diamond Berkovich indenter. A maximum applied force of 5 mN and a hold time of 20 s were chosen for these tests. The nanohardness and Young's modulus of the tested bulk hydride sample were derived from the indentation load and displacement data recorded during the measurements following the Oliver–Pharr method [100]. The Young's modulus of some virgin and hydried Zr-4
plate samples was also measured using the impulse excitation technique with a GrindoSonic instrument (LEMMENS Company, Belgium).

Tensile samples with a rectangular cross-section of 3 mm × 2 mm and a gauge length of 10 mm were machined from the Zr-4 plate samples containing various hydrogen contents, in accordance with the AS 1391-2007 standard. The tensile tests were carried out at room temperature with an Instron 5967 universal testing machine at an extension rate of 0.50 mm min\(^{-1}\). The bulk strain on the sample during the tensile test was monitored using a strain gauge.
Chapter 4

Hydriding of the Nanostructured Zircaloy-4 Prepared by High-pressure Torsion (HPT): Effect of the HPT Processing and the Hydrogen-induced Structure and Mechanical Property Changes

4.1 Introduction

Nanostructured Zircaloy-4 (Zr-4) material was recently successfully prepared [101] by high-pressure torsion (HPT), which is a severe plastic deformation (SPD) technique that refines the grain sizes of metallic materials down to the nanometer regime [102]. The main reason for conducting the HPT work is that the produced nanostructured materials have better resistance to radiation damage than their coarse-grained counterparts [103]. It should be noted that, although the strength of this nanocrystalline Zr-4 material is improved, the comprehensive properties should be carefully evaluated before considering its practical applications in nuclear reactors, especially the resistance to hydride embrittlement. This is because the hydride-related embrittlement would significantly reduce the ductility and fracture toughness of the material. The HPT-processed Zr-4 material may have a high susceptibility for the hydride formation, as the SPD could induce a large concentration of defects acting as potential nucleation sites of hydrides. Thus, it is of great significance in both technical and scientific aspects to perform the in-depth investigations concerning hydriding and its effects on structural...
and mechanical properties of HPT Zr-4, which would enhance our understanding on the hydride formation behaviours in severely deformed zirconium alloys with nanostructure and potential deformation texture.

In the current chapter, we aim to ascertain the following two questions:

(i) what is the effect (if any) of HPT on the hydride formation in Zr-4?

(ii) what changes in terms of structure and mechanical property for the HPT-processed Zr-4 would be incurred by the introduction of hydrogen?

We first conducted a comparative study to clarify the issue (i). The hydride precipitation behaviours (hydride phase evolution, morphology and concentration) of the original and HPT-produced Zr-4 samples at the same hydriding conditions were compared, in order to reveal the influence of HPT preprocessing on the hydride formation. Subsequently, to answer the issue (ii), the hydriding processing–microstructure–property relationship of the HPT material was thoroughly investigated. The structural evolutions of the HPT samples possessing the nanocrystalline structure due to thermal effects during hydriding were also discussed.

4.2 Experimental Procedures

4.2.1 Samples

The Zr-4 disk samples (diameter 10 mm and thickness 0.8 mm) were used in this study. The starting samples exhibit an equiaxed \( \alpha \)-Zr grain structure with diameters from \( \sim 10 \) to \( \sim 20 \ \mu \text{m} \) (Fig. 4.1a). Unconstrained HPT processing on some disk samples was
conducted at room temperature under a pressure of 3.8 GPa. Detailed microstructural characterisation of the HPT materials in Ref. [101] revealed that the HPT samples exhibit a homogenous nanocrystalline structure with grain sizes of ~100 nm after 5 revolutions HPT processing (Fig. 4.1b).

**Figure 4.1** (a) microstructure of the initial Zr-4 disk observed with SEM; (b) microstructure of the 5-revolution HPT disk observed by transmission electron microscopy [101].

### 4.2.2 Processing

The as-received and HPT-processed samples were initially ground to remove the native oxide layer present on the surface, and then subjected to hydrogen charging in a Sieverts furnace using high purity hydrogen (99.9%) at hydrogen pressures of 10, 15 and 20 atm. For hydriding, the samples were soaked at 450 °C for 15 h followed by furnace cooling to room temperature with a cooling rate of ~2.2 °C min\(^{-1}\). To separately track the structural evolution of the Zr-4 matrix induced by the thermal effect during hydriding, two HPT samples were vacuum annealed at 450 °C for 15 h. One vacuum
annealed sample was further hydrided under 15 atm hydrogen pressure using the same hydriding procedure.

### 4.2.3 Characterisation

The phase identification of the Zr-4 disks before and after hydriding was performed by X-ray diffraction (XRD) using a GBC MMA X-ray diffractometer with Cu K\(\alpha\) radiation (\(\lambda = 1.5418\) Å) at 28.6 mA and 35 kV, using a continuous-scan mode at 1° min\(^{-1}\). The microstructure of cross-sections of Zr-4 samples was examined by mounting them in epoxy, polishing according to standard metallographic techniques and finishing on 1200 grit silicon carbide paper. Samples were etched with a solution consisting of 10 ml HF, 100 ml HNO\(_3\) and 100 ml distilled water for 30 s and observed using a JEOL JSM-6490LA scanning electron microscopy (SEM). Two approaches were applied to estimate the hydride volume fraction and hydrogen content ([H]) achieved for each hydrided sample. The first approach compares the integrated intensities of specific XRD peaks using the calculation method described in Ref. [27], and another one is based on the analysis of SEM micrographs using an image processing and analysis software (ImageJ) [104]. Details about these two methods could be found in Appendix B. The Vickers microhardness was measured using a LECO M-400-H1 microhardness tester at a load of 0.3 kg and an indentation dwelling time of 12 s. At least 10 indents were taken for each sample. A nanoindentation test on the polished cross-section of the 20 atm hydrided HPT sample was performed using a Hysitron TI 900 TriboIndenter with a diamond Berkovich indenter. The nanoindentation measurements were conducted on 24
different points of the sample using a loading-unloading test mode at a test force of 5 mN and a hold time of 20 s. During the tests, the indentation load and displacement were recorded. The raw data were then applied to construct the load-displacement plots. The Young’s modulus $E$ and nanohardness $H$ of the sample were calculated from load-displacement curves using the Oliver–Pharr method [100].

The bulk texture of samples was measured using neutrons at a wavelength of 2.414 Å on Wombat, the high intensity powder diffractometer at the OPAL reactor of the Australian Nuclear Science and Technology Organisation [85]. With the samples mounted on an Eulerian cradle, diffraction patterns including a set of chosen diffraction peaks for the pole figure analysis were recorded using a position sensitive area detector, covering an in-plane range of 120° in diffraction angle $2\theta$. For the pole figure measurements, samples were tilted ($G = 0°90°$) and rotated ($\Omega = 0°360°$) in equal-distance steps, typically on a $15° \times 5°$ grid in a three-dimensional orientation sphere, while the $\gamma$ angle was fixed at 27.6°. Diffraction data were analysed to determine the orientation distribution function (ODF) using the software packages 2DiffCalc [91] and MTEX [92], and the pole figures were then calculated from the determined ODF.

**4.3 Effect of High-pressure Torsion on Hydride Formation**

In this section, a comparative study was conducted to investigate the effect of HPT preprocessing on the hydride precipitation behaviour in Zr-4 during gaseous hydrogen
charging.

### 4.3.1 Phase and Microstructural Characterisation

Fig. 4.2 shows the XRD patterns of the as-received Zr-4 disk and corresponding hydried samples prepared under different hydrogen pressures. A single hexagonal close-packed (hcp) $\alpha$-Zr (JCPDS Card No. 05-0665) was clearly detected in the as-received sample, and face-centred cubic (fcc) $\delta$-ZrH$_{1.66}$ (JCPDS Card No. 34-0649) and $\tilde{\alpha}$-Zr were identified in the hydried samples at hydrogen pressures of 15 and 20 atm, whereas no distinct hydride peaks were observed in the 10 atm hydried sample (Fig. 4.2). Moreover, the XRD semi-quantification evaluation on the hydride contents and hydrogen concentrations suggested that as the hydriding pressure rose from 15 to 20 atm,

![Figure 4.2 XRD patterns of the as-received and corresponding hydried samples under different hydrogen pressures.](image)
atm, the δ-hydride volume fraction increased from 2% to 6% ([H] increased from 313 to 945 wt. ppm). Typical cross-sectional microstructures of the as-received Zr-4 disks hydrided at various hydrogen pressures are provided in Fig. 4.3. In conjunction with this microstructural characterisation (Fig. 4.3), we could find that the formation of hydrides and the hydride morphology and concentration were closely related to the applied hydrogen pressure. At a relatively low hydrogen pressure of 10 atm, no hydrides were observed within the U-Zr matrix (Fig. 4.3a), verifying the XRD identification (Fig. 4.2).

Figure 4.3 SEM micrographs showing typical microstructures on the cross-sections of hydrided samples without HPT preprocessing under different hydrogen pressures: (a) 10 atm; (b) 15 atm and (c) 20 atm.
As the hydrogen pressure increased to 15 atm, needle-like hydrides appeared with most hydride needles connected with the adjacent ones (Fig. 4.3b). With further increasing the hydrogen pressure to 20 atm, the hydride platelets became thicker and, meanwhile, a hydride network was developed, exhibiting a higher hydride concentration (Fig. 4.3c).

Fig. 4.4 shows the XRD patterns of HPT samples before and after hydriding under various hydrogen pressures. It is evident that after HPT processing the sample maintained a single $\alpha$-Zr, and the $\delta$-ZrH$_{1.66}$ emerged after hydriding the HPT samples at hydrogen pressures of 10 and 15 atm. The XRD estimation of the $\delta$-hydride volume fractions showed that the elevation of hydriding pressures from 10 to 15 atm resulted in the increase of the hydride volume fractions from 3% to 16% ([H] increased from 470 to 2554 wt. ppm). Interestingly, with further increasing the hydrogen pressure to 20 atm,

![XRD patterns of the unhydrided and hydrided HPT samples at various hydrogen pressures.](image)

**Figure 4.4** XRD patterns of the unhydrided and hydrided HPT samples at various hydrogen pressures.
the hydried sample was fully indexed to the tetragonal \((I4/mmm)\) \(\text{\(\bar{U}\)}\)ZrH\(_2\) (JCPDS Card No. 17-0314), implying the formation of pure \(\text{\(\bar{U}\)}\)hydride at an even higher hydrogen content (~21,600 wt. ppm for pure \(\text{\(\bar{U}\)}\)ZrH\(_2\)). This is in good agreement with the previous results that \(\text{\(\bar{U}\)}\)hydrides were precipitated at very high hydrogen concentrations [27,49].

The metastable \(\varepsilon\)-Zr\(_2\)H [32] and \(\delta\)-ZrH [105] phases were not observed in the present hydriding condition. Generally, a greater concentration of hydrides could be achieved at a higher hydriding pressure for both the as-received and HPT samples. This trend may be explained by the higher hydrogen absorption of the material at the elevated hydriding pressure, according to the Sievert’s law [106] which is expressed as: \(C_\text{H} = k \cdot p_{\text{H}_2}^{1/2}\), where \(C_\text{H}\) is the atomic percentage of hydrogen dissolved in Zircaloy, \(k\) is the Sievert’s constant, and \(p_{\text{H}_2}\) is the hydrogen partial pressure. When the concentration for the absorbed hydrogen exceeds the terminal solid solubility (TSS), hydrides will precipitate and, therefore, the greater hydrogen absorption at a higher hydrogen pressure will lead to the formation of a larger amount of hydrides.

Fig. 4.5 shows the effect of hydrogen charging pressure on the cross-sectional microstructures of HPT disks. The common acicular or platelet-like hydrides were clearly visible on cross-sections of the 10 and 15 atm hydried HPT disks. For the sample hydried at 10 atm, the hydride needles and nearly equiaxed \(\text{\(\bar{U}\)}\)Zr grains were clearly observed (Figs. 4.5a and b). For the 15 atm hydried sample, a high concentration of hydride platelets was formed (Fig. 4.5c), and some long hydride plates were observed to possess tangled short-platelet branches, as shown in Fig. 4.5d.
Extensive SEM observations also revealed the relatively uniform distribution of hydride needles or platelets throughout the HPT disks at 10 and 15 atm. According to the quantitative analysis of several low-magnification SEM micrographs at 10 and 15 atm

![SEM micrographs showing typical microstructures on cross-sections of hydrided HPT Zr-4 samples at hydrogen pressures of (a) 10; (c) 15 and (e) 20 atm. (b) and (d) are local magnifications of (a) and (c), respectively.](image)

**Figure 4.5** SEM micrographs showing typical microstructures on cross-sections of hydrided HPT Zr-4 samples at hydrogen pressures of (a) 10; (c) 15 and (e) 20 atm. (b) and (d) are local magnifications of (a) and (c), respectively.
(the representative images are shown in Figs. 4.5a and c) using the approach provided in Appendix B, the hydride volume fraction significantly increased from 4% to 21% as the applied hydrogen pressure raised from 10 to 15 atm. It should be noted that these estimated values of hydride volume fractions are slightly higher than those evaluated from the XRD tests. This is probably related to the uncertainty of the measurement based on the SEM micrographs taken from the etched microstructure, as few hydrides could be generated due to the etching process [107]. As the hydrogen pressure increased to 20 atm, the platelet-morphology hydride identified as Ŷ-ZrH$_{1.66}$ developed into the pure Ŷ-ZrH$_2$ (Fig. 4.4), and long microcracks were present on the microstructure of the Ŷ-ZrH$_2$ sample. No apparent grain structure of Ŷ-ZrH$_2$ was revealed (Fig. 4.5e), similar to Xu and Shi’s observation on Ŷ-ZrH$_{1.83}$ [108]. The microstresses arising from the volume expansion of the Ŷ-hydride formation and thermal stresses during hydriding are believed to be responsible for the microcrack network development in the pure Ŷ-hydride microstructure (Fig. 4.5e).

4.3.2 Comparative Analysis and Verification

A comparison of the microstructural characterisation results of the hydrided samples clearly implies that more hydrides tend to form in the HPT samples than that in the as-received samples when hydrided at the same hydrogen pressures. Note that the severe plastic deformation of the HPT samples will generate a large number of defective grain boundaries and other lattice defects (e.g. vacancies and dislocations), which is
believed to be responsible for the enhanced potential for the hydride formation in the HPT samples. First, these defects could act as fast hydrogen diffusion channels [109,110] and hydrogen traps [111,112], significantly promoting the formation of hydrides. Second, the presence of large amount of defects (especially the dislocations) provides sufficient favourable nucleation sites for hydrides, enhancing the hydride nucleation [34,113]. At a low hydrogen pressure of 10 atm, presumably the concentration of absorbed hydrogen during hydriding is below the terminal solid solubility (TSS) of hydrogen at the given hydriding conditions based on the evidence that no hydrides were formed in the as-received samples (Figs. 4.2 and 4.3a). However, for the HPT sample hydrided at 10 atm, the local hydrogen concentrations in the regions of the sample with a high defect density may exceed the TSS of hydrogen due to the hydrogen trapping effect by defects, thereby leading to the precipitation of some hydrides within the HPT matrix at the low hydrogen pressure (Figs. 4.4 and 4.5a-b). With further increasing the hydrogen pressures (>10 atm), higher hydrogen uptake is yielded, favouring the hydride formation in both the as-received and HPT samples. Furthermore, due to the combined effects of the large concentration of lattice defects induced by HPT (acting as hydrogen traps and effective hydride nucleation sites), the nucleation and subsequent growth of hydrides are facilitated in the HPT samples. Consequently, higher hydride contents were obtained in the HPT samples than that in the as-received samples when hydrided at the same conditions. The aforementioned analysis regarding the role of HPT preprocessing on the hydride formation could be
supported by the results presented in Fig. 4.6. Fig. 4.6a shows the cross-section microstructure of the HPT disk after vacuum annealing at 450 °C for 15 h. The equiaxed ŪZr grains were clearly present in this microstructure, suggesting the emergence of recrystallisation after annealing. The vacuum-annealed disk is further hydried at 15 atm using the identical hydriding process for the HPT samples. In this instance, only few hydride platelets with an estimated volume fraction of 2% were observed on the cross-section (Fig. 4.6b). Compared with the HPT sample without prior annealing treatment, the recrystallised sample exhibited the enhanced resistance to hydride formation at a hydriding pressure of 15 atm. It is reported that dislocations are favourable sites for hydride nucleation, which can effectively accommodate the misfit strain associated with the hydride precipitation [34]. During the prior recrystallisation annealing, the annihilation of dislocations in the HPT samples is initiated, inducing the lack of preferred nucleation sites for hydrides and resultant limited hydride formation.

**Figure 4.6** SEM images showing characteristic microstructures of the vacuum-annealed HPT sample before (a) and after (b) hydriding at a hydrogen pressure of 15 atm.
after hydriding (Fig. 4.6b). The result provided in Fig. 4.6 confirmed that, from an inverse side, the large concentration of lattice defects induced by HPT processing impart the higher potential for the hydride precipitation in the HPT material compared with samples without HPT processing.

4.4 Mechanical Property and Structure Changes

The metallographic studies described in Section 4.3 have revealed the significant changes in the microstructure of HPT samples after the hydriding treatment at various hydrogen pressures. In this section, we would further investigate the influences of hydriding on the mechanical properties, ÜZr grain structure and texture of the HPT Zr-4 material.

