

Micromechanics, Microstructure and Formation of Zirconium Hydrides in Nuclear Fission Applications



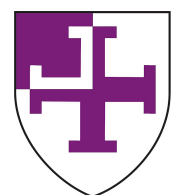
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ABSTRACT

Hydride formation in zirconium based nuclear fuel cladding can lead to reduction of ductility and fracture toughness. This detrimental effect of hydrogen embrittlement is critically dependent on the morphology of hydrides in microscale and the Zr/hydride dual-phase microstructure. In this work Zr hydride thin film samples were prepared for microstructural and micromechanical characterisation. The microstructure near the Zr/hydride interface was examined with the use of scanning electron microscopy (SEM) and electron backscatter diffraction (EBSD). A new model was developed to account for the effect of concentration-dependent diffusion on the formation of hydride precipitates. Microcantilever tests and nanoindentation were carried out to compare the deformation properties of the δ -hydride with those of the α -Zr. Pre-notched microcantilevers were fabricated in the individual phases and across the phase boundary with the use of focused ion beam (FIB). The experimental results show that the δ -hydride exhibits isotropic micromechanical properties. All the 2-4 μm wide δ -hydride microcantilevers underwent brittle fracture and the conditional fracture toughness is 1.8-2.0 $\text{MPa}\cdot\text{m}^{1/2}$ in a variety of crystallographic directions. The Young's modulus of the δ -hydride is 88-94 GPa and its proportional limit in microscale (1016-1189 MPa) is approximately double that of the α -Zr (401-600 MPa). The indentation size effect (ISE) was experimentally investigated and the hardness increased by 65% to 5.1 GPa when the indenter penetration depth was reduced from 5 μm to 0.5 μm . Despite interfacial microvoids and secondary hydride microcracks were observed after applying the bending load, the interface-notched dual-phase microcantilevers predominantly underwent plastic deformation without primary crack propagation.

GLOSSARY OF ABBREVIATION

AFM	Atomic Force Microscopy
ASTM	American Society for Testing and Materials
bcc	Body Centred Cubic
CRSS	Critical Resolved Shear Stress
CSM	Continuous Stiffness Measurement
DHC	Delayed Hydride Cracking
EBSD	Electron Backscatter Diffraction
EDS	Energy Dispersive Spectroscopy
fcc	Face Centred Cubic
fct	Face Centred Tetragonal
FE(M)	Finite Element (Method)
FESEM	Field Emission Scanning Electron Microscopy
FIB	Focused Ion Beam
FTCS	Forward-Time-and-Central-Space
GND	Geometrically Necessary Dislocation
hcp	Hexagonal Close Packed
ISE	Indentation Size Effect
ICDD	International Centre for Diffraction Data
LEFM	Linear Elastic Fracture Mechanics
OM	Optical Microscopy
PDF	Powder Diffraction File
ppm (wt)	Parts per Million (by Weight)
SEM	Scanning Electron Microscopy
TEM	Transmission Electron Microscopy
TSS(P/D)	Terminal Solid Solubility (for Precipitation/ for Dissolution)
UTS	Ultimate Tensile Strength
XRD	X-ray Diffraction

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1 INTRODUCTION

The use of nuclear fission power for electricity generation has received ongoing attention with growing concern about energy consumption and carbon dioxide emission. In 2014, a net capacity of 376 GW electric output, or 6.2% of the worldwide capacity, was provided by 438 operating nuclear power reactors around the world. The International Atomic Energy Agency also estimated a 2-68% growth in capacity by 2030 [1]. Since nuclear fission relies on the number of available neutrons to produce a sustainable chain reaction, fuel cladding materials should be transparent to neutrons in order to maintain an efficient operation [2]. Zirconium has a low neutron absorption cross-section and good mechanical properties at the operating temperature of about 300°C. Its various alloys are therefore widely selected for the manufacture of cladding in conventional types of nuclear fission reactors such as pressurised water reactors and boiling water reactors.

Zirconium alloys react with coolant water to form hydrogen during the reactor service. Hydrogen can diffuse into the metal lattice and precipitate as microscale hydrides. The presence of hydrides is deleterious to ductility leading to low fracture toughness and sudden failures at a small strain [3], [4]. This effect of hydrogen embrittlement correlates with the hydride morphology and the microstructure of the material. Hydrides are also associated with delayed hydride cracking (DHC), which is a time-dependent sub-critical crack growth process resulting from the formation of brittle hydrides and their subsequent failures near a crack tip [5]. Measurements on the micromechanical properties of zirconium hydrides are therefore essential for a better understanding of these detrimental effects on the material performance.