4.4.1 Mechanical Property

Fig. 4.7 displays the variation in the microhardness of HPT disks before and after hydrogen charging at different pressures. Note that the original HPT sample possessed a superior average microhardness of 293 HV$_{0.3}$ (Fig. 4.7) due to a significant grain refinement and generation of high dislocation density after HPT deformation [102,114]. As expected, a relatively low microhardness of 201 HV$_{0.3}$ was measured for the HPT sample after vacuum annealing (Fig. 4.6a) and, moreover, furthering hydriding the annealed HPT sample at 15 atm led to the formation of few hydrides (Fig. 4.6b) and hence a low microhardness of 218 HV$_{0.3}$ was attained. When hydriding the HPT disks
with the applied hydrogen pressure varied from 10 to 15 atm, the average microhardness of the samples elevated from 203 to 292 HV$_{0.3}$ (Fig. 4.7). Compared with the vacuum-annealed HPT sample, it is obvious that no apparent microhardness increase is observed for the 10 atm hydrided HPT sample with a very low fraction of hydrides, while significant hardening is induced by the precipitation of large amounts of hydrides in the hydrided HPT sample at 15 atm (Figs. 4.5a-d). The hydrides precipitation during cooling introduces local stresses (due to hydrides volume expansion) and dislocations [33,37], contributing to the potential hardening effect of hydrides.

The pure ŨZrH$_2$ attained at 20 atm (Figs. 4.4 and 4.5e) exhibited an exceptionally high average microhardness of 470 HV$_{0.3}$ (Fig. 4.7). In this case, the microhardness

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**Figure 4.7** Vickers microhardness of the hydrided and unhydrided HPT samples. Error bars in the microhardness data show one standard deviation.
indentation with a well-defined microcarck morphology was observed (Fig. 4.8). Such indentation crack development is driven by the residual stress field in the material, and the crack extending length is related to the material crack propagation resistance [115]. The fracture toughness $K_{IC}$ of $\hat{\Theta}$hydride can be estimated following the indentation microfracture method and using the expression [108,115]:

$$K_{IC} = \frac{E}{c} \left(\frac{P}{H}\right)^{1/2},$$

where $E$ is the Young's modulus, and $H$ is the hardness, $P$ is the indentation load (in the present Vickers microhardness test the applied load $P$ is 0.3 kg), $c$ is the length of the radial cracks, and $\xi$ is a constant related to the geometry of the indenter (for Vickers indenters $\xi$ is 0.016). The crack length $c$ was evaluated as ~43.2 $\mu$m from the SEM micrograph showing the microhardness impression and crack morphology (Fig. 4.8).

The $E$ and $H$ of the $\hat{\Theta}$ZrH$_2$ material were determined by applying nanoindentation tests on various positions of its polished section, as shown in Fig. 4.9. During each nanoindentation measurement, an indentation load-displacement curve was recorded (a representative load-displacement curve is shown in the inset in Fig. 4.9), from which the corresponding $E$ and $H$ values could be determined [100]. The average values of $E$ and $H$ for $\hat{\Theta}$ZrH$_2$ were 78.5 GPa and 5.4 GPa, respectively. Adopting the above the experimental results, the fracture toughness $K_{IC}$ of the $\hat{\Theta}$ZrH$_2$ was estimated to be 0.63 MPa m$^{1/2}$, which was close to the reported $K_{IC}$ value of the $\hat{\Theta}$ZrH$_{1.83}$ material (0.74 MPa m$^{1/2}$) [108].
Figure 4.8 SEM image of a Vickers microhardness indentation of the 20 atm hydrided HPT sample (pure $\text{UZrH}_2$), the arrows show the presence of microcracks.

Figure 4.9 Young's modulus and nanohardness of the 20 atm hydrided HPT sample (pure $\text{UZrH}_2$) measured by nanoindentation tests, the inset shows a representative indentation load-displacement curve.
4.4.2 $\alpha$-Zr Grain Structure

The interesting features found in the 10 atm HPT sample are the equiaxed $\alpha$-Zr grains formation and significant microhardness degradation compared with the original HPT sample (Figs. 4.5a-b and 4.7). It was accordingly inferred that a low temperature recrystallisation of the HPT Zr-4 matrix occurred at 450 °C during hydriding, as the typical recrystallisation temperature range of conventional cold deformation Zr-4 is between 470 and 650 °C [116,117]. The high stored energy in HPT deformation, as the driving force for recrystallisation, could stimulate the occurrence of recrystallisation at a low temperature. Moreover, for the HPT-processed metals, Zhilyaev et al. [102] reported that the recrystallisation temperature decreased when the accumulated strain $\varepsilon'$ rose above ~5, herein $\varepsilon'$ was estimated from the relationship: $\varepsilon' = \ln(2^\pi Nr/h)$, where $N$ is the number of whole revolutions imposed on the disk sample, and $r$ and $h$ are the radius and thickness of the disk, respectively. Based on this criterion, it was reasonable to consider that the recrystallisation of HPT samples with $\varepsilon'$ reaching ~5.28 occurred during hydriding. The occurrence of recrystallisation caused the prominent decrease in microhardness of the HPT sample after hydriding at 10 atm (Fig. 4.7). The comparable microhardness of the 15 atm HPT sample to that of the HPT matrix (Fig. 4.7) is a consequence of the combined effects of the precipitation hardening of the large concentration hydrides and the recrystallisation softening of the matrix. It should be indicated that the recrystallised $\alpha$-Zr grains were not evident at 15 atm, as they were masked by the concentrated hydrides (Figs. 4.5c and d).
4.4.3 Texture

Figs. 4.10a and b show the (0002) and (10\bar{1}0) pole figures of the starting HPT disk before and after vacuum annealing. The HPT disk only presented a strong (0002) basal texture having the pole maximum of 4 multiples of the random distribution (m.r.d.) along the axial direction (AD) of the disk (Fig. 4.10a). With the emergence of significant recrystallisation after annealing (Fig. 4.6a), the (0002) basal texture was weakened in comparison to the initial deformation texture and, meanwhile, a prismatic (10\bar{1}0) texture was developed (Fig. 4.10b). The basal pole figure displayed a broad pole maximum (3 m.r.d.) parallel to the tangential (TD\hat{\theta}) and radial (RD\hat{\theta}) plane\(^1\) and also a retained weak pole along AD. The (10\bar{1}0) pole figure showed a clear maximum along AD. This texture evolution result is rational crystallographically, which gives us the confidence that our neutron texture measurements and data analyses are correct. More importantly, it reveals that the development of (10\bar{1}0) component parallel to AD is at the expense of the (0002) deformation component parallel to AD, manifesting that the [0002] grain orientations rotate by \(\sim 90^\circ\) around a <10\bar{1}0> axis during recrystallisation. This characteristic rotation has been previously reported in Ti and Zr during the recrystallisation process [118]. Further investigation is required to understand the origin of this rotation of the [0002] grain orientations in HPT Zr-4 after recrystallisation. Fig. 4.10c displays a representative neutron diffraction pattern of the

\(^1\) The tangential and radial directions of the HPT disks are abbreviated as TD\hat{\theta} and RD\hat{\theta} respectively, to avoid the confusion with the rolling (RD) and transverse directions (TD) of the plate samples in Chapters 5-7.
Figure 4.10
Figure 4.10 Basal (0002) and prismatic (10\bar{T}0) pole figures of the $\tilde{\text{U}}$-Zr phase determined by neutron diffraction for the (a) starting HPT Zr-4 disk; (b) vacuum-annealed HPT sample and (d) HPT sample hydrided at the hydrogen pressure 15 atm. (c) a neutron diffraction pattern obtained from the 15 atm hydrided HPT sample. (e) (111) pole figure of the $\tilde{\text{U}}$-ZrH$_{1.66}$ precipitated in the 15 atm hydrided HPT sample. The sample reference frame for direct pole figures is shown on the right of (e).

15 atm hydrided HPT sample, with the background fitted using the 2DiffCalc routine [91]. Diffraction peaks for texture analysis were indexed, including (0002), (10\bar{T}0) and (10\bar{T}1) peaks of $\tilde{\text{U}}$-Zr and (111) peak of $\tilde{\text{U}}$-ZrH$_{1.66}$ (Fig. 4.10c). As the hydride peak intensity is low in neutron diffraction essentially due to the small coherent neutron scattering cross-section of hydrogen (1.757 barn [119]), only the strongest (111) peak of $\tilde{\text{U}}$-ZrH$_{1.66}$ was unambiguously identified in the 15 atm hydrided HPT sample. The calculated (0002) and (10\bar{T}0) pole figures of $\tilde{\text{U}}$Zr and (111) pole figure of $\tilde{\text{U}}$ZrH$_{1.66}$ for the 15 atm hydrided HPT sample are demonstrated in Figs. 4.10d and e, respectively. The observed $\tilde{\text{U}}$-hydride in the 15 atm hydrided HPT sample showed a relatively weak
(111) texture (pole maximum 2 m.r.d.) compared with the basal texture of the initial HPT disk. Through the texture analysis (Figs. 4.10a, d and e), the $\bar{\tau}(111)/\bar{\tau}(0001)$ orientation relationship is found, which is also supported by the previous studies using electron backscatter diffraction (EBSD) [39,40] and synchrotron [63] techniques. This hydride-matrix orientation correlation essentially results from the preferred lattice matching of the involved $(0001)_{\alpha Zr}$ and $\{111\}_{\delta ZrH_{1.66}}$ atomic planes [33]. Besides, the developed recrystallisation basal and prismatic textures of $\bar{\tau}$Zr under vacuum and 15 atm hydrogen atmospheres are similar (Figs. 4.10b and d) in dominant shape and intensity. The main differences are that along AD a stronger (0002) pole and weaker (10$\bar{1}$0) pole of $\bar{\tau}$Zr are observed for the 15 atm hydrided HPT sample than those for the vacuum-annealed sample. It is considered that the hydrogen solute atoms dissolved in Zr-4 lattice during hydriding at 15 atm hydrogen, may retard the recrystallisation to some extent [120] and hence preserving more [0002] grain orientations along AD (Fig. 4.10d). Furthermore, hydrogen in solid solution plays an inhibiting role on the static recovery by limiting climb or annihilation of the dislocations, which is linked to the recrystallisation phenomenon [121,122]. Although one might argue that during cooling the precipitation of $\bar{\tau}$-hydrides representing a large volume expansion (17.2% [33]) relative to the $\bar{\tau}$-Zr matrix may exert intergranular compressive stresses on surrounding $\bar{\tau}$Zr grains which increase the driving force of recrystallisation, few hydrides are precipitated at the recrystallisation temperature of 450 °C and thus induce low internal stresses and insignificant effects on the resultant texture evolution.


4.5 Conclusions

In this chapter, a comparative study was initially conducted to investigate the effect of HPT preprocessing on the hydride precipitation behaviour in Zr-4 during gaseous hydrogen charging. Overall, when hydriding at the same hydrogen pressures, more hydrides tended to precipitate in the HPT samples compared to that of the samples without HPT preprocessing. The HPT samples exhibited the enhanced potential for the hydride formation. This results from comprehensive effects of a large concentration of defects induced by HPT (acting as hydrogen traps and hydrogen fast diffusion channels and providing preferred hydride nucleation sites), promoting the nucleation and subsequent growth of hydrides in the HPT samples. Another but the primary concern for the work in this chapter was the study on the microstructural, textural and mechanical properties of the gaseously hydrided HPT-processed Zr-4 disks at different hydrogen pressures. The Ũ\(\text{ZrH}_{1.66}\) hydrides formed at 10 atm hydrogen pressure showed the needle-like morphology while thick Ũ-hydride platelets developed at 15 atm. A large volume fraction of Ũ-hydrides (~21%) precipitated at 15 atm, leading to the prominent enhancement in microhardness of the vacuum-annealed HPT sample. At 20 atm, pure Ũ\(\text{ZrH}_2\) was attained possessing a high microhardness of 470 HV\(_{0.3}\) and an estimated fracture toughness of 0.63 MPa m\(^{1/2}\). The HPT disk presents a strong (0002) basal texture along AD and due to the recrystallisation occurred during hydriding, the [0002] grain orientations rotated by ~90° around a \(<10\bar{1}0>\) axis, leading to the developments of (0002) pole maxima perpendicular to AD and (10\(\bar{1}0\)) component along AD. The
precipitated Ũ-hydrides displayed a relatively weak (111) texture compared with the basal texture of the HPT Zr-4 disk and followed the Ũ(111)/Ũ(0001) orientation relationship with the Ũ-Zr matrix.
Chapter 5

Microstructure and Texture Analysis of the δ-hydride Precipitation in Annealed Zircaloy-4 Materials

5.1 Introduction

Hydride-induced embrittlement has been recognised as one of the most important reasons causing the failure in zirconium alloys, which are core structural materials used extensively in nuclear reactors. The hydrogen ingress and subsequent hydride precipitation in Zr alloys under the reactor service conditions are normally inevitable, mainly attributed to the strong affinity of Zr with hydrogen and the low solubility of hydrogen in the Zr matrix (less that 10 wt. ppm at room temperature [123]). Due to the intrinsic brittleness of hydrides at low temperature, the hydride formation may severely embrittle the Zr matrix, leading to the substantial losses of ductility, impact and fracture toughness. When the concentration of the hydride precipitates reaches a critical value, a slow crack propagation process called delayed hydride cracking (DHC) may be initiated in the Zr alloy components with certain levels of internal/external stresses [82,124,125]. The initiation of DHC may gradually degrade the structure integrity of the components and thus reduce their useable lifetime. Considering the technological importance of this hydride-assisted cracking issue, the precipitation behaviour of hydrides and their induced embrittlement in Zr alloys have been the subject of extensive research work [8,40,41,45,51,60].
Previous results demonstrated that the hydride precipitation in Zr alloys is a complicated process. The morphology, distribution and crystallographic features of hydrides are influenced by several factors including the hydriding conditions, matrix microstructure and texture [8,105,126]. For instance, the formation of the equilibrium face-centred-cubic (fcc) δ-hydride phase is favoured by slow cooling rates and high hydrogen contents, whereas the metastable tetragonal (P4_2/n) γ-hydride phase tends to precipitate under quenching conditions [105]. The frequently reported orientation relationship (OR) of the δ-hydride with the α-Zr matrix is δ(111)∥α(0001), although some other crystallographic correlations (such as δ(111)∥α(1010)) are occasionally observed. Qin et al. [40] assumed that the various alloy compositions and hydrogen concentrations of hydrided Zr alloys used in different work may alter the matching of atom patterns and spacings at the hydride-matrix interface and lead to the variation of the OR. The δ-hydrides display a common acicular or platelet morphology as seen in optical metallographic examinations, and transmission electron microscopy (TEM) observations revealed that, the optically visible hydrides are often composed of stacks of smaller hydrides which may have different crystallographic orientations [47]. Besides, it is worth noting that the δ-hydride precipitation is accompanied by a significant volume expansion (i.e. dilatational strain) that requires both the elastic and plastic accommodation by the hydride and the surrounding α-Zr matrix during the hydride precipitation process [33,127,128]. The states of the internal stress in the δ-hydride precipitated in Zircaloy-4 (Zr-4) and Zr-2.5Nb alloys, generated as a result of the elastic
accommodation behaviour, were evaluated in the recent work by Santisteban and Vicente Alvarez et al. [126,129], uncovering the magnitude and nature of the stresses existed within hydrides. However, not much information about the response of the plastic accommodation (e.g. generation of misfit dislocations) for the hydride formation in Zr alloys is available in the open literature [60], although this knowledge is needed for better understanding on the subtle microstructural features and the brittle characteristics of hydrides formed in situ in Zr alloys. Another concern is that the potential developments of the crystallographic texture of hydrides, taking into account the presence of Ú-Zr matrix texture produced in the thermo-mechanical processing steps of the material and the existing preferred OR between hydride and matrix. Several research works have reported the hydride texture measured in hydrided Zr alloys using synchrotron X-ray diffraction [63,126,129] and neutron diffraction [46]. In order to enhance the understanding on the general characteristics and origin of the hydride texture, it might be still necessary to perform further texture analysis on both the hydride and matrix phases in various Zr alloys with apparently different matrix texture, and the comparison between the produced new results with those have been reported would be of great interest.

In this chapter, we presented a comprehensive microstructure and texture analysis on two hydrided Zr-4 materials containing high contents of hydrogen (~2000 wt. ppm) primarily by neutron diffraction and electron microscopy. The bulk textures of the hydride and Ú-Zr matrix phases were determined in order to understand the
characteristics and origin of the hydride texture. The neutron diffraction line profile analysis combined with the high-resolution transmission electron microscopy (HRTEM) investigation was also performed aiming to reveal the potential generation and distribution of misfit dislocations in the hydride and adjacent $\tilde{\text{U}}\text{Zr}$ matrix resulting from the plastic accommodation of the substantial dilatational strains associated with the hydride transformation.

### 5.2 Experimental Procedures

#### 5.2.1 Sample Preparation

Commercial Zr-4 materials (ASTM Grade R60804, purchased from Wah Chang, USA) in two thermal-mechanical states, i.e. hot-rolled and annealed plate (referred to as plate hereinafter) and hot-extruded and annealed round bar (referred to as bar), were used in this study; the chemical composition is given in Table 5.1. The Zr-4 plate was annealed in the range 760 and 810 °C for 1.5 h and the bar treated at 700 °C for 3 h. The microstructures of both types of Zr-4 materials are similar (Fig. 5.1), both consisting of equiaxed $\tilde{\text{U}}\text{Zr}$ grains that are typical of annealed Zr-4 materials.

| Table 5.1 Chemical composition of Zr-4 used in the present chapter. |
|-------------------------|----------------|----------------|----------------|----------------|----------------|
| Element                | Sn (wt.%) | Fe (wt.%) | Cr (wt.%) | O (wt.%) | Zr (wt.%) |
| Content                | 1.56      | 0.22       | 0.11       | 0.14       | Balance       |
Figure 5.1 SEM micrographs showing typical microstructures (a) on the RD-TD section of the Zr-4 plate matrix and (b) on the cross-section of the Zr-4 bar matrix. RD and TD indicated in (a) represent the rolling direction and transverse direction of the plate, respectively.

Several test samples with dimensions of 12 mm × 6 mm × 2 mm (from the original plate) and 10 mm × 1 mm (from the bar material) were machined out by wire-cutting for hydrogen charging experiments. The length, width and thickness directions of the produced rectangular-shaped pieces correspond to the rolling direction (RD), transverse direction (TD), and normal direction (ND) of the initial plate, respectively, and the axial direction of the disks is parallel to the extrusion direction (ED) of the original bar. Samples for hydrogenation were first immersed in an acid solution consisting of 10 ml HF, 45 ml HNO$_3$ and 10 ml distilled water for 2 min to remove the oxide layer present on the surface that was generated during wire-cutting, and then gaseously hydrided in a Sieverts device (Advanced Materials Corporation, USA) using high purity hydrogen (99.9%) at a pressure of 20 atm. Three identical thermal cycling processes were
conducted to prepare the hydrided samples. For each thermal cycle, the samples were soaked at a temperature of 450 °C for 5 h, followed by furnace cooling with an approximate cooling rate of 2.2 °C min\(^{-1}\).

5.2.2 Microstructural Characterisation

The microstructures of hydrided Zr-4 samples were characterised using optical microscopy (OM), scanning electron microscopy (SEM), electron backscatter diffraction (EBSD) and TEM. For the OM and SEM observations, Zr-4 samples after hydriding were cut, mounted in epoxy and polished according to standard metallographic techniques. These samples were further etched with a solution consisting of 10 ml HF, 100 ml HNO\(_3\) and 100 ml distilled water for 30 s and then observed using a Leica DMRM OM under polarised light and by a JEOL JSM-6490LA SEM operated at 20 kV. The EBSD measurement of a hydrided plate sample was performed using a Zeiss Ultra Plus field emission gun SEM equipped with an Oxford/HKL system operating at 30 kV. Samples for EBSD analysis were prepared by mechanical grinding and further electropolishing applying an electrolyte consisting of 95% CH\(_3\)OH and 5% HClO\(_4\) at 30 V DC and at 25 °C. A detailed description of the preparation procedures for the EBSD samples is given in Appendix A. A step size of 0.25 μm was used for EBSD scans and the acquired EBSD data were processed with the software packages HKL Channel 5 and MTEX [92]. The interior grain structures of hydrided Zr-4 material were investigated using a high-resolution JEOL JEM-3000F TEM and thin foil samples
sectioned from the rolling-normal plane of a hydrided plate sample. The TEM thin foils were prepared by twin-jet electropolishing using a Struers TenuPol-5 electropolisher and an electrolyte containing 75% CH$_3$COOH and 25% HClO$_4$ at 25 °C.

5.2.3 Bulk Texture Measurements

The macroscopic texture of the virgin and hydrided samples was measured using neutron diffraction at a beam wavelength (\(\lambda\)) calibrated to be 2.414 Å on the high intensity powder diffractometer Wombat [85] at the Australian Nuclear Science and Technology Organisation. The tested samples were mounted on an Eulerian cradle and their corresponding diffraction images were recorded using a position sensitive area detector. For the complete pole figure measurements, samples were tilted (\(\chi = 0°-90°\)) and rotated (\(\phi = 0°-360°\)) in equal-distance steps, typically on a 15° × 5° grid in a three-dimensional orientation sphere. Each diffraction image was equally divided into three sections and a diffraction pattern was constructed from each section. Subsequently, the resultant diffractograms were analysed to extract pole figure data including the diffraction peak integral intensity and pole figure coordinates using the software package 2DiffCalc [91]. The generated pole figure data belonging to the same phase were used to determine the orientation distribution function (ODF) adopting the MTEX algorithm [92]. No sample symmetry was imposed to calculate the ODF in the present analysis.
5.2.4 Neutron Diffraction Patterns Analysis

The representative neutron diffractograms extracted from the texture measurements were also used for the line broadening analysis of the diffraction peak profile. The profile of all the accessible peaks from the observed phases was fitted using a Pseudo-Voigt function and the background was fitted assuming a linear shape. The peak parameters including the peak position, integral intensity and breadth were determined by this fitting. The instrumental effect on the line broadening was corrected to reveal the physical broadening of diffraction peaks through the measurement on a stress free and coarse-grained NIST standard LaB$_6$ powder sample. The inherent correlation of the defined physical broadening of peak profiles with the average coherent domain size ($D$) and mean microstrain ($\langle \varepsilon^2 \rangle^{1/2}$) of different phases in the sample can be described by the Scherrer and Wilson equation [130]

$$\frac{\beta_{hkl}^2}{\tan^2 \theta_{hkl}} = \frac{\mathcal{A}_{hkl}}{D_{hkl} \tan \theta_{hkl} \sin \theta_{hkl}} + 16\langle \varepsilon_{hkl}^2 \rangle$$  \hspace{1cm} (5.1)

where $2\theta_{hkl}$ is the peak position and $\beta_{hkl}$ is the integral breadth of the physical broadening peak profile, and $D_{hkl}$ and $\langle \varepsilon_{hkl}^2 \rangle^{1/2}$ denote the coherent domain size and mean lattice strain of the grains in the $\langle hkl \rangle$ crystallographic direction, respectively. By performing a linear least-square fit to the plot of $\beta_{hkl}^2/\tan^2 \theta_{hkl}$ vs $\mathcal{A}_{hkl}/(\tan \theta_{hkl} \sin \theta_{hkl})$ for all measured peaks of the same phase in the sample, the average coherent domain size and $D$ and microstrain $\langle \varepsilon^2 \rangle^{1/2}$ can be calculated from the slope and the intercept, respectively.

Additionally, the obtained neutron diffractograms of the hydrided samples were
also analysed using the Rietveld refinement technique implemented in the LANL code General Structure Analysis System (GSAS) [131] for the determination of hydride phase fractions.

**5.3 Results and Discussion**

**5.3.1 Phase Analysis**

Figs. 5.2a and b show the typical neutron diffraction patterns for the hydrided plate and bar samples, respectively. The diffraction peaks corresponding to the hexagonal close-packed (hcp) $\tilde{\text{H}}\text{Zr}$ (JCPDS Card No. 05-0665) and the fcc $\tilde{\text{H}}\text{ZrH}_{1.66}$ (JCPDS Card No. 34-0649) were generally identified in both hydrided samples (see the representatively indexed pattern in Fig. 5.2a). The presence of $\tilde{\text{H}}$-hydrides was unambiguously manifested by the detected $\tilde{\text{H}}$-hydride diffraction peaks with relatively low intensities, including the $\tilde{\text{H}}$(111), $\tilde{\text{H}}$(200) and $\tilde{\text{H}}$(311) peaks. No other hydride phases (such as $\gamma$-$\text{ZrH}$ and $\text{ZrH}_{2}$) were observed in this study. The diffractograms presented here are also used for the diffraction line profile analysis that will be described in Section 5.3.5. Further, the Rietveld refinement of the representative neutron diffraction patterns of the hydrided Zr-4 samples was performed to quantify the formed hydrides using GSAS [131]. This analysis approach is based on the proportional relationship between the weight fraction of a phase and the scale factor derived from the Rietveld analysis, which can be given by [9,132]:

$$W_p = S_p(ZMV)_p / \sum_i S_i(ZMV)_i$$  (5.2)
Figure 5.2 (a) The GSAS Rietveld refinements of typical neutron diffractograms acquired from the texture measurements of different hydrided samples: (a) hydrided plate and (b) hydrided bar. The diffraction peaks corresponding to $\delta$-Zr and $\delta$-hydride were representatively indexed in (a). Each graph shows the measured data points (+ symbols), the fitted line (continuous line through the measured data points) and their difference curve.
where $W_p$ is the relative weight fraction of phase $p$ in a multiphase system with $n$ phases, and $S$, $Z$, $M$, and $V$ are, respectively, the Rietveld scale factor, the number of formula units per cell, the mass of the formula unit (in atomic mass units) and the unit cell volume (in Å$^3$). Through this analysis the weight fractions of the $\delta$-$\text{ZrH}_{1.66}$ phase in the hydrided plate and bar materials are determined to be 10 wt.% and 14 wt.%, respectively; and the corresponding hydrogen contents can thus be estimated to be 1787 and 2500 wt. ppm.

### 5.3.2 Microstructure Observation

The typical microstructures of Zr-4 plate and bar materials subjected to hydrogen charging are presented in Figs. 5.3 and 5.4, respectively. Both hydrided samples exhibited characteristic microstructures with a large amount of platelet-like hydrides in the form of intergranular and intragranular precipitates embedded in the $\delta$-$\text{Zr}$ matrix. Specifically for the hydride plate, the polarised-light micrographs (Figs. 5.3a and b) taken from the ND-RD and RD-TD sections showed that hydride platelets tended to align close to the RD of the plate as the hydrides preferred to form with its longitudinal direction parallel to the direction of prior sample strain [50,54]. As apparently revealed in the plate RD-TD sectional microstructure with some relatively coarse platelets highlighted by black ellipses (Fig. 5.3b), the precipitated hydride platelets demonstrated different thickness. This discrepancy reflected from metallographic observations is the indication of the actual variation in the hydride platelet thickness and/or the different
spatial arrangement of hydrides. On the ND-TD section of the plate (Fig. 5.3c) and the cross-section of the bar (Fig. 5.4), the intergranular hydrides were predominantly precipitated and formed a continuous network along the grain boundaries. It is worth

**Figure 5.3** SEM and polarised-light micrographs of the hydrided Zr-4 plate observed on various sections: (a) ND-RD section; (b) RD-TD section; (c) ND-TD section. (d) is a high magnification image taken on the RD-TD section, demonstrating a clear evidence of hydrides being restricted within individual $\bar{\alpha}$Zr grains. The apparent transgranular hydride is indicated by a black arrowhead and some coarse hydrides are highlighted by black ellipses in (b). SEM images are taken under backscattered electron imaging mode. RD, TD and ND are the plate rolling, transverse and normal directions, respectively.
mentioning that, due to the intrinsic brittle nature of Ū-hydrides either at room temperature or high temperature as indicated by the extremely low fracture toughness (~1 MPa m$^{1/2}$ at 20 °C and ~3 MPa m$^{1/2}$ at 300 °C [133]), they may act as fracture initiators in the hydrided materials under the stress loading conditions. The microstructural configuration with the intergranular hydride network (Figs. 5.3c and 5.4) may cause the significant intergranular fracture under the application of stress and thus induce the serious degradation of the structural integrity or even the failure of the component. Besides, a common structural feature in two hydrided materials was that most intragranular hydrides were restricted within individual grains, with the exceptions of few interlinked hydrides (indicated by the black arrowhead in Fig. 5.3b) passing through the grain boundaries. Note that the interlinked hydrides were precipitated in the adjacent grains exhibiting the similar colour in the polarised-light micrograph (Fig. 5.3b) which implies the low misorientation. These results are consistent with the suggestion that grain boundary misorientation is an important factor governing the development of interlinked hydride configuration [134]. The microstructure observation on the RD-TD section at a higher magnification, as shown in Fig. 5.3d, further revealed the typical hydride features that the majority of intragranular hydrides were constrained in individual ŪZr grains and the transgranular hydrides were seldom appeared. Moreover, as obviously seen in Figs. 5.3c and 5.4b, the intergranular hydrides are normally thicker than the intragranular ones, as the grain boundaries are favourable sites for the hydride precipitation [40].
Figure 5.4 (a) Low and (b) high magnification SEM micrographs showing typical microstructures on the cross-section of hydrided Zr-4 bar. The micrographs are taken in secondary electron imaging mode.

The $\bar{\alpha}$-$\bar{Zr}$ and $\delta$-hydride phases present in the hydrided Zr-4 sample were also identified by indexing the Kikuchi patterns with the EBSD system, as shown in Fig. 5.5. An all Euler map taken from the RD-TD section of the hydrided Zr-4 is displayed in Fig. 5.6a, where $\bar{\alpha}$-$Zr$ grains are mapped with different colour code based on their crystal orientations represented by Euler angles whereas $\delta$-hydride grains are marked with black colour. The characteristic intergranular and intragranular hydrides were also observed, and the constrained growth feature of intragranular hydrides by the surrounding $\bar{\alpha}$-$Zr$ grain boundaries with large misorientation was confirmed. Moreover, the hydride crystallographic orientations with respect to the $\bar{\alpha}$-$Zr$ matrix are determined using poles figures calculated from the EBSD measurement. At all locations (Fig. 5.6a) the intergranular and intragranular $\bar{\delta}$-hydrides were found following the $\bar{\delta}(111)//\bar{\alpha}(0001)$ orientation relationship (OR) with the surrounding $\bar{\alpha}$-$Zr$ grains, as representatively
illustrated in Fig. 5.6b. This OR result is in line with the previous studies using TEM [47,135] and due to the statistically more sufficient observations of the EBSD map (Fig. 5.6a), it reliably reveals the common OR between Û-hydride and the matrix in hydried Zr-4 alloy. Fig. 5.6c shows the hydride orientation map which is coloured using the all Euler colouring scheme and superimposed on the band contrast (BC) map of ÛZr grains.

Most hydride platelets, including the longest one (denoted by the arrow A) observed in Fig. 5.6c which had the length of ~10 μm, exhibited the single orientation, and such

![Figure 5.5](image.png)

**Figure 5.5** Typical Kikuchi patterns recorded during the EBSD measurement on the hydried Zr-4 plate sample: (a) Kikuchi pattern of a matrix (left) indexed as ÛZr (right) and (b) Kikuchi pattern of a precipitate (left) indexed as ÛZrH_{1.66} (right).
orientation behaviour was also reported for the Ú-hydride platelets in Zr-2.5Nb alloy by the EBSD measurements [38]. Apart from the majority of hydride platelets with the single orientation, individual platelets having different orientations were occasionally observed. As indicated in Fig. 5.6c, a long hydride plate was found to have two short strings (marked by arrows e and f) demonstrating the clearly distinct orientation. According to the Euler angles of the hydride strings from the EBSD data, the misorientation angle between them was calculated to be ~60° with a rotation axis of <111> and, interestingly, these two hydride strings maintained the Ú(111)/Ú(0001) correlation with the surrounding Ú-Zr grains according to the stereographic projection analyses illustrated in Fig. 5.6d. The precipitation of hydride strings in the same Ú-Zr grains but with varied orientation, which is analogous to the formation of martensite variants in ferrous alloys, promotes the self-accommodation of strain arising from the large volume expansion of Ú-hydrides (17.2% [33]) relative to the Ú-Zr matrix. Our EBSD result (Figs. 5.6a and c) reveals that, in most cases, the intergranular and intragranular hydride platelets characterised by the single orientation in individual platelets were observed, as the dilatational strain associated with the formation of Ú-hydrides could be favourably accommodated by the grain boundary itself or by the elastic distortion/plastic deformation (i.e. the generation of misfit dislocations) in the involved Ú-Zr and Ú-hydrider grains [8,41,128]. In addition to the observed single orientation of most individual Ú-ZrH_{1.66} platelets, the BC map of Fig. 5.6e implies another interesting microstructural feature of the hydrided plate, i.e. the BC of Ú-hydrider
(reflected by the corresponding BC value) is generally weaker than that of ĢZr. It should be mentioned that the BC depends on the sample surface quality, the measurement conditions as well as microstructural characteristics (lattice distortion or dislocation density) [136]. As the hydride demonstrated commonly weaker BC compared with that of ĢZr in the same EBSD measurement (Fig. 5.6e), it is reasonable to derive that relatively high lattice distortion (strain or dislocation) may exist in the Ģ-hydride phase. Furthermore, Fig. 5.6f shows the distribution of the BC values along the white dashed line (BBÔ that crosses the region with ĢZr and Ģ-hydride (Fig. 5.6e). To exclude the subtle influence of grain orientation on BC, the distribution of the BC parameter in different phases was fairly compared within one ĢZr grain region (Fig. 5.6f). This comparison consistently suggested the generally stronger BC of ĢZr in comparison to that of Ģ-hydride. Also, the relatively low BC value was detected in a narrow ĢZr region (~0.25 μm) near the hydride/matrix interface.

Figure 5.6
Figure 5.6 EBSD results for the hydrided Zr-4 plate: (a) all Euler map in which the black coloured regions correspond to the $\delta$-ZrH$_{1.66}$ grains; (c) hydride orientation map coloured using the all Euler colouring scheme, superposed on the band contrast (BC)
map of Ũ-Zr grains; (b and d) stereographic projections of Ũ-ZrH\textsubscript{1.66} and Ũ-Zr grains illustrating the orientation relationship between Ũ-ZrH\textsubscript{1.66} and Ũ-Zr; (e) BC map of the matrix and Ũ-hydrides and (f) the distribution of BC value along the line BB\textsubscript{0} in (e) which crosses the region with Ũ-Zr and Ũ-hydride. The microstructure shown in (a) and (c) was reconstructed from the EBSD data by the HKL Channel 5 software, while the reconstruction of the microstructure in (e) was achieved using the MTEX algorithm [92].