Recent advances in focused ion beam (FIB) techniques coupled with nanoindentation systems have allowed microscale specimens of complex geometries to be fabricated and tested [6], [7]. Direct loads applied on these specimens can produce the load-displacement relationship for extracting the specific properties of the material. This micromechanical testing method combined with advanced microstructural analysis techniques enables investigation of zirconium hydrides at the scale of their microstructures.

The present experimental study demonstrates the use of precision testing methods for micro-mechanical characterisation of zirconium hydrides. Advanced imaging and characterisation techniques such as scanning electron microscopy (SEM) and electron backscatter diffraction (EBSD) were used for examination of the zirconium-hydride dual-phase microstructure. This study covers the mechanisms for hydrogen diffusion and a new computational model for simulating the hydrogen concentration profile. Nanoindentation and microcantilever specimens were used to determine the elastic and plastic properties at various crystallographic orientations relative to the stress system. The deformation properties of the localised region alongside the phase boundary are presented with discussions on the corresponding findings.

2 LITERATURE REVIEW

2.1 Zirconium

2.1.1 Selection of Zirconium for Nuclear Fuel Cladding

Zirconium alloys are widely used as fuel cladding materials for nuclear fission applications mainly because of their low neutron absorption cross-section (Figure 2.1), high service temperature, good mechanical properties, high corrosion resistance and high radiation resistance [2], [8]. The combination of these properties made its various alloys become the main fuel cladding materials by the mid-1960s [2]. However Zr has complex corrosion mechanisms that are accompanied by the ingress of hydrogen. This may lead to embrittlement and DHC due to hydride formation in the matrix [4]. It remains as a challenge to improve the performance of Zr alloys for the potential future Generation-IV fission reactors with an expected operating temperature over 350°C [9].

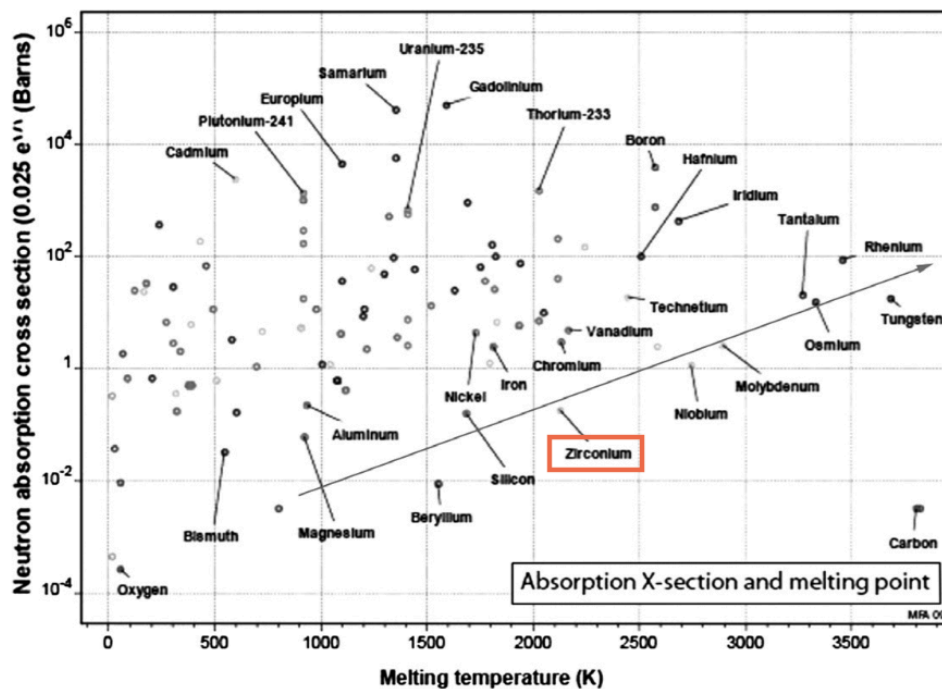


Figure 2.1 Neutron absorption cross-section against melting temperature of pure elements [2].

2.1.2 Mechanical Properties and Slip Systems

A variety of experimental methods have been employed to study the mechanical properties of Zr and its alloys as summarised in Table 2.1. The characteristic length scales of samples are specified in the table since some properties are dependent on the deformation volume. This specimen size effect is introduced in Sections 2.4.1 and 2.4.3.

Table 2.1 Mechanical properties of Zr and its alloys

Properties	Range	Measurement methods	Materials	References
Yield strength (MPa)	205-310	Macroscopic tensile test*	Zr	[8], [10]
	250-550	Macroscopic tensile test*	Zircaloy-4	[8], [11]–[14]
	530	Micro-compression test (micropillars with a diameter of $\sim 2.7 \mu\text{m}$)	Zircaloy-4	[15]
	780	Nanoindentation (peak load is 7 mN and radius of the plastic zone is $\sim 2 \mu\text{m}$)	Zr	[16]
Ultimate tensile strength (MPa)	380-450	Macroscopic tensile test*	Zr	[8]
	400-520	Macroscopic tensile test*	Zircaloy-4	[8], [11]–[14]
Microhardness (GPa)	0.9-1.7	Vickers hardness test and pulse technique	Zr	[17]–[19]
Nanohardness (GPa)	2.9-4.9	Nanoindentation (the peak load is 1 mN and the indentation depth is $\sim 0.1 \mu\text{m}$)	Zr	[16][17]
Young's modulus (GPa)	80-126	Ultrasonic wave, pulse technique, resonance technique and micro-bending test ($0.5\text{-}10 \mu\text{m}$ wide microcantilevers)	Zr	[8], [16], [18], [20]–[22]
	95-97	Frequency oscillator technique	Zircaloy-2, Zr-2.5Nb	[23], [24]
Shear modulus (GPa)	32-37	Ultrasonic wave and pulse technique	Zr	[8], [18], [20]
	34-36	Frequency oscillator technique	Zircaloy-2, Zr-2.5Nb	[23]
Poisson's ratio	0.32-0.35	Pulse technique and resonance technique	Zr	[8][20]

* The macroscopic tensile tests were carried out at a strain rate in the range from 10^{-4} to 10^{-2} s^{-1} .

Slip systems and deformation twinning have been studied in order to understand the anisotropic deformation behaviour of Zr and its alloys. The $\langle a \rangle$ prismatic slip is the most reported slip type in polycrystalline samples at room temperature [22], [25]–[27]. The $\langle a \rangle$

basal slip and the $\langle c+a \rangle$ pyramidal slip were mainly observed at elevated temperature or under specific circumstances [22], [28], [29]. The critical resolved shear stress (CRSS) for the $\langle a \rangle$ prismatic slip was found to be notably lower than other slip systems for microscale specimens in the work of Gong et al. [22]. A pronounced difference in the CRSS among various slip systems is also observed in macroscopic experiments [27], [28], [30], [31] (Table 2.2). Some important crystallographic planes and directions are illustrated in Figure 2.2.

Table 2.2 Deformation systems in Zr. Reproduced from the work of Ballinger et al. [26]

Type	Direction	Plane	Crystallographic description	Temperature range	Stress range
Slip	$\langle a \rangle$	Prismatic	$\{10\bar{1}0\}\{1\bar{2}10\}$	All	Lowest
	$\langle a \rangle$	Basal	$\{0001\}\{1\bar{2}10\}$	High	
	$\langle c+a \rangle$	Pyramidal	$\{10\bar{1}1\}\{11\bar{2}3\}$ $\{11\bar{2}1\}\{11\bar{2}3\}$	Intermediate High	High High
Tensile twinning	$\langle c+a \rangle$	Pyramidal	$\{10\bar{1}2\}\{1\bar{0}11\}$ $\{11\bar{2}1\}\{1\bar{1}26\}$	Intermediate Low	
Compressive twinning	$\langle c+a \rangle$	Pyramidal	$\{11\bar{2}2\}\{1\bar{1}23\}$ $\{10\bar{1}1\}\{1\bar{0}12\}$	Low to intermediate Intermediate to high	