Fig. 5.7a provides a bright-field TEM image recorded from the hydrided plate sample, showing an example of the subtle microscopic structure of a Ũ-hydride platelet with two developed branches. A selected-area electron diffraction (SAED) pattern taken from the hydride and matrix in Fig. 5.7a is presented in Fig. 5.7b, from which the OR between the hydride and the Ũ-Zr matrix can be identified as Ũ(111)/Ũ(0001) and Ũ(1\overline{1}0)/Ũ[\overline{1}2\overline{0}]. This hydride-matrix OR is in agreement with the finding from the present EBSD observations (Figs. 5.6b and d) and was also reported in previous studies on hydrided Zircaloy-2 [42,43,137] and Zr-2.5Nb [38] alloys. The prevalence of this crystallographic relation, as schematically shown in Fig. 5.8 [138], is essentially due to the preferred lattice matching of the involved (0001)Ũ-Zr and {111}Ũ-ZrH\textsubscript{1.66} atomic planes, which could contribute to minimising the strain energy for the Ũ-Zr (hcp) Ũ-ZrH\textsubscript{1.66} (fcc) phase transformation [33,39].
Figure 5.7 (a) A bright-field TEM image and (b) the corresponding composite SAED pattern showing the $\delta$-ZrH$_{1.66}$ platelets formed in the $\bar{\delta}$Zr matrix of the hydried plate. Note that some corrosion pits appear in the $\bar{\delta}$Zr matrix, as indicated by black arrowheads in (a), and they were probably generated in the twin-jet thinning process for the TEM sample preparation.

Figure 5.8 Schematic drawing showing the orientation relationship between $\bar{\delta}$Zr and $\bar{\delta}$ZrH$_{1.66}$ [138].
5.3.3 Texture Evaluation

In order to gain an insight into the characteristics and origin of the hydride texture, it is essential to perform the texture analysis on both the hydride precipitate and the matrix phases in different textured Zr-4 materials. Fig. 5.9a and 5.10a show the (0002) and (10\(\bar{1}\)0) \(\bar{U}\)Zr pole figures for the virgin Zr-4 plate and bar materials, respectively, and Fig. 5.9b and 5.10b display the (111) and (200) pole figures of \(\bar{U}\)ZrH\(_{1.66}\) formed in the corresponding two hydrided materials. Pole figures presented here were recalculated from the ODF determined using the software MTEX [92] and the original pole figure data obtained by neutron diffraction. For the \(\bar{U}\)Zr texture, a total of nine diffraction peaks of the \(\bar{U}\)Zr phase as detected in Fig. 5.2, including (10\(\bar{1}\)0), (0002), (10\(\bar{1}\)1), (10\(\bar{1}\)2), (11\(\bar{2}\)0), (10\(\bar{1}\)3), (20\(\bar{2}\)0), (11\(\bar{2}\)2) and (20\(\bar{2}\)1) were used for the determination of the ODF, whereas for the \(\bar{U}\)-hydride only the (111), (200) and (311) peaks could be used. The measured texture for both phases is expected to have high accuracy as 1512 different sample orientations were involved in the present full texture measurements. Table 5.2 summarises some quantitative details about the texture (pole figure maxima, ODF maxima and texture index). As clearly indicated by the pole figures in Figs. 5.9a and 5.10a, the initial plate and bar materials had the distinctly different crystallographic texture (especially the basal texture), which essentially resulted from their diverse thermomechanical treatments. For the virgin plate, the (0002) basal planes present the double pole maxima lying on the ND-TD plane of the plate at angles of around ±30° to the ND, and the prismatic (10\(\bar{1}\)0) planes show a strong pole along the RD (Fig. 5.9a) [9].
The $\bar{U}$Zr texture for the plate is similar to that observed in the cold-rolled zirconium sheet using the high-energy X-ray diffraction [139], and this reported result is in good agreement with the previous finding of Carr et al. [140] on the same material but measured by the time-of-flight neutron diffraction, indicating the reliability of our neutron texture measurements and data processing. In contrast to the plate material, the \{0002\} basal planes and the prismatic poles (i.e. the $<10\bar{1}0>$ crystal directions) of $\bar{U}$Zr grains in the starting bar material are dominantly aligned parallel to the ED of the bar (Fig. 5.10a), demonstrating the typical features of fiber texture. Besides the evident difference in the shape of $\bar{U}$Zr pole figures, the intensity of the $\bar{U}$Zr texture for the bar material is slightly weaker than that for the plate, as revealed by the parameters quantitatively describing the sharpness of the texture listed in Table 5.2 (for example the texture index for the bar material is 1.9 while for the plate 2.1).

For the measured texture of $\bar{U}$ZrH$_{1.66}$ phase in two hydrided materials, some relevant characteristics can be captured by current observations (Fig. 5.9b and 5.10b) and through the comparison with previous studies [63,126]. The $\bar{U}$-hydrides in hydrided samples both presented a weak texture, manifested by the relatively low values of texture parameters listed in Table 5.2. For example, the pole maximum is 1.7 multiples of the random distribution (m.r.d.) and texture index is 1.2 for the texture of $\bar{U}$-hydrides in the hydrided plate, slightly larger than the corresponding values for the texture of $\bar{U}$-hydrides of the hydrided bar (pole maximum 1.6 m.r.d. and texture index 1.1). Vicente Alvarez et al. [63] performed the texture analysis of a hydride blister in a
Zr-2.5Nb tube with an apparently shaper Û-Zr texture (texture index ~7) compared with that for two Zr-4 materials in this work, using synchrotron X-ray diffraction, which implied a weak Û-hydride texture with texture index of ~2.3. This result, together with the present findings of the Û-hydride texture (Figs. 5.9b and 5.10b), suggests that Û-hydrides precipitated in various zirconium alloys generally exhibited a weak texture with the intensity remarkably lower than that of the Û-Zr matrix. Based on Vicente Alvarez et al.’s suggestion [63], the marked decrease in the intensity of Û-hydride texture was related to the cubic symmetry of the Û-hydride phase and the existed OR between Û-Zr and Û-hydride, which involves different precipitation variants. Moreover, Santisteban et al. [126] reported the Û-hydride texture obtained from a warm-rolled Zr-4 plate containing only 180 wt. ppm of hydrogen by synchrotron X-ray diffraction, very similar to that measured from the hydrided plate in our experiment (Fig. 5.9b) with an approximate hydrogen content of 1787 wt. ppm. They also identified the weak texture characteristics of Û-hydrides with the pole maxima of 2.3 m.r.d. and texture index of 1.22. These observations regarding the Û-hydride texture from two Zr-4 plate materials referred above with the expected similar matrix texture revealed that the Û-hydride texture is basically independent of the hydrogen content, which was also verified by the previous investigation on a hydride blister in Zr-2.5Nb [63]. Further, the most interesting observation of the Û-hydride texture is that the (111) pole figure of Û-hydrides almost resembles the feature of (0002) Û-Zr pole figure for the corresponding virgin material in terms of the dominant shape and locations of local pole maxima (Figs.
5.9a, b and 5.10a, b). This pole figure result can be properly explained by considering the OR between the \( \delta \)-hydride and \( \tilde{\Upsilon} \)-Zr matrix as suggested by the EBSD and TEM measurements (Figs. 5.6b, d and 5.7b). Following the procedure described in Ref. [63,126], the theoretical (111) and (200) pole figures of \( \delta \)-hydrides in the hydrided plate and bar materials (as illustrated in Figs. 5.9c and 5.10c, respectively) were calculated from the \( \tilde{\Upsilon} \)-Zr ODF of the relevant virgin Zr-4, by applying the common orientation relation between \( \tilde{\Upsilon} \)-Zr and \( \delta \)-hydride reported in the present work, i.e. \( \tilde{\Upsilon}(111)//\tilde{\Upsilon}(0001) \) and \( \tilde{\Upsilon}(1\bar{1}0)//\tilde{\Upsilon}(1\bar{1}2\bar{0}) \). The \( \tilde{\Upsilon} \)-Zr ODF of the starting Zr-4, not shown here, was estimated from the pole figure data from the current neutron diffraction experiments using MTEX [92]. The measured and simulated \( \delta \)-hydride pole figures in two cases generally exhibited the good coincidence in the primary pole intensity and submaxima locations, as indicated in Figs. 5.9b, c and 5.10b, c. These findings suggest that the \( \delta \)-hydride commonly obeys the \( \tilde{\Upsilon}(111)//\tilde{\Upsilon}(0001) \) and \( \tilde{\Upsilon}(1\bar{1}0)//\tilde{\Upsilon}(1\bar{1}2\bar{0}) \) OR with the \( \tilde{\Upsilon} \)-Zr matrix of Zr-4 under the present hydriding conditions. Especially, the texture results in Figs. 5.10b and c prove that this OR is valid in the case of the hydrided bar material although the direct measurement of the OR for the hydride precipitation in this material is not performed in this work. Overall, the analysis aforementioned regarding the macroscopic texture for both phases reveals that (i) the \( \delta \)-hydride texture is predominantly determined by the texture of the \( \tilde{\Upsilon} \)-Zr matrix resulting from the inherent matrix/precipitate OR observed, but its intensity is normally very weak relative to that of the \( \tilde{\Upsilon} \)-Zr matrix texture; and (ii) the \( \tilde{\Upsilon} \)-Zr\( _{1.66} \) phase, precipitated in the present
hydriding conditions without imposing the external stress on the samples, generally follows the $\tilde{\alpha}(111)///\tilde{\alpha}(0001)$ and $\tilde{\alpha}[1\bar{1}0]///\tilde{\alpha}[1\bar{1}20]$ OR with the $\tilde{\alpha}$-Zr matrix of Zr-4.

Figure 5.9 Experimental pole figures of different phases determined by neutron diffraction: (a) $\tilde{\alpha}$-Zr phase of the virgin Zr-4 plate [9]; (b) $\tilde{\alpha}$-hydride phase precipitated in the plate. (c) Predicted pole figures of the $\tilde{\alpha}$-hydrides formed in the plate, obtained by applying the $\tilde{\alpha}(111)///\tilde{\alpha}(0001)$ and $\tilde{\alpha}[1\bar{1}0]///\tilde{\alpha}[1\bar{1}20]$ orientation relationship to the ODF
of the $\tilde{\UZr}$ phase in the plate. The plate rolling direction (RD) and transverse direction (TD) are indicated, the normal direction (ND) is in the centre.

**Figure 5.10** Pole figures of different phases determined by neutron diffraction: (a) $\tilde{\UZr}$ phase of the virgin Zr-4 bar; (b) $\tilde{\u}$-hydride phase precipitated in the bar. (c) Predicted pole figures of the $\tilde{\u}$-hydrides formed in the bar, obtained from the experimental ODF of the $\tilde{\UZr}$ phase in the extruded bar and the $\tilde{\u}(111)/\tilde{\U}(0001)$ and $\tilde{\u}[1\bar{1}0]/\tilde{\U}[1\bar{1}0]$
orientation relationship. The extrusion direction (ED) and tangential direction (TD) of the bar material are indicated, the radial direction is in the centre.

Table 5.2 Quantitative information for the measured texture of different phases in the virgin and hydrided Zr-4 plate and bar materials.

<table>
<thead>
<tr>
<th>Phases</th>
<th>Pole figure Max (m.r.d.)</th>
<th>ODF Max (m.r.d.)</th>
<th>Texture index</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ū-Zr in the virgin plate</td>
<td>4.5</td>
<td>5.1</td>
<td>2.1</td>
</tr>
<tr>
<td>Ū-ZrH_{1.66} in the hydrided plate</td>
<td>1.7</td>
<td>2.2</td>
<td>1.2</td>
</tr>
<tr>
<td>Ū-Zr in the virgin bar</td>
<td>3.5</td>
<td>3.8</td>
<td>1.9</td>
</tr>
<tr>
<td>Ū-ZrH_{1.66} in the hydrided bar</td>
<td>1.6</td>
<td>2.1</td>
<td>1.1</td>
</tr>
</tbody>
</table>

5.3.4 Local Misorientation Distribution

Fig. 5.11a displays a local misorientation map of the hydrided Zr-4 plate sample. This local misorientation map is constructed using the kernel average misorientation approach implemented in HKL Channel 5, in which each pixel in the map is coloured as a function of the average misorientation between the given pixel and all of its neighbors. The misorientation greater than 5°, which might be generated at the neighbouring grain [141], is excluded for this map construction. Combined with the corresponding EBSD phase map (Fig. 5.6a), it is obvious that the hydrides generally exhibited a higher misorientation, and the specific intragranular misorientation profiles for Ū-Zr and Ū-hydride shown in Fig. 5.11b also verified this point. The larger misorientation developed in hydrides is probably attributed to the accumulation of considerable plastic
strain and the attendant generation of misfit dislocations in hydrides [38,60], which could effectively accommodate the substantial dilatational misfit strain associated with the $\tilde{\alpha}$-Zr (hcp) $\rightarrow$ $\tilde{\delta}$-ZrH$_{1.66}$ (fcc) transformation.

Figure 5.11 (a) Local misorientation map of the hydrided Zr-4 plate and (b) the average intragranular misorientation distribution in the $\tilde{\alpha}$-Zr matrix and $\tilde{\delta}$-hydride phases.
5.3.5 Dislocation Density Estimation

The observed general characteristics of hydrides in terms of low BC (Fig. 5.6e) and high intragranular misorientation (Fig. 5.11) are rationalised by the neutron diffraction line profile analysis on the hydrided Zr-4 materials described in this section that attempt to quantify the dislocation densities in both Ũ-hydride and Ū-Zr matrix phases. Table 5.3 summarises the quantitative microstructural parameters of different phases in the hydrided materials (plate and bar) obtained from the line profile analysis on the measured neutron diffractograms displayed in Fig. 5.2. Results show that, for both hydrided materials, the average coherent domain size \(D\) of Ũ-hydride (~20 nm) is much smaller than that of Ū-Zr (~80 nm). For the diffraction peak profile analysis, the determined coherent domain size corresponds to subgrains and dislocation cells [142]. The fine hydride platelets with thickness of ~50 nm as seen in Fig. 5.7a are obviously responsible for the low \(D\) value of the hydride. In contrast, the calculated mean lattice microstrain \(\langle \varepsilon^2 \rangle^{1/2}\) of the Ũ-hydride is significantly larger than that of the Ū-Zr matrix of hydrided materials, possessing the value approximately 2.6–4.4 times that of Ū-Zr (Table 5.3). The average dislocation density \(\rho\) in different phases of the hydrided materials, which correlates with the determined average coherent domain size and mean microstrain can be estimated via the relationship [143-145]:

\[
\rho = \frac{2\sqrt{3}\langle \varepsilon^2 \rangle^{1/2}}{Db}
\]

(5.3)

where \(b\) is the magnitude of the Burgers vector of the dislocations \((b = 0.3378\) nm for Ũ-hydride and \(b = 0.5147\) nm for Ū-Zr). The calculated \(\rho\) of Ũ-hydride and Ū-Zr phases in
hydrided materials is also listed in Table 5.3. In the case of the hydrided plate, it is found that the calculated $\rho$ in $\bar{\eta}$-hydride ($15 \times 10^{14} \text{m}^{-2}$) is around an order of magnitude higher than that in $\bar{\eta}$Zr ($0.44 \times 10^{14} \text{m}^{-2}$), and similar situation is also observed for the hydrided bar material with the average dislocation densities in the $\bar{\eta}$-hydride and $\bar{\eta}$Zr phases estimated to be $11.6 \times 10^{14} \text{m}^{-2}$ and $0.96 \times 10^{14} \text{m}^{-2}$, respectively. Note that the value of the average dislocation density evaluated from the neutron diffraction line profile analysis is usually only semiquantitative. However, the comparison between the dislocation densities of the $\bar{\eta}$-hydride and $\bar{\eta}$Zr phases in the same hydrided material is valid as they are measured and analysed in a consistent way [146].

Table 5.3 Microstructural parameters of the hydrided Zr-4 plate and bar samples determined by the neutron diffraction line profile analysis.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Phases</th>
<th>$\bar{\eta}$-Zr in the hydride plate</th>
<th>$\bar{\eta}$ZrH$_{1.66}$ in the hydrided plate</th>
<th>$\bar{\eta}$-Zr in the hydrided bar</th>
<th>$\bar{\eta}$ZrH$_{1.66}$ in the hydrided bar</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D$ (nm)</td>
<td></td>
<td>88</td>
<td>17</td>
<td>61</td>
<td>21</td>
</tr>
<tr>
<td>$\langle \varepsilon^2 \rangle^{1/2}$ (%)</td>
<td></td>
<td>0.057</td>
<td>0.25</td>
<td>0.087</td>
<td>0.23</td>
</tr>
<tr>
<td>$\rho$ ($10^{14}$ m$^{-2}$)</td>
<td></td>
<td>0.44</td>
<td>15</td>
<td>0.96</td>
<td>11.6</td>
</tr>
</tbody>
</table>

A complementary high-resolution TEM (HRTEM) analysis on the hydrided Zr-4 plate sample was further conducted to reveal the local distribution of dislocations in the $\bar{\eta}$-hydride and $\bar{\eta}$Zr phases. A typical Fourier-filtered HRTEM image from a hydride platelet in the hydrided plate sample is provided in Fig. 5.12a, showing a significant
accumulation of dislocations. By contrast, the examples of the $\bar{\text{U}}$Zr grains in the hydrided plate containing only a few dislocations are shown in Figs. 5.12b and c. The rough imaging locations of the original HRTEM images of Figs. 5.12a, b and c are marked in Fig. 5.7a with (1), (2) and (3), respectively. Fig. 5.12d illustrates the indexed electron diffraction patterns acquired from the Fourier transformation of the corresponding HRTEM images, affirming that the analysed region of HRTEM corresponded to the single constitution phase ($\bar{\text{U}}$ZrH$_{1.66}$ or $\bar{\text{U}}$Zr). As representatively demonstrated in Figs. 5.12a-c, extensive HRTEM investigations in a large area of the hydrided plate sample suggested that the dislocation density in the hydride grains is predominantly higher than that in the $\bar{\text{U}}$Zr grains. Also, no twinning or stacking fault is found in the $\bar{\text{U}}$-hydride and $\bar{\text{U}}$Zr grains, which is probably related to the high stacking fault energy of the material at room temperature. The combination of these observations and the neutron diffraction line profile analysis provided the solid evidence to support that the misfit strains accompanied with the hydride transformation are dominantly accommodated by the generation of a significant amount of dislocations inside the hydrides, contributing to the development of large misorientation in hydrides (Fig. 5.11).