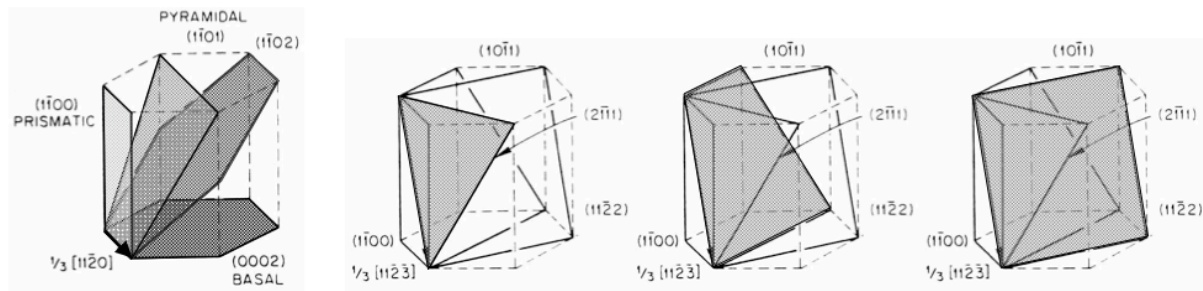


Figure 2.2 Illustration of some crystallographic planes and directions of the α -Zr lattice.

2.2 Zirconium Hydrides

2.2.1 Hydrogen Solubility and Hydride Precipitation

Hydrogen diffuses into zirconium claddings to form hydrides when its concentration exceeds the terminal solid solubility (TSS). The TSS of H in Zr is high at elevated temperature, for instance, 50-120 ppm wt at 300°C; but it drops rapidly to 0.1-0.4 ppm wt at room temperature [32], [33]. The true equilibrium value of TSS, however, may be difficult to measure due to the large local volume expansion associated with hydride formation (Section 2.2.3 and Table 2.3) [34]. Figure 2.3 shows the linear fits for the logarithm of TSS against the reciprocal temperature. The terminal solid solubility for precipitation during cooling (TSSP) is higher than that for dissolution during heating (TSSD) at any given temperature. The variation in TSSP measurements obtained from different studies partly arises from the difference in the thermal histories [33].

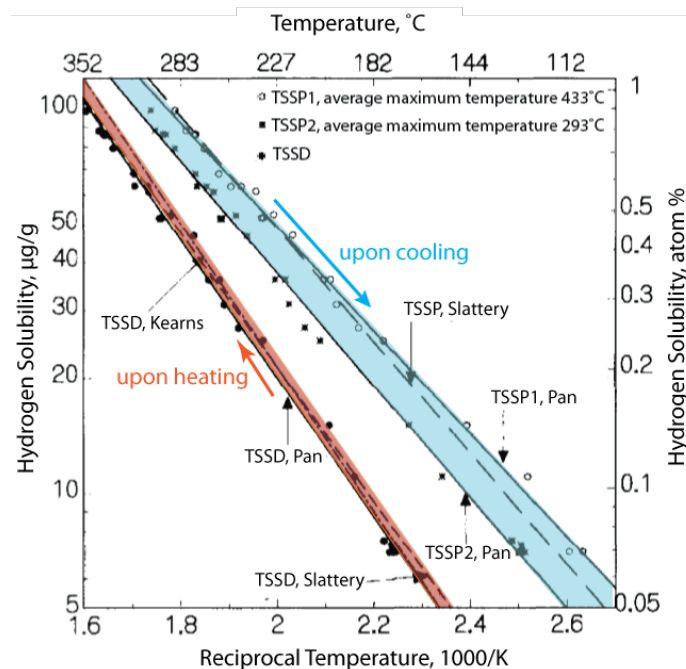


Figure 2.3 Terminal solid solubility for precipitation (TSSP) is higher than that for dissolution (TSSD) in a range of temperatures. The difference between TSSP1 and TSSP2 indicates that the hydrogen solubility increases at a given temperature during cooling when the maximum temperature of the prior thermal cycle increases [32], [33], [35].

2.2.2 Zr-H Phase System

The equilibrium phase diagram of the Zr-H system is shown in Figure 2.4 [36]. It consists of two allotropic Zr phases, α -Zr (hcp) and β -Zr (bcc), and three hydride phases. Zr undergoes martensitic transformations from β -Zr to α -Zr if quenched from elevated temperature. The eutectoid decomposition of $\beta \rightarrow \alpha + \delta$ occurs at $\sim 550^\circ\text{C}$ and ~ 37.5 at% H [4]. The α -Zr can take certain amount of hydrogen up to 5.9 at% H in the solid solution at 550°C . The $\alpha/(\alpha+\delta)$ solvus boundary can be considered as the TSS for hydrogen (Figure 2.3). The β -Zr exists above 550°C which is higher than the current reactors' operating temperature of $\sim 300^\circ\text{C}$. Apparently it has received fewer attentions than the α -Zr. The γ -hydride is probably a metastable phase produced by martensitic shear transformation below $\sim 286^\circ\text{C}$ as denoted by the dotted line in the phase diagram [4], [36]. It tends to form at a high cooling rate ($>2^\circ\text{C}/\text{min}$) [37]. The stability of the γ -hydride has raised much discussion [38], [39]. A narrow γ -hydride phase region at the H/Zr atomic ratio of ~ 1.0 was proposed by Mishra et al. [40] however the phase stability was questioned in some other studies [41], [42]. Lanzani and Ruch [43] reviewed the specimen composition reported in the literature and pointed out that the amount of impurities and alloying elements appears to be a determining factor; the experimental evidence supported that the γ -hydride is an equilibrium phase in high purity Zr while it is metastable in less pure Zr.