It is thus reasonable to deduce that, besides the intrinsic brittle characteristics of hydrides, the pileup of dislocations in hydrides may be another important factor leading to their negligible plasticity at room temperature [8,107,133,147]. In addition, a comparison of the HRTEM images of Figs. 5.12b and c taken from $\bar{\text{U}}$-Zr grains close to and far away from the $\bar{\text{U}}$-Zr/$\bar{\text{U}}$-hydride interface, respectively, implies that more
Figure 5.12 Typical Fourier-filtered high-resolution TEM (HRTEM) images of the hydrided plate sample showing the local dislocation distribution in the (a) δ-hydride grain; (b) δ-Zr grain far way from the δ/δ interface; (c) δ-Zr grain near the δ/δ interface. Dislocation cores are indicated using "T". Note that the approximate imaging locations of the original HRTEM images of (a), (b) and (c) are marked in Fig. 5.7a, by (1), (2) and (3), respectively. (d) shows three Fourier transformed electron diffraction patterns I, II and III, obtained from the corresponding HRTEM images of (a), (b) and (c), respectively.
dislocations tend to be generated in the matrix near the $\overline{\Gamma}\overline{\Gamma}$ interface compared with that far away from the interface, which was a common phenomenon as noted in detailed HRTEM observations. This finding explains the detected weak BC for the $\overline{\Gamma}$-Zr grain region in the vicinity of hydrides in the EBSD measurement (Fig. 5.6f). Moreover, consistent with Bai et al.'s suggestion [60], this observation indicates the occurrence of the local plastic deformation of the matrix due to the volume dilatation induced by the hydride, which was recognised as another means (besides the generation of misfit dislocations in hydrides) for the accommodation of misfit strains associated with the hydride precipitation in Zr-4.

5.4 Conclusions

The microstructure characteristics and crystallographic texture of various hydrided Zr-4 materials (hot-rolled and annealed plate, and hot-extruded and annealed round bar) containing high concentrations of hydrogen ($\sim$2000 wt. ppm) were investigated in detail by neutron diffraction and microscopy. Both intragranular and intergranular platelet-like precipitates (identified as $\overline{\Gamma}$-ZrH$_{1.66}$) were observed. Most intragranular hydrides were restricted within individual $\overline{\Gamma}$-Zr grains, and the intergranular ones tended to form a continuous network along grain boundaries in the present high hydrogen content condition. This study successfully determined the bulk texture of $\overline{\Gamma}$-hydrides by neutron diffraction, advancing the use of neutron diffraction for the investigation of the hydride-forming materials with high hydrogen contents. The results showed that
δ-hydrides generally presented a weak texture that was dependent on that of the Ū-Zr matrix. This dependence essentially originated from the existed common Ū(111)//Ū(0001) and Ū[110]/Ū[1120] OR between the Ū-Zr matrix and Ū-hydride as revealed in the present TEM and EBSD measurements. The neutron diffraction line profile analysis in conjunction with the HRTEM observations on the hydrided samples presented the solid evidence that the dislocation density in the hydride was notably higher than that in the Ū-Zr matrix phase. The average dislocation density in the hydride was evaluated to be around one order of magnitude higher than that in the matrix. The HRTEM investigations also demonstrated that more dislocations were normally generated in the Ū-Zr matrix near the Ūū interface compared with that far away from the interface, indicating the local plastic deformation of the matrix. The generation of significant amount of misfit dislocations in hydrides as well as the local plastic deformation in the matrix is considered as the consequence induced by the accommodation of the large misfit strains associated with the hydride precipitation in the Zr-4 matrix.
Chapter 6

Hydride Distribution and Macroscopic Orientation in Zircaloy-4

6.1 Introduction

As demonstrated in the previous investigations [39,49,51] and our present work in Chapters 4 and 5, the hydride precipitation in Zircaloy-4 (Zr-4) could be typically revealed using various techniques such as X-ray diffraction (XRD), optical or electron microscopy and electron backscatter diffraction (EBSD). Sufficient information in terms of the phase, morphology and size of hydrides, and the orientation relationship (OR) between the hydride and matrix phases can be derived from these studies. For example, the thin platelet morphology of δ-hydride (ZrH\textsubscript{1.66}), the most common hydride phase in practical reactor conditions [41], has been directly observed through the destruction metallographic examination using optical or scanning electron microscopy (SEM). Nevertheless, due to the restricted areas of detection, the hydride distribution on the macroscopic or spatial scales cannot be well examined by the approaches above. Neutron tomography, as a non-destructive tool for materials testing, enables the inspection of bulk samples containing low-atomic-number elements (especially hydrogen) beneath the matrixes. This technique has been used to investigate the formation of hydride blisters [99] and hydrogen concentration [148-150] in zirconium alloys. The characterisation using neutron tomography and other metallographic detection methods could essentially provide an overall description of the spatial
distribution and microstructural features of hydrides. The clarification of the hydride
distribution in zirconium alloys is of great significance as this distribution feature could
strongly influence the material performance (especially the ductility). Besides the
hydride distribution, the hydride macroscopic orientation also has an important impact
on the material behaviour. The significant degradation of the ductility in zirconium
alloys occurs when the precipitated hydride platelets are oriented normal to the loading
stress [69]. The main factors reported to affect the orientation of hydride platelets in
zirconium alloys are the crystallographic texture of the matrix, prior deformation and
applied stress [36,58]. For example, upon the application of a sufficiently high stress
during hydriding, the hydride platelets tend to precipitate perpendicular to the tensile
stress direction or parallel to the compressive stress direction [36,51,126]. Most of
previous investigations concerning the hydride orientation in zirconium alloys focused
on the reorientation of hydrides due to the application of the stress during hydriding,
while less attention has been given to evaluate the influence of the prior deformation on
the hydride orientation. In particular, there is a lack of understanding on the
crystallographic features for the hydrides with different orientations (e.g. the preferred
hydride-matrix OR) that were potentially induced by the prior deformation. Further
work is required to improve the understanding on the possible changes in the hydride
orientation behaviour caused by the prior deformation in zirconium alloys.

In the current chapter, the hydride distribution features in bent and unbent Zr-4
plate samples subjected to gaseous hydrogen charging were investigated using neutron
tomography combined with the conventional approaches of SEM and XRD. In addition, the effects of the prior bending deformation on the hydride orientation and the hydride-matrix crystallographic orientation relation in the bent sample were analysed.

6.2 Experimental Procedures

6.2.1 Sample Preparation

Two kinds of samples with different geometries were produced from hot-rolled and annealed Zr-4 plate material with a chemical composition of Zr$_{98.11}$Sn$_{1.56}$Fe$_{0.22}$Cr$_{0.11}$O$_{0.14}$ (wt.%). In consistence with the expressions in Chapter 5, the rolling, transverse and normal directions of the plate are abbreviated as RD, TD and ND, respectively. One type of samples had irregular shapes and a maximum length of ~12 mm along the plate RD, while another type consisted of thin plates with the thickness of ~1.8 mm along the TD. The prepared thin plates were further bent using the equipment schematically illustrated in Fig. 6.1. The pre-strain ($\hat{\epsilon}$) generated in the bent plate samples was estimated to be ~8%, following the relationship [151]: $\hat{\epsilon} = [2(R_1/h) + 1]^{\frac{1}{2}}$, where h is the sample thickness and $R_1$ is the radius of curvature of the bent sample. Note that the appreciable local plastic deformation was observed on the surface region of the bent sample where the bending force was imposed during the bending deformation (Fig. 6.1). The produced bent and unbent samples were first immersed in an acid solution of 10 ml HF, 45 ml HNO$_3$ and 10 ml distilled water for 2 min to remove the native oxide layer present on the surface, and then gaseously hydrided in a Sieverts apparatus (Advanced
Materials Corporation, USA) using high purity hydrogen (99.9%) at pressures of 10 and 20 atm, respectively. Three identical thermal cycling processes were implemented to prepare the hydrided samples. For each thermal cycle, the samples were soaked at a temperature of 450 °C for 5 h, and then furnace cooled to room temperature with a cooling rate of ~2.2 °C min⁻¹. The prepared hydrided samples with and without the prior bending deformation will be denoted as hydrided bent and unbent plate samples, respectively, hereinafter in this chapter.

![Figure 6.1 Schematic illustration of the equipment used for the preparation of the Zr-4 bent plate sample [151]. The length, thickness and width directions of the plate sample to be bent correspond to the RD, TD and ND, respectively.](image)

6.2.2 Characterisation

The neutron tomography investigations on the hydrided samples were conducted at the ICON beamline (SINQ, PSI Villigen, Switzerland) using the micro-tomography
setup [98]. The sample stage used for this experiment consists of a motorized positioning system and a turn-table allowing the tomographic imaging in the range of 360°. A detector system based on a combination of a scintillator screen and a CCD-camera was applied to acquire the images for tomography. The ultrasonic cleaning of the hydrided samples was performed before the neutron tomography experiments to remove the potential contamination on the sample surface. During the tomographic imaging, the sample was rotated about its axis at a given angular step of 0.3° and radiographic projections were taken for each rotation step. These radiographs were then reconstructed to obtain the three-dimensional (3D) tomographic images of the sample using the reconstruction software MuhRec2 [152] and the visualisation tool VGStudio MAX 2.1 package.

Samples for metallographic examinations were cut, mounted in epoxy casts, and then mechanically polished to 1200 grit silicon carbide paper, followed by chemical etching using a solution consisting of 10 ml HF, 100 ml HNO₃ and 100 ml distilled water for 30 s. Microstructures of hydrided samples were characterised using a JEOL JSM-6490LA SEM and a Zeiss Ultra Plus field emission gun SEM. The EBSD measurements were conducted using an Oxford/HKL system, installed on the Zeiss Ultra Plus field emission gun SEM. Experimental details of the sample preparation for EBSD examination are presented in Appendix A. EBSD scans were obtained at a step size of 0.5 μm. The acquired EBSD data were processed with the HKL Channel 5 and MTEX [92] software packages. The Vickers microhardness of hydrided samples was
determined using a LECO M-400-H1 microhardness tester with a 0.3 kg load. The phase identification was performed using a GBC MMA X-ray diffractometer with Cu K\(\alpha\) radiation (\(\lambda = 0.15418\) nm) at 28.6 mA and 35 kV.

6.3 Results and Discussion

6.3.1 Hydride Distribution Observation

Fig. 6.2 presents the characteristic microstructure obtained on the RD-TD section of the hydrided unbent plate sample. The distribution of hydride platelets was relatively homogeneous on this section. In addition, the hydride distribution near the surface region of the hydrided unbent plate sample was examined along its ND-TD section. As revealed in Fig. 6.3, the hydride concentration in this near-surface region was significantly higher than that observed on the RD-TD section (Fig. 6.2). More interestingly, the local inhomogeneous hydride distribution and attendant hydride concentration gradient along the thickness direction (ND) were detected in Fig. 6.3a.

![Figure 6.2](image.png)

**Figure 6.2** Typical SEM micrograph of the hydrided unbent plate taken on the RD-TD section.
Three regions with apparently different microstructural features can be clearly observed in Figs. 6.3b-d, i.e. Region (I): near the sample surface, hydrides locally concentrate and form the almost dense hydride layer (Fig. 6.3b); Region (II): below the dense hydride layer, the hydride volume fraction decreases progressively (Fig. 6.3c) and Region (III): far away from the surface, less-concentrated hydrides exhibiting a relatively uniform distribution in the Zr-4 matrix (Fig. 6.3d). It is well known that a nearly dense hydride layer (called hydride rim) usually appears near the outer surface of the zirconium alloy cladding materials in the reactor service conditions, mainly owing to the radial temperature gradient present during the operation [4,153]. This hydride layer was also observed in the previous studies [27,153,154] and the current work (Fig. 6.3a) under the artificial gaseous hydriding conditions. However, in the current hydriding conditions (soaked at 450 °C for 5 h in each thermal cycle), no significant temperature gradient could be present in the hydrided sample, given the fact that the sample size is in the order of millimeters. On the other hand, it is speculated that hydrides will first form at the surface region naturally because the solid solubility limit of hydrogen (i.e. the hydrogen saturation) will be reached there first. In addition, it is considered that the hydrogen concentration gradient plays a key role in affecting the diffusion of hydrogen and as a result, the effective hydrogen diffusion coefficient in the highly hydrided zone should be smaller than that in the region with lower hydride density, resulting in a blocking effect for hydrogen ingress into the bulk of the sample and the attendant preferential hydride accumulation near the surface.
Figure 6.3 SEM images taken near the surface of the hydrided unbent plate: (a) a low-magnification image showing the local inhomogeneous hydride distribution; (b-d) enlarged micrographs corresponding to three regions (I-III) marked in (a), respectively. All micrographs are taken on the ND-TD section of the hydrided sample.

Fig. 6.4 further depicts the microhardness profile measured along the thickness direction (ND) on the ND-TD section of the hydrided unbent plate. This reveals, in conjunction with the SEM studies on microstructural features of the indentation morphology and hydride distribution at the various positions (insets in Fig. 6.4), that there is a strong correlation between the microhardness and hydride volume fraction. At the position (~938 μm from the surface) with low hydride content, the microhardness of
205 HV_{0.3} was measured, whereas the highly concentrated hydrides near the sample surface (at a distance of ~150 μm from the surface) resulted in the microhardness as high as 297 HV_{0.3}. As indicated by the microstructures of indentations (insets in Fig. 6.4), the accumulated hydrides enhanced the resistance to the local plastic deformation, thereby leading to the elevation of the microhardness.

Figure 6.4 Vickers microhardness of the hydrided plate sample as a function of the distance from the sample surface along the thickness direction (normal direction). The insets are SEM micrographs showing the corresponding microstructures and indentation morphologies at various locations.

Fig. 6.5 shows a view of the reconstructed 3D volume and various tomographic slices of the hydrided unbent plate sample. Since hydrogen has a much higher neutron attenuation coefficient than that of zirconium [99], the areas of higher attenuation
shown as lighter gray in the reconstructed grayscale images indicate the presence of hydrides. The existence of an inhomogeneous spatial distribution of hydrides could be clearly identified from these tomographic images (Fig. 6.5). Thin hydride layers were directly observed on the sample surfaces, which further verified the fact that some hydride layers appeared on the surface as previously implied by the sectional microstructural examination (Fig. 6.3a). Besides the "surface effect" detected, it appears to be another "edge effect" for the hydride formation. Specifically, the concentrated hydrides precipitated at the edges (Figs. 6.5b and c) and the sharp corner (Fig. 6.5d) of the sample. It is considered that the likely occurrence of 3D diffusion of hydrogen at sample edges (two adjacent free surfaces) and the corner (three or more adjacent free surfaces) enhanced the hydrogen ingress into the sample and subsequently facilitated the formation of concentrated hydrides at these regions (Figs. 6.5b-d).

The hydride distribution in the hydrided bent plate was also inspected using neutron tomography, and the acquired tomographic images are shown in Fig. 6.6. This 3D reconstruction result reveals a concentrated hydride layer located at only one side of the bent plate sample (marked by arrowheads in the left image in Fig. 6.6). To ensure this observation was real and not an artifact of the 3D reconstruction, the phase analysis of the hydrided bent sample was carried out. As indicated by the dashed rectangular boxes in the right image in Fig. 6.6, the hydrided bent plate sample was cut into three pieces (marked as plate piece A₁, A₂ and A₃, as shown in Fig. 6.6) to facilitate the phase detection on different regions of the sample using XRD. It should be mentioned that,
Figure 6.5 (a) A neutron tomographic reconstruction of the hydrided unbent plate sample. The coordinate systems for the real sample (RD-TD-ND) and the slicing of the reconstructed volume (X-Y-Z) are both marked. (b) XY slice; (c) XY slice and (d) YZ slice images showing the non-uniform hydride distribution in the sample.

for the XRD measurement of the plate piece A1, the sample was orientated such that the X-ray beam was incident on the surface with the presence of the hydride layer as identified by neutron tomography (Fig. 6.6). Typical XRD patterns of two plate pieces (A1 and A2) sectioned from two sides of the bent plate are depicted in Fig. 6.7. For the plate sample A1, the strong diffraction peaks corresponding to hexagonal close-packed (hcp) Ú-Zr (JCPDS Card No. 05-0665) and face-centered cubic (fcc) Ú-ZrH1.66 (JCPDS Card No. 34-0649) were identified (Fig. 6.7a). In contrast, only the diffraction peaks of
\( ^{\text{\textsuperscript{\textit{U}}}Zr \text{ were detected in the plate piece A}}_2 \text{(Fig. 6.7c). Moreover, according to the XRD semi-quantitative evaluation approach described in Appendix B, the average } ^{\text{\textsuperscript{\textit{U}}}\text{hydride volume fraction in the diffracted region of the plate sample A}}_1 \text{ was estimated to reach a high level of 22\%. These XRD analysis results are consistent with the findings by neutron tomography (Fig. 6.6), suggesting that a significant hydride accumulation was only present in the plate piece A}_1, \text{ at least on its surface region considering the limited penetration depth of the laboratory X-ray Cu K}_{\text{\textsuperscript{\textit{U}}}\text{radiation in the hydrided Zr-4 samples (~10 \mu m [155])}}. \text{ Further, the measured surface of the plate A}_1 \text{ was ground to remove a layer with a thickness of ~15 \mu m, and the resultant sample was further tested by XRD. Interestingly, only the } ^{\text{\textsuperscript{\textit{U}}}Zr \text{ peaks while no hydride peaks were detected in the corresponding diffraction pattern shown in Fig. 6.7b. The XRD results reported above}}

**Figure 6.6** Views of the reconstructed 3D volume of the hydrided bent sample obtained by neutron tomography. The dashed rectangular boxes in the right image indicate the sectioning of the samples for the subsequent XRD measurements (Fig. 6.7).
confirmed that the concentrated hydrides appeared on the surface of the plate A1. At this stage, it is reasonable to conclude that a concentrated thin hydride layer was present on the surface of the plate piece A1, based on the consistent XRD and neutron tomography experimental results (Figs. 6.6 and 6.7). It was noted that the concentrated hydride region appeared in the hydrided plate A1 corresponds to the marked plastic deformation area created due to the application of the bending force during the preparation of the bent sample, as previously stated in Section 6.2.1. Wang et al. [46,156] suggested that the occurrence of the significant plastic deformation promoted the hydrogen ingress and the subsequent hydride precipitation in Zr-4, as the attendant microstructural defects in the plastic deformation could act as hydrogen traps and provide favourable nucleation sites for hydrides. It is thus considered that the inhomogeneous hydride distribution on the surface of the hydrided bent sample (Fig. 6.6) is related to the occurrence of the localised plastic deformation existed in the sample, contributing to the formation of the concentrated hydride layer in the hydrided plate piece A1. Unlike the observations of the apparent concentrated hydride layers on the surfaces of the hydrided unbent plate sample at a hydrogen pressure of 20 atm and of the hydrided plate piece A1, no appreciable hydride precipitation/accumulation was observed on the surface of the hydrided plate A2, as indicated by the neutron tomography and XRD results (Figs. 6.6 and 6.7c). This is probably attributed to the facts that no prominent plastic deformation was occurred in this sample and a relatively low hydrogen pressure of 10 atm was used for hydriding. In this situation, limited hydrogen ingress and hydride precipitation in
this sample is expected (i.e. the surface effect is weak for this case). Fig. 6.8 illustrates the microstructure on the longitudinal-section of the plate piece A₂, and it reveals that only a small amount of hydride platelets (representatively marked with arrowheads) were precipitated. The hydride volume fraction in the sample A₂ is believed to be below the detection limit of the present XRD measurement, leading to the absence of the hydride peaks in the observed diffraction pattern (Fig. 6.7c).

Figure 6.7 XRD patterns of the plate pieces A₁ and A₂ sectioned from the hydrided bent plate sample as indicated in Fig. 6.6: plate piece A₁ (a) before and (b) after surface grinding; (c) plate piece A₂.
Figure 6.8 SEM micrograph showing the typical microstructure on the longitudinal-section of the plate piece A₂ sectioned from the hydrided bent sample as indicated in Fig. 6.6.

6.3.2 Hydride Orientation Analysis

For the hydrided Zr-4 plate without the prior bending deformation before hydriding (i.e. the hydrided unbent plate), as shown in Fig. 6.2, the precipitated hydride platelets normally tended to align along the RD direction in the RD-TD plane, in line with the observations in Figs. 5.3b and d (see Chapter 5). However, for the hydrided bent plate, extensive metallographic investigations reveal that the formed hydride platelets exhibited the varied orientations along the thickness direction (TD) at the part of the sample with the evident prior bending deformation (i.e. the plate piece A₃ indicated in Fig. 6.6). In this section, the microstructural observations in three different regions (termed as top, middle and bottom regions as indicated in Fig. 6.9) of the plate piece A₃, which represent the typical hydride orientation changes in this sample, will be presented and discussed.
Figure 6.9 A low-magnification view of the longitudinal-section for the plate piece A₃ sectioned from the hydrided bent plate sample, showing the approximate regions of the microstructural characterisation.

Fig. 6.10 shows the typical SEM micrographs taken from the top, middle and bottom regions of the plate piece A₃ (as illustrated in Fig. 6.9). The hydride platelets were found to exhibit the different orientations in various areas, which can be described specifically in the following:

(i) in the top region (Fig. 6.10a), most hydride platelets were oriented roughly along the RD of the initial plate (i.e. the direction of the prior tensile strain as expected in this region);

(ii) in the middle region (Fig. 6.10b), the random hydride orientation was observed;

(iii) in the bottom region (Fig. 6.10c), the hydrides tended to align close to the TD (i.e. the direction of the prior compressive strain).

Compared with the hydride orientation on the RD-TD plane of the hydrided unbent plate (Fig. 6.2), one can find that the prior bending deformation on this sample caused
the subsequent precipitation of hydride platelets to align parallel to the direction that the Zr-4 flowed during deformation. The identical effect of the prior deformation on the hydride orientation was recognised by many studies on various zirconium alloys [52-55], but unfortunately little explanation for this phenomenon was given in these investigations.

![Figure 6.10 SEM images showing the variation of the hydride orientation in different regions of the plate piece A3 as indicated in Fig. 6.9: (a) top region; (b) middle region; and (c) bottom region. The gray dots appeared in the micrographs are regarded as hydrides that are oriented perpendicular to the RD-TD plane.](image-url)
Due to the strong influence of the hydride orientation on the mechanical properties of hydrided zirconium alloys \[69\], it is of great significance to perform the crystallographic analysis on the precipitated hydrides with different orientations, which may assist in understanding this prior strain-induced hydride orientation behaviour. By means of the EBSD technique, the crystallographic measurements were conducted on the illustrated three regions in Fig. 6.9 of the plate A3. The obtained EBSD phase maps corresponding to the top, middle and bottom regions of the bent plate piece A3 (Fig. 6.9) are shown in Figs. 6.11a-c, respectively. The indexing of the Kikuchi patterns recorded during the measurements reveals the phase composition of $\delta$ZrH$_{1.66}$ and $\alpha$Zr in this sample. Further, the crystallographic OR of the $\delta$-hydride precipitate (the red grain in Fig. 6.11) with the surrounding $\delta$Zr matrix in various regions was analysed using the stereographic projection method \[42\]. As representatively illustrated in Fig. 6.12a, the hydrides and the matrix followed the $\delta$$(111)/\alpha(0001)$ OR at all locations of the top region of the bent plate piece. In the middle region, apart from the prevailing $\delta$$(111)/\alpha(0001)$ OR (Fig. 6.12b), another two important orientation correlations of $\delta$$(111)/\alpha(10\bar{1}0)$ (Fig. 6.12c) and $\delta$$(111)/\alpha(10\bar{1}1)$ (Fig. 6.12d) were also observed. By contrast, as typically depicted in Fig. 6.12e, the primary OR in the bottom region was $\delta$$(111)/\alpha(10\bar{1}0)$, and the secondary OR in this region was identified as $\delta$$(111)/\alpha(10\bar{1}1)$ (Fig. 6.12e). These results, which were derived from the extensive analysis of the precipitated hydrides observed in the EBSD maps (Fig. 6.11), reveal an interesting fact that the variation of the hydride orientation is accompanied by the change in the
selection of the preferred hydride-matrix OR. Moreover, the preferential hydride-matrix OR appears to be dependent on the nature of the prior bending strain, i.e. the primary OR tends to transit from $\bar{\eta}(111)/\bar{\eta}(0001)$ under the tensile strain in the top region to $\bar{\eta}(111)/\bar{\eta}(10\bar{1}0)$ under the compressive strain in the bottom region. The similar

![Figure 6.11](image)

**Figure 6.11** EBSD maps illustrating the microstructure in various regions of the plate piece A3 shown in Fig. 6.9: (a) top region; (b) middle region and (c) bottom region. The hydrides are marked with the red colour.
transition of the preferred hydride-matrix OR was also observed in the normal circumferential hydride and the reoriented radial hydride precipitated under the hoop stress during hydriding in Zr-4 cladding tubes [44]. These observations suggest that the change of the preferred hydride-matrix OR may be a common crystallographic feature associated with the variation in the hydride orientation as a result of the application of the stress during hydriding or the prior bending deformation before hydriding.

Figure 6.12 (a-f) Stereographic projection analysis results showing the crystallographic orientation relationship between the $\delta$-ZrH$_{1.66}$ and $\delta$-Zr grains at the indicated locations in Fig. 6.11.
Additionally, to clarify whether the crystallographic texture of the matrix plays a role on the variation of the hydride orientation, the local $\tilde{\gamma}$-Zr microtextures of the illustrated three regions in Fig. 6.9 were evaluated from the recorded EBSD data using the MTEX package [92]. The obtained $\tilde{\gamma}$-Zr pole figures for the three regions of the hydrided bent plate are provided in Fig. 6.13. It was found that the analysed local areas displayed quantitatively similar microtextures characterised by the concentrated basal poles oriented close to the ND direction. Note that the hydriding treatment of the bent Zr-4 plate sample at 450 °C would not induce the significant recrystallisation or texture development [51]. Based on this fact and the result in Fig. 6.13, it is reasonable to speculate that there is no significant variation of the through-thickness texture for the bent plate. This is also the expected situation for the bent plate with a minor bending strain of ~8% as described in Section 6.2.1. The local texture analysis mentioned-above indicates that the variation of the macroscopic hydride orientation does not necessarily require the cooperation of the appreciable change in the local texture of the $\tilde{\gamma}$-Zr matrix. In other words, the prior strain before hydriding exerts more significant influence on the hydride orientation than does the crystallographic texture of the matrix, in agreement with the previous finding [36].
Figure 6.3 Pole figures determined by EBSD, illustrating the $\bar{U}$Zr microtexture in various regions in the plate piece $A_3$ indicated in Fig. 6.9: (a) top region; (b) middle region and (c) bottom region.

6.4 Conclusions

In the current chapter, the hydride precipitation and distribution behaviours in the
bent and unbent Zr-4 plates were studied using a combination of the XRD, SEM and neutron tomography techniques. This work promises to study the spatial distribution of hydrides in Zr-4 after gaseous hydrogen charging. The influence of the prior bending deformation before hydriding on the hydride orientation in the bent sample was also analysed. The principal conclusions drawn from this study are summarised as follows:

(1) The inhomogeneous hydride distribution was evidenced in two types of hydried samples. Thin hydride layers on the sample surface and concentrated hydrides at the edges/corner were clearly observed for the unbent plate hydrided under a hydrogen pressure of 20 atm. This localised hydride accumulation was presumably attributed to the preferential hydrogen accumulation and saturation in these regions. For the hydrided bent sample at a relatively low hydrogen pressure of 10 atm, a thin hydride layer was observed only at the side with the significant surface plastic deformation generated during bending.

(2) The hydride orientation in the bent sample was shown to be consistent with the direction of the maximum tensile and compressive strain induced by the bending deformation. Compared with the crystallographic texture of ŭ-Zr matrix, the prior bending strain before hydriding appears to play a more significant role in determining the hydride orientation in the bent sample.

(3) Associated with the variation of the hydride orientation in the bent sample, the preferred orientation relationship between the precipitated ŭ-hydride and ŭ-Zr matrix transited from ŭ(111)/Ũ(0001) in the tensile strain region to ŭ(111)/Ũ(1010) in the
compressive strain region of the sample.
Chapter 7

Hydride Precipitation and its Influence on Mechanical Properties of Notched and Unnotched Zircaloy-4 Plates

7.1 Introduction

Zirconium alloys are used extensively as nuclear fuel cladding and fuel assembly components because of their unique combination of low neutron absorption cross-section, good corrosion resistance and attractive mechanical properties. One factor that needs to be considered for zirconium alloy components during service is the hydrogen absorption and the subsequent precipitation of hydrides, which severely degrades the ductility and fracture toughness of the material. Moreover, some zirconium alloy components are susceptible to a crack initiation and propagation process called delayed hydride cracking (DHC), potentially reducing their usable lifetime [10,157]. Due to its technological importance, the hydride-induced embrittlement in zirconium alloys has attracted considerable attention in recent decades [8,10,68,73,158]. Previous research efforts have established that the degree of the embrittlement depends mainly on the features of the hydrides that formed in alloys, such as the hydride orientation, distribution, precipitation location and amount [10,40,133]. It has been found that closely spaced hydride platelets are more detrimental to tensile ductility than widely spaced hydrides [68,73]. Additionally, Qin et al. [40] suggested that the intergranular hydrides may be more deleterious to ductility than the intragranular ones. A brittle
fracture behaviour tends to result when a continuous hydride network forms in the microstructure [8,70]. More interestingly, zirconium alloys may undergo an abrupt ductile-to-brittle transition at room temperature when the hydride or hydrogen content in the material reaches a critical level [8,65,67,70,158]. The sensitivity to hydride embrittlement in zirconium alloys is influenced by multiple factors, including the material microstructure and testing conditions. For example, Bai et al. [8] suggested that the use of fine microstructures with long elongated grains in the loading direction may delay the ductility reduction of hydrided Zircaloy-4 (Zr-4). Huang and Yeh [158] found that a premature brittle-to-ductile transition occurred in a hydrided Zr-4 sample at room temperature when it was tested in the hydrogen atmosphere with a pressure of 1010 kPa. It is important to note that in previous studies the evaluation of the influence of hydride precipitation on the mechanical behaviour of zirconium alloys was normally conducted through the uniaxial tensile tests on hydrided samples with relatively uniform distribution of hydrides [8,65,67,70,158]. However, as indicated by Bertolino et al. [64], the homogeneous hydride distribution may not properly represent the actual hydride distribution present in the components under service conditions. In fact, the inhomogeneous hydride distribution in the in-service component has been recognised, with the representative example of the formation of macroscopic hydride blisters in zirconium alloy pressure tubes [63]. It is therefore essential to evaluate the distribution features of hydrides formed under different hydriding conditions (e.g. in the presence/absence of stress gradients), and its potential impact on the failure
micromechanisms of hydrided zirconium alloys, in order to obtain an in-depth understanding on the hydride embrittlement phenomenon in these materials.

In this chapter, a notched Zr-4 plate with the inclusion of a wedge in the notch was prepared and then subjected to gaseous hydriding. The notched sample was designed to induce stresses at the notch tip and to enable the potential effect of the stress on the hydride precipitation and distribution features in the sample to be studied. Some unnotched plates charged with various hydrogen contents and relatively uniform hydride distribution were also prepared and the mechanical behaviours of these unnotched samples after hydriding were evaluated by the uniaxial tensile tests. The main objective of the present study was to ascertain the influences of hydride precipitation and its distribution features on the mechanical properties and fracture modes of hydrided Zr-4 plates.

7.2 Experimental Procedures

7.2.1 Material

Hot-rolled and annealed Zr-4 plate material (ASTM Grade R60804, purchased from Wah Chang, USA) was used in this study. The chemical composition of the Zr-4 plate was Zr-1.56Sn-0.22Fe-0.11Cr-0.14O (wt.%), and the plate exhibited a typical recrystallised microstructure characterised by the equiaxed ÚZr grain structure with an average grain size of ~10 μm, as shown in Fig. 7.1. The crystallographic texture of the Zr-4 plate was measured in this thesis work by neutron diffraction and the (0002) and
(10\overline{1}0) and pole figures are demonstrated in Fig. 5.9a (see Chapter 5). It may be noted that the dominant texture feature is the (0002) two pole maxima inclined at about ±30° from the plate normal direction (ND) and extended towards the transverse direction (TD); moreover, there is a (10\overline{1}0) prismatic maximum along the rolling direction (RD).

Figure 7.1 Typical microstructure of the Zr-4 plate matrix observed on different sections: (a) RD-TD section and (b) RD-ND section. The rolling direction (RD), transverse direction (TD) and normal direction (ND) are indicated.

7.2.2 Hydriding Procedures

Prior to the gaseous hydrogen charging, the Zr-4 samples were immersed in an acid solution consisting of 20 ml HF, 90 ml HNO₃ and 20 ml distilled water for 2 min to remove the oxide layer present on the surface. Two sets of plate samples were prepared for hydriding. A notched sample with the geometry schematically shown in Fig. 7.2 was first produced, and a wedge-shaped 316 stainless steel sample with a wedge angle of ~30° was pressed into the notch. The localised plastic deformation occurred near the
edges of the notch during the assembling process due to the larger size of the steel wedge than that of the notch. The as-prepared whole sample (referred to as notched sample in the following text) was hydrided using high purity hydrogen (99.9%) in a Sieverts device (Advanced Materials Corporation, USA) under a pressure of 60 atm. It was soaked at a temperature of 450 °C for 24 h and then cooled down to room temperature in the furnace with an estimated cooling rate of 2.2 °C min$^{-1}$. After hydriding, a short macroscopic crack extending along the pre-existed notch direction was observed on the notched sample (Fig. 7.2) and, subsequently, the entire through-thickness rupture of this sample was achieved by hand. Besides, a batch of unnotched plate samples was hydrided in a self-developed furnace at ANSTO with a chamber volume of 100 cm$^3$. They were exposed to the high purity hydrogen gas (99.9%) at 1 atm and maintained at 520 °C, followed by furnace cooling to room temperature with an approximate cooling rate of 1 °C min$^{-1}$. Depending on the exposure
time, the obtained hydrogen contents for this batch of samples varied from 25 to 850 wt. ppm, as determined by hot vacuum extraction using a LECO hydrogen analyser with an error of ~5 wt. ppm.

7.2.3 Mechanical Property Testing

To understand the premature rupture behaviour of the notched sample after hydriding, mini-tensile tests on the unnotched plate samples charged with different hydrogen contents were performed. Miniature tensile samples with the geometry depicted in Fig. 7.3 were prepared and tested in accordance with the AS 1391-2007 standard. The length and width directions of the tensile samples were parallel to the TD and RD of the plates, respectively. The gauge length was 10 mm. The mini-tensile tests were carried out at room temperature on an Instron 5967 universal testing machine at an extension rate of 0.50 mm min$^{-1}$. The 0.2% offset yield strength ($\sigma_{0.2}$) and ultimate tensile strength ($\sigma_{UTS}$) were determined from the recorded load-extension curves. The elongation and reduction of area were calculated from the dimensional measurements of the original and ruptured tensile samples. For the ruptured notched sample, the reduction of area was also evaluated via the pre- and post-crack measurements. The Young’s modulus ($E$) of the virgin Zr-4 plate and the hydried sample containing 850 wt. ppm of hydrogen were determined by the impulse excitation technique using a GrindoSonic instrument (LEMMENS Company, Belgium), in order to monitor the possible changes in $E$ induced by the hydride precipitation. The measurements of $E$
were conducted at room temperature along the RD and TD directions of the plates.

![Image of tensile test samples](image)

**Figure 7.3** The geometry of mini-tensile test samples. The width and length directions of the tensile sample correspond to the RD and TD of the plate, respectively.

### 7.2.4 Microstructural Characterisation

The microstructures of hydrided Zr-4 samples were examined by mounting them in epoxy, polishing according to metallographic techniques and finishing on 1200 grit silicon carbide paper. The polished samples were etched with a solution containing HF, HNO₃ and H₂O in a volume ratio of 1:10:10 for 30 s and observed using a JEOL JSM-6490LA scanning electron microscopy (SEM). The fracture surfaces of the tensile samples after testing or the notched sample after hydriding were examined under SEM. X-ray diffraction (XRD) measurements of the hydrided samples was performed by a GBC MMA X-ray diffractometer with Cu Kα radiation (λ = 1.5418 Å) at 28.6 mA and 35 kV, using continuous-scan mode at 1° min⁻¹. An additional diffraction measurement
of the notched sample after hydriding was conducted using neutrons at a wavelength of 2.414 Å and a beam size of 20 mm × 60 mm on Wombat, the high intensity powder diffractometer at the Australian Nuclear Science and Technology Organisation [85]. By analysing the acquired neutron diffraction pattern using the Rietveld refinement technique implemented in the GSAS code [131], the phase fraction of hydrides formed in the notched sample was quantified. The Rietveld phase quantification method enables the accurate phase analysis without the requirement of standards or laborious experimental calibration procedures [132]. The description of the basis of this approach could be found in Section 5.3.1 (see Chapter 5).

7.3 Results and Discussion

7.3.1 Mechanical Properties

Fig. 7.4 shows the changes of strength and ductility of the hydrided Zr-4 plates with the charged hydrogen contents up to 850 wt. ppm. There is an overall trend that the ultimate tensile strength (\(\sigma_{UTS}\)) was slightly increased by increasing the hydrogen content, while the 0.2% yield stress (\(\sigma_{0.2}\)) was almost independent of the hydrogen content (Fig. 7.4a). Additionally, Table 7.1 lists the Young\(\varepsilon\) modulus (\(E\)) of the unhydrided Zr-4 plate and hydrided sample with a hydrogen concentration of 850 wt. ppm. It shows that \(E\) was almost unchanged before and after hydriding, with the typical \(E\) value maintained at a level of ~94 GPa. Grange et al. [65] proposed that this observation accounted for the fact that \(\sigma_{0.2}\) remained nearly independent of the hydrogen
content (Fig. 7.4a). Further, the stable elastic modulus before and after hydriding indicated that the elastic modulus of hydride and Zr-4 matrix were similar, both having

![Graph](image)

**Figure 7.4** Effect of hydrogen content on the mechanical properties of the hydrided Zr-4 samples: (a) ultimate tensile strength and yield strength; (b) elongation and reduction of area.
a magnitude of ~94 GPa. This conclusion is also supported by a recent study on the hydrided Zircaloy-2 by synchrotron X-ray diffraction, showing that the hydride modulus was around 100 GPa [107]. Regarding the observed slight elevation of tensile strength with an increase in the hydride amount, two major explanations have been proposed in the literature for this strengthening effect. One suggestion is that the hydrides precipitated in the Zr-4 matrix normally possessed higher strength [79] than that of the surrounding matrix and hence acting as the reinforcing phase and resulting in the mechanical strengthening of the hydrided material. Another suggestion is that a large number of dislocations were generated in the Ú-Zr matrix during the hydride formation, contributing to the strengthening of hydrided Zr-4 [37,60]. The generation of the dislocations in the matrix is a consequence of the accommodation of the dilatational misfit strain associated with the hydride precipitation, and has been evidenced by transmission electron microscopy (TEM) investigations [37,60]. Although the strength of hydrided samples was insignificantly affected by the hydrogen content, the ductility reflected by the elongation and reduction of area (RA) values was closely linked to the hydrogen concentration (Fig. 7.4b). Specifically, the tensile ductility of hydrided plates generally diminished with increasing hydrogen concentration (i.e. hydride content). Note that the virgin Zr-4 had excellent ductility, represented by a high RA of 53% and elongation of 31%. Minor reductions in these values were found for the hydrided plate with a low hydrogen content of 25 wt. ppm. As the hydrogen content increased to 110 wt. ppm, the RA decreased by ~9% whereas the elongations only reduced by ~1%
compared with the initial values, which suggested that the effect of hydrogen on RA is more distinct than that on elongation [158]. At a high hydrogen concentration of 850 wt. ppm, the elongation and RA drastically reduced to 5% and 10%, respectively, indicating the substantial loss of ductility. Furthermore, for the hydrided notched sample, the RA was close to zero based on the pre- and post-crack measurements, revealing that a ductile-to-brittle transition occurred in this case.

**Table 7.1** The Young's modulus ($E$) of the virgin Zr-4 plate and hydrided plate containing 850 wt. ppm of hydrogen. The measurements are performed at room temperature along the RD and TD of plates.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$E$ measured along RD (GPa)</th>
<th>$E$ measured along TD (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Virgin Zr-4 plate</td>
<td>94.8</td>
<td>94.5</td>
</tr>
<tr>
<td>Hydrided Zr-4 plate with 850 wt. ppm H</td>
<td>94.1</td>
<td>94.1</td>
</tr>
</tbody>
</table>

### 7.3.2 Hydride Phase Identification

As the type of hydrides precipitated in zirconium alloys depends on the cooling rate applied during hydriding and the achieved hydrogen content [10,27,105], it is necessary to identify the hydride phase present in the hydrided samples. Fig. 7.5 depicts the typical XRD patterns of hydrided Zr-4 plates containing various hydrogen contents. The diffraction peaks corresponding to hexagonal closed-packed (hcp) ŪZr (JCPDS Card No. 05-0665) were generally identified in all hydrided samples. Besides the Ū-Zr
Figure 7.5 Typical XRD patterns of hydrided samples containing various hydrogen contents.

diffraction peaks, relatively weak peaks corresponding to face-centered cubic (fcc) \( \tilde{\nu} \)-\( \text{ZrH}_{1.66} \) (JCPDS Card No. 34-0649) were also detected in the hydrided sample containing 850 wt. ppm H. For the samples with hydrogen contents in the range of 25–450 wt. ppm, the hydride phase was not detectable by the present XRD measurements (the representative XRD pattern of the sample with 450 wt. ppm H was shown here). This is related to the low volume fractions of hydrides for the samples with low levels of hydrogen (\( \tilde{\nu} \)-450 wt. ppm). Nevertheless, it is rational to assume that \( \tilde{\nu} \)-hydrides were present at low hydrogen concentrations (\( \tilde{\nu} \)-450 wt. ppm), as the slow cooling rate applied in the hydriding process (1 °C min\(^{-1}\)) favoured the formation of the equilibrium \( \tilde{\nu} \)-\( \text{ZrH}_{1.66} \) phase [10,41]. For the notched sample after hydriding, the evident
diffraction peaks for the $\delta$-ZrH$_{1.66}$ phase were detected, which was also manifested by the neutron diffraction measurement, as revealed in Fig. 7.6. Considering that only $\delta$-hydrides were present in the samples and the hydrogen solubility in the Zr-4 matrix was very low (less than 10 wt. ppm at room temperature [27,123]), it is safe to conclude that a greater concentration of hydrides were precipitated at higher hydrogen levels. Further, the Rietveld refinement analysis, which allows the quantification of phase fraction, was performed on the recorded neutron diffraction data (Fig. 7.6). The refinement result showed a weight fraction of 11 wt.% for $\delta$-ZrH$_{1.66}$ phase, corresponding to a hydrogen content of 1965 wt. ppm. As the neutron diffraction data

Figure 7.6 The GSAS refinement of the neutron diffraction pattern measured from the notched sample after hydrogen charging. The graph shows the measured data points (+ symbols), the refinement result (fitted line) and their difference curve. The $\chi^2$ parameter, a metric indicating the goodness of fit between the actual data and the fitted pattern, was 2.1 in this work.
representing the information from the bulk sample were used in the Rietveld phase quantitative analysis, the high accuracy of the determined hydride content should be expected. Based on this quantitative analysis, it is reasonable to consider that, compared with other hydrided samples in this study, a higher hydrogen concentration, i.e. a larger amount of hydrides was attained for the notched sample after hydriding under a hydrogen pressure as high as 60 atm.

### 7.3.3 Metallographic and Fractographic Observations

#### 7.3.3.1 Hydrided Plates Containing 25–850 wt. ppm of Hydrogen

Fig. 7.7 shows the typical microstructures of the Zr-4 plates with hydrogen contents ranging from 110 to 850 wt. ppm. The common acicular or platelet-like hydrides were clearly observed and, as expected, the distribution density of hydrides steadily increased with increasing hydrogen concentration. In addition, the microscopic features of the hydrides in terms of the precipitation sites and alignments exhibited some distinct variations with hydrogen contents. At a relatively low hydrogen content of 110 wt. ppm, the randomly distributed grain boundary hydride platelets were predominantly observed (Fig. 7.7a). This result supported the previous suggestion that grain boundaries (GBs) may be preferred sites for hydride formation relative to the intra-grain region [35,40]. As the hydrogen content was increased to 380 or 450 wt. ppm, intergranular hydrides as well as the gradual development of intragranular hydride needles were observed (Figs. 7.7b and c). According to the theoretical analysis by Qin et al. [40], the favourable GBs
for the precipitation of intergranular hydrides were essentially those lying on the basal plane of the matrix (the usual habit plane of hydrides [39]) and having a high energy. When a high level of hydrogen (≥80 wt. ppm) was introduced into the matrix, the preferred GBs sites tended to exhaust for the formation of intergranular hydrides, and the excess hydrogen could promote the development of intragranular hydrides (Figs. 7.7b-d). At an even higher hydrogen content of 850 wt. ppm, the intergranular and intragranular hydrides were both frequently observed. These hydride platelets became thicker and were preferentially aligned along the RD of the plate (Fig. 7.7d). The

![SEM micrographs showing typical hydride morphologies in the hydrided Zr-4 plates with various hydrogen contents: (a) 110; (b) 380; (c) 450 and (d) 850 wt. ppm.](image)

**Figure 7.7** SEM micrographs showing typical hydride morphologies in the hydrided Zr-4 plates with various hydrogen contents: (a) 110; (b) 380; (c) 450 and (d) 850 wt. ppm.
microstructure of the plate with a very low hydrogen concentration of 25 wt. ppm was similar to that of the virgin plate (Fig. 7.1a), demonstrating little or no evidence of hydrides. Apart from the hydrides primarily concerned, it can be noted that the initial equiaxed U\textsuperscript{Zr} grain structure was maintained after hydriding.

To investigate the fracture behaviours of hydrided Zr-4 and understand the hydride-induced embrittlement, the fracture surfaces of hydrided plates with different hydrogen contents (≤850 wt. ppm) were examined, as illustrated in Fig. 7.8. At a low hydrogen content of 25 wt. ppm, the hydrided plate clearly underwent a ductile fracture process, evidenced by the abundant dimple structures with a mean size of ~10 \( \mu \)m present in the fracture surface (Fig. 7.8a). When the hydrogen content rose to 110 wt. ppm, some secondary cracks appeared (Fig. 7.8b) while the fracture surface still dominantly contained dimpled regions. It is also found that some short secondary cracks (pointed in Fig. 7.8b) were coincident with the hydride precipitation sites, which implied that the hydrides contributed to the development of secondary cracks. At a hydrogen concentration of 450 wt. ppm, besides the dimple structures and secondary cracks, some cleavage facets around the cracks were distinctly observed, as indicated by arrows in Fig. 7.8c. In contrast, the fracture surface at an even higher hydrogen level of 850 wt. ppm exhibited the brittle features, characterised by considerable cleavage facets and longer secondary cracks along the crack propagation direction (Fig. 7.8d). In this case, small-sized and shallow dimple structures were occasionally observed in the surface (Fig. 7.8e), suggesting the abrupt reduction of ductility.
The hydrides present in zirconium alloys are recognised as a fracture initiator because of their intrinsic brittleness, as reflected by the low fracture toughness of the order of 1 MPa m^{1/2} at room temperature [159]. It has been reported that the presence of brittle hydride phase, which provides an easy crack path, played a key role in determining the fracture micromechanisms and ductility of hydrided zirconium alloys [8,50,158]. The combination of metallographic and fractographic investigations (Figs. 7.7 and 7.8) explicitly suggested that the fracture behaviour of hydrided Zr-4 plates under uniaxial tension loading were closely related to the hydride concentration (i.e. hydrogen content). With increasing hydrogen content, the fracture mode experienced a successive change from a pure ductile fracture (25 wt. ppm) to a mixture of ductile and brittle fracture (450 wt. ppm), and then to a near complete brittle fracture (850 wt. ppm).

At the low hydrogen level of 25 wt. ppm, negligible hydrides were formed, thereby leading to less degradation of ductility (Fig. 7.4b) and the resultant ductile fracture (Fig. 7.8a). At 450 wt. ppm H, in conjunction with the metallographic observation (Fig. 7.6c), it could be confirmed that the crack path primarily followed the brittle hydrides, which ruptured by cleavage, whereas the ductile matrix between hydrides fractured by microvoid coalescence. As the hydrogen content is increased to 850 wt. ppm, the brittle fracture of hydrides with a high concentration in this situation may lead to the prevalence of cleavage and, moreover, as these hydrides were preferentially aligned along the RD of the plate (Fig. 7.6d), the long secondary crack could be progressively generated through linking up the adjacent fractured hydrides arranged in the crack.
Figure 7.8 SEM images showing characteristic fracture surfaces of hydried plates containing different hydrogen contents: (a) 25; (b) 110; (c) 450 and (d) 850 wt. ppm. (e) shows the occasionally observed dimple structures at 850 wt. ppm. Crack growth direction is from bottom to top.
direction (Fig. 7.8d). Furthermore, the almost complete brittle behaviour exhibited in this case coupled with the drastic reduction of ductility (Fig. 7.4b), indicated that critical hydrogen content beyond which the ductile-to-brittle transition occurred at the uniaxial tensile condition was approaching 850 wt. ppm.

7.3.3.2 Notched Plate after Hydriding

Figs. 7.9b-e display the characteristic microstructures for the hydrided notched sample at various regions. The hydride morphology and distribution features at these selectively observed areas clearly exhibit some differences (Figs. 7.9b-e). Nevertheless, a close comparison of Fig. 7.7 and Figs. 7.9b-e reveals that the average concentration of hydrides in the notched plate was generally higher than that in other hydrided plates investigated here, consistent with the hydride quantification analysis via neutron diffraction (Fig. 7.6). At the region below the fracture surface (i.e. the RD-ND section), a great amount of grain boundary hydrides were precipitated, forming a continuous network along grain boundaries and, meanwhile, many long intragranular hydrides going from side to side of individual $\tilde{U}$Zr grains and near dense hydride regions were present (Fig. 7.9b). The brittle hydrides distributed in this manner significantly destroyed the microstructural integrity of the initial material. At the region far from the notch edge (indicated by $\tilde{B}_1\tilde{O}$ in Fig. 7.9a), the microstructure consisted of many long hydride platelets, which tended to align along the RD of the plate (Fig. 7.9c). Also, the hydride concentration in this area seems to be lower than that in the region below the
Figure 7.9 (a) Schematic illustrating the region with marked plastic deformation in the notched Zr-4 plate generated during the installation of large-sized steel wedge and the biaxial tensile stress concentration area around the notch resulting from the thermal expansion of steel wedge during hydriding; (b-d) SEM images showing the hydride morphologies in the hydrided notched plate at different regions: (b) below the fracture surface and close to the root of the notch; (c) far from the notch edge, as indicated by
in (a); (d) near the notch edge, as marked by \( \text{B}_2 \) in (a); and (e) near the edge of the developed crack, as indicated by \( \text{B}_3 \) in (a).

fracture surface (Fig. 7.9b). It was believed that the concentration of biaxial tensile stress at the root of the notch generated by the inserted steel wedge (schematically shown in Fig. 7.9a) enhanced the hydrogen diffusion during hydriding towards the notch root [124] and, accordingly, resulting in a considerably higher concentration of hydrides precipitated in the area below the fracture surface (Fig. 7.9b). Although the direct measurement of the stress state around the notch root was presently unrealised in this work, it is reasonable to assume that, the pre-existed notch (Fig. 7.2) introduced a biaxial tensile stress distribution with a stress concentration at the root of the notch during hydriding (Fig. 7.9a). On one hand, the constrained 316 stainless steel wedge in the designed notch possesses a high linear thermal expansion coefficient \( (17.5 \times 10^{-6} \, ^\circ\text{C}^{-1}) [160] \), nearly three times the value for Zr-4 \( (6 \times 10^{-6} \, ^\circ\text{C}^{-1}) [161] \). Consequently, the steel wedge effectively exerted a compressive force to the surrounding Zr-4 plate during hydriding at 450 °C and, accordingly, generating the biaxial tensile stress at the root of the notch. On the other hand, previous theoretical and experimental studies have confirmed the existence of biaxial tensile stress concentration at the root of the notch [162]. At the area near the notch edge (marked by \( \text{B}_2 \) in Fig. 9a), a considerable number of long hydride platelets that aligned along the RD of the plate was present in the microstructure and, interestingly, a hydride content gradient was
observed, showing a greater concentration of hydrides at the position approaching the notch edge (Fig. 7.9d). As previously stated, the marked plastic deformation regions around the notch edges were created (Fig. 7.9a) due to the forced fit of the large-sized wedge into the notch. The plastic deformation is normally accompanied by the generation of microstructural defects (e.g. vacancies and dislocations), which could act as hydrogen traps [111,112] and provide preferred hydride nucleation sites [34,113], thereby facilitating the formation of more hydrides at the position close to the notch edge (Fig. 7.9d). At the region near the crack edge (indicated by Fig. 7.9d in Fig. 7.9a), a similar microstructure to that of Fig. 7.9d was found, demonstrating numerous hydride platelets with a pronounced orientation along the RD and a decreasing hydride content along the direction from the crack to the extreme of the sample (Fig. 7.9e). Based on Figs. 7.9d and e, it is important to point out that the plane stress state supposed in the thin notched sample contributes to the marked orientation of hydrides formed near the notch/crack edges, yielding a dominant orientation of hydrides perpendicular to the stress component direction.

Fig. 7.10a depicts the fracture surface for the hydrided notched sample. Extensive flat cleavage facets appeared in the fracture surface while no microvoid coalescence was found, demonstrating a complete brittle fracture behaviour (Fig. 7.10a). A close examination of Fig. 7.10a also reveals that many cleavage facets were surrounded by short secondary cracks. Combined with the metallographic finding that a continuous hydride network was formed in this case (Fig. 7.9b), it was considered that the fracture
path for this notched sample mainly followed the intergranular hydrides, leading to the emergence of extensive cleavage facets with sizes comparable to that of the $\bar{\alpha}$-Zr grains (Fig. 7.10b). In addition, a high-magnification SEM micrograph (Fig. 7.10b) shows that many secondary cracks almost perpendicular to the crack propagation direction are present in the brittle facet area, implying that this area is much more brittle than the surrounding areas. These secondary cracks were identified to coincide with the locations of some intergranular hydrides (Fig. 7.9b), which indicates that the fracture of intragranular hydrides also occurred during the rupture process of the notched sample.

For the notched plate, it was notable that the crack was prematurely initiated and propagated along the notch direction during hydriding at 450 °C and under a high hydrogen pressure of 60 atm (Fig. 7.2). This may be attributed to a synergistic effect of hydrogen gas and tensile stress concentration at the root of notch in the sample (Fig. 7.9a). The metallographic observation (Fig. 7.9b) showed that a great concentration of

![Figure 7.10](a) SEM image showing typical fracture surface of the ruptured notched plate after hydriding; (b) is a local magnification of (a). Crack growth direction is from bottom to top.
hydrides tended to accumulate at the region near the root of the notch, resulting from the
enhanced hydrogen diffusion by the tensile stress concentration at this region. According to Huang and Yeh’s study [158], it was thought that these concentrated hydrides may be instantly cracked because of the stress concentration at the notch root, i.e. the delayed hydride cracking (DHC) occurs. This hydride cracking was possible at the hydriding temperature of 450 °C because the δ-hydride (ZrH_{1.66}) remains brittle in tension up to 500 °C [80] with the fracture toughness varying slightly from 1 MPa m^{1/2} at room temperature to 3–4 MPa m^{1/2} at 300 °C [133]. Therefore, many microcracks could be generated by the fracture of the accumulated hydrides (Fig. 7.10). During the hydriding process using a high hydrogen pressure, the occurrence of DHC associated with the microcracks acting as short circuits for the further hydrogen penetration into the region ahead of the notch root [158] promotes the continuous hydride precipitation at the notch tip. Again, the cracking of these precipitated hydrides could be triggered by the concentrated stress. Due to this repeated hydride formation and fracture process, the crack propagation could be progressively realised through the fracture of hydrides (i.e. DHC), which was promoted by the tensile stress concentration. However, the DHC only occurs when hydride concentration increases to a critical value under certain stress level. Further, as the stress concentration was only limited in the region near the notch root, the propagation of the crack may be arrested when the crack tip reaches the regions with a low level of stress, so only a short flaw was developed during hydriding (Fig. 7.2). After hydriding, the ease in breaking this thin notched sample as well as the measured
value of RA approaching zero reveals that the notched sample became totally brittle, in agreement with the fractographic analysis (Fig. 7.10). Although the actual hydrogen content in the hydrided notched sample was not measured, it is reasonable to consider that this sample had a very high hydrogen content, at least, exceeding 850 wt. ppm, based on the combined metallographic and neutron diffraction analyses (Figs. 7.6 and 7.9b-d). Overall, two main factors, i.e. the very high hydrogen concentration achieved in this thin notched sample (thickness ~0.8 mm) and the formation of a continuous hydride network on the section along the thickness direction, contributed to the emergence of a rapid ductile-to-brittle transition at room temperature and the resultant through-thickness brittle failure for the hydrided notched sample.

7.4 Conclusions

In this chapter, the hydride precipitation and its influence on the mechanical properties of the hydrided Zr-4 plates with various hydrogen contents were investigated at room temperature. Special attention was devoted to the analysis of the hydride distribution features and premature cracking behaviour in a designed notched plate. The most important conclusions are summarised in the following:

(1) Hydrides exerted only minor influences on the ultimate tensile strength and yield stress of the hydrided Zr-4 plates containing hydrogen contents up to 850 wt. ppm.

(2) The uniaxial tensile ductility of the hydrided plates was significantly degraded by the hydride precipitation. The fracture mode and the degree of embrittlement were
closely dependent on the hydrogen content.

(3) Under the uniaxial tensile condition, the hydrided plate with 850 wt. ppm H exhibited a negligible ductility with the elongation of 5% and reduction of area of 10%, leading to almost completely brittle fracture behaviour.

(4) For the hydrided notched plate, the tensile stress concentration associated with the notch tip promoted the hydride accumulation at the region near the notch tip and the premature crack propagation through the hydride fracture during hydriding. The eventual brittle through-thickness failure for this notched sample was mainly ascribed to the formation of a continuous hydride network on the thickness section and the obtained very high hydrogen concentration (estimated to be 1965 wt. ppm).
Chapter 8

Summary and Outlook

This final chapter presents a general summary of this thesis work and provides some suggestions for the potential future work on the hydride embrittlement in zirconium alloys.

8.1 General Summary

This research work investigated the hydride precipitation behaviours (the hydride phase, morphology, distribution and crystallographic texture, etc.) in Zircaloy-4 (Zr-4) materials with different thermo-mechanical states (i.e. the high-pressure torsion processed, hot-rolled and annealed, and hot-extruded and annealed), and analysed the influence of the hydride precipitation on the mechanical properties of Zr-4 materials. A general summary of the principal results obtained from this work is presented as follows:

(1) The nanostructured Zr-4 materials prepared by high-pressure torsion (HPT) exhibited the lower resistance to the hydride precipitation compared with the samples without HPT processing.

(2) For different Zr-4 materials investigated, the precipitated $\tilde{\delta}$-ZrH$_{1.66}$ platelets predominantly followed the $\tilde{\delta}(111)/\tilde{\delta}(0001)$ and $\tilde{\delta}(110)/\tilde{\delta}(1120)$ orientation relationship with the $\tilde{\delta}$-Zr matrix of the materials.

(3) The $\tilde{\delta}$-hydride displayed a weak macroscopic texture which was determined by the
$\bar{U}Zr$ matrix, and this dependence essentially originated from the observed predominant orientation correlation between $\bar{U}Zr$ and $\bar{U}$-hydride.

(4) The experimental data revealed a heavily dislocated structure of the $\bar{U}$-hydrides with an estimated average dislocation density of one order of magnitude higher than that in the $\bar{U}Zr$ matrix.

(5) The natural accumulation of hydrides occurred on the surface and at the edges/corner of the Zr-4 plate samples under the current gaseous hydriding conditions with a relatively high hydrogen pressure of 20 atm. It was also shown that after gaseous hydriding, hydrides tend to locally accumulated in the regions of the plate samples with the presence of tensile stress concentration or marked compressive plastic deformation.

(6) The bending deformation before hydriding in the bent plate sample induced the subsequent precipitation of hydride platelets aligned parallel to the direction of the prior tensile or compressive strain. Associated with the variation of the hydride orientation in different regions of the bent plate sample, the preferred crystallographic orientation relationship between $\bar{U}$-hydride and $\bar{U}Zr$ matrix transited from $\bar{U}(111)/\bar{U}(0001)$ in the tensile strain region to $\bar{U}(111)/\bar{U}(10\bar{1}0)$ in the compressive strain region.

(7) For the hydrided Zr-4 plates with the hydrogen contents ranging from 25 to 850 wt. ppm, the uniaxial tensile tests showed that the precipitated hydrides had an insignificant effect on the tensile strength, while the ductility was severely degraded with increasing hydrogen content.

(8) The hydrided plate containing a hydrogen content of 850 wt. ppm exhibited a
negligible ductility, resulting in almost completely brittle fracture behaviour in the tensile test. It is concluded that the critical hydrogen content beyond which the ductile-to-brittle occurred in the investigated Zr-4 plate under the uniaxial tensile testing and room temperature conditions was approaching 850 wt. ppm.

8.2 Suggestions for Future Work

The present research has made good progress towards the goal of understanding the hydride precipitation and induced embrittling effect in zirconium alloys. However, the understanding obtained on this phenomenon is still incomplete, due to the lack of experimental data under other testing and hydriding conditions and the relevant analyses. The areas requiring future studies in order to improve our understanding on this topic are suggested and described in the following.

(1) Hydride formation in irradiated zirconium alloys. The current work is concerned about the hydride precipitation behaviour in unirradiated zirconium alloys. Under practical in-reactor service conditions, the zirconium alloys applied are subjected to intense neutron radiation, which would lead to the significant changes in the irradiated microstructure (e.g. the formation and growth of dislocation hoops). Based on the present investigation, it is speculated that the generation of the irradiation-induced lattice defects may enhance the potential for the hydride precipitation in irradiated materials than that in unirradiated counterparts. It would be technologically useful to study the irradiation effect on the hydride formation in zirconium alloys, which would
contribute to the understanding of the hydride embrittlement behaviour in actual zirconium alloy components after a period of service in nuclear reactors.

(2) **The dislocation structure in hydrides in zirconium alloys.** The work in Chapter 5 presented a semi-quantitative estimation result for the average dislocation densities in hydrides. There is need to obtain more precise quantitative information of the average dislocation densities in hydrides determined by the line profile analysis of high resolution neutron or X-ray diffraction patterns of hydrided samples. Additional experimental work by transmission electron microscopy is also required to observe the dislocation morphology and to determine the dislocation type (Burgers vector).

(3) **Quantitative analysis of the influence of prior deformation on the macroscopic orientation of hydrides.** As revealed in Chapter 6 of this thesis, the appreciable bending deformation in Zr-4 plate samples prior to hydriding leads to a preferential alignment of hydrides that a majority of hydride platelets are aligned parallel to the direction of the maximum strain (both for tensile and compressive strain). Due to the difficulty in the measurement of the complex strain distribution in the investigated thin bent sample (~1.8 mm thick), the quantitative correlation between the prior strain on the degree of the preferential alignment of hydrides along the principal strain direction is unclear. Experimental work is needed to quantify the effect of the prior strain on the macroscopic orientation of hydrides using tensile or compressive deformed samples with various levels of prior strain before hydriding.

(4) **High temperature mechanical behaviour studies of hydrided material.** It is also
important to study the mechanical behaviour of hydrided materials with a large range of hydrogen contents (up to thousands of wt. ppm) at service temperature (~300 °C) of a power nuclear reactor. Further works are required to understand the embrittling effect of hydrides at elevated temperature and to rationalize the influence of the hydrided microstructure (hydride phase, morphology and distribution, etc.) on the macroscopic mechanical properties and fracture micromechanisms of the hydrided materials with various hydrogen contents at the high temperature.
Appendix A

Sample Preparation Method for the EBSD Measurement

This appendix presents details on the preparation technique of hydrided Zircaloy-4 samples for the EBSD measurements that were performed in Chapters 5 and 6. The main steps of grinding and polishing procedures are listed in Table A.1.

Table A.1 Detailed procedures used for the preparation of hydrided Zircaloy-4 samples in the EBSD measurement.

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<th>FG 3</th>
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<td>Grinding Paper</td>
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<td>SiC 1200#</td>
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<tr>
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<td>----------</td>
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<td>150rpm Counter-Rotation</td>
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<td>5 - 15 mins</td>
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</table>
Appendix B

Approaches for the Quantification of Hydrides in Zirconium Alloys Based on XRD and SEM Techniques

The hot vacuum extraction technique used in Chapter 7 allows the accurate determination of hydrogen concentrations in zirconium alloys, but the samples were destroyed in the analysis process. In Chapters 5 and 7, a few hydrided Zircaloy-4 (Zr-4) samples were tested using neutron diffraction, and the Rietveld quantitative phase analysis from the acquired neutron diffraction data was performed to evaluate the formed hydride contents. However, the measurement opportunities with neutron diffraction are not easily available. Some alternative approaches based on the conventional XRD and SEM techniques were also used in this work (Chapters 4 and 6) for the quantitative estimation of the hydride/hydrogen content in zirconium alloys, and a detailed description of these approaches is provided in this appendix.

Approach Based on the X-ray Diffraction

In this method, the conventional X-ray diffraction patterns for hydrided Zr-4 samples are analysed to quantify the hydride volume fractions, which are correlated with the hydrogen contents of these samples. For the hydrided samples that are analysed using this method in the current work (see Chapters 4 and 6), only one type of hydrides (\(\delta\)-ZrH\(_{1.66}\)) was present, so it was not necessary to consider \(\gamma\) and \(\epsilon\) hydrides to calculate the hydrogen content for each sample. The quantitative phase analysis for the \(\delta\)-hydride
volume fractions and hydrogen contents is performed by comparing the integrated intensities of the δ-hydride and δZr peaks, and the volume ratio of δ-ZrH$_{1.66}$ and δZr phases can be estimated according to the following equation [27,84]:

\[
\frac{V_\delta}{V_\delta} = \frac{I_{(111)}^\delta}{I_{(002)}^\delta} \times \frac{R_{(002)}^\delta}{R_{(111)}^\delta} = \frac{I_{(111)}^\delta}{I_{(002)}^\delta} \times \frac{P[F_{\delta}]^2 \left( \frac{1 + \cos^2 2\theta}{\sin^2 \theta \cos \theta} \right)^{e^{-2M}}}{P[F_{\alpha}]^2 \left( \frac{1 + \cos^2 2\theta}{\sin^2 \theta \cos \theta} \right)^{e^{-2M}}} \times \frac{T_{(002)}^\delta}{T_{(111)}^\delta} \tag{A.1}
\]

where, for a specific peak, $g$ is the unit cell volume ($m^3$), $|F_{\delta}|^2$ is the structure factor, $P$ is the multiplicity factor, $\left( \frac{1 + \cos^2 2\theta}{\sin^2 \theta \cos \theta} \right)$ is the angle factor, $e^{-2M}$ is the temperature factor and $T$ is the texture factor. Most parameters involved in equation A.1 could be found in Ref. [27], except the texture factor $T$. It is rationally assumed that $T_{(002)}^\delta = T_{(111)}^\delta$, as a strong orientation relation between the δ-hydride and the δZr matrix, i.e. δ(111)/δ(0001), was captured in this thesis (see Chapters 4 and 5). From the calculation results of $V_\delta$, the corresponding hydrogen contents $[H]$ were then estimated using the following equation [27]:

\[
[H] = [H]^\delta \cdot V_\delta \cdot \frac{\rho_{\delta}}{\rho_{\delta Zr} \cdot (1 - V_\delta) + \rho_{\delta} \cdot V_\delta} \tag{A.2}
\]

where $[H]^\delta$ is the hydrogen content of δ-ZrH$_{1.66}$ phase, $\rho_{\delta}$ is the density of δ-hydride at room temperature (~5.65 g/cm$^3$), and $\rho_{\delta Zr}$ is the density of δ-Zr at room temperature (~6.51 g/cm$^3$).

**Approach Based on the Image Analysis**

In this approach, the hydride volume fractions of the hydrided Zr-4 samples are
quantitatively estimated based on the analysis of SEM micrographs taken from the etched microstructure of these samples, using the image processing and analysis software (ImageJ [104]). The general procedure for the hydrides volume fraction analysis using ImageJ is described in Fig. A.1. In order to minimise the measurement error, it is suggested to analyse at least 3 low-magnification SEM micrographs (the images with a magnification of 500 times were used for the current work) taken from different locations of the samples, and the reported hydride volume fraction is the average of these measurements. The hydrogen content can then be estimated from the determined hydride volume fraction using equation A.2 given in this section.

Figure A.1 A typical example showing the sequence of steps for the hydrides volume fraction determination in hydrided Zr-4 samples using the ImageJ software [104].
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