The δ -hydride exists as a single equilibrium phase with a limited range of hydrogen concentration of ~ 61 - 63 at% at room temperature but stable δ -hydrides coexist with the α -Zr over a wide range of hydrogen concentration and temperature. This $(\alpha+\delta)$ phase region receives the most attention because of the operating condition of a nuclear reactor. Hydrided zirconium having a composition in this $(\alpha+\delta)$ phase region is usually referred to as ZrH_x ,

where x denotes the range of the bulk H/Zr ratio, due to its non-stoichiometric composition.

The ϵ -hydride is another stable hydride at H/Zr > 1.74 (63.5 at%) at room temperature [44].

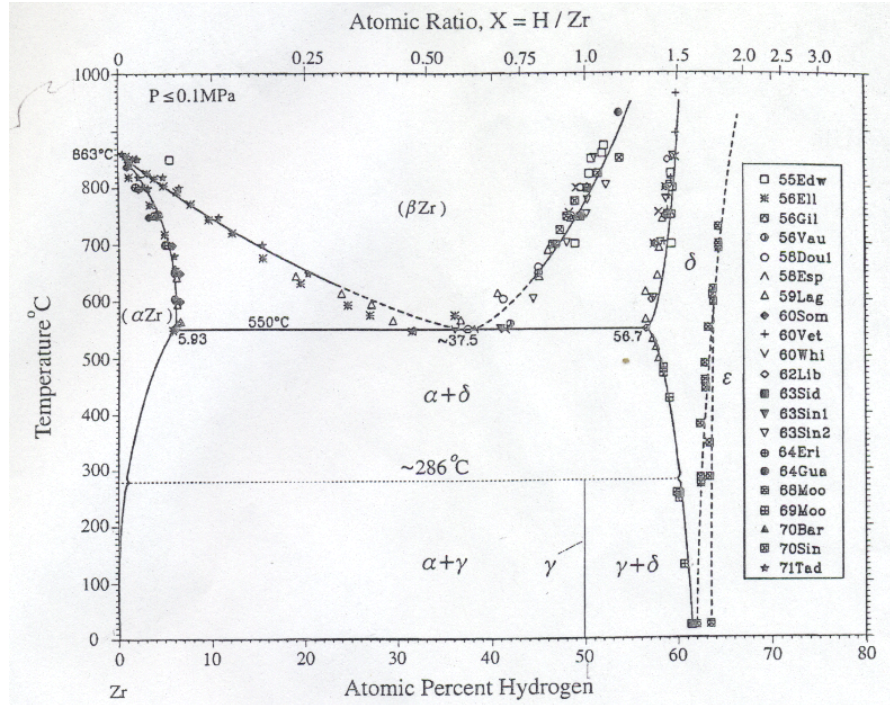


Figure 2.4 Zr-H binary phase diagram [36].

2.2.3 Crystallographic Properties and Relationships

The δ -hydride has a disordered fcc structure of CaF_2 type where H atoms occupy 6 to 7 out of 8 tetrahedral interstices in each unit cell at room temperature (Figure 2.5) [45]. Some of its crystallographic properties are summarised in Table 2.3. The precipitation of the δ -hydride is favoured under the conditions of low cooling rate, high hydrogen concentration or when tensile stress is applied [42], [46]–[48]. The volume change associated with the formation of the stable δ -hydride, 17%, is higher than that of the γ -hydride, 13% (Table 2.3). This misfit during precipitation allows work done by external tensile forces to lower the activation barrier to precipitation [4]. The hydrides therefore tend to nucleate preferentially in a region where local tensile stresses are applied [46], [47] (See Figure 2.13).

Table 2.3 Crystallographic properties of the α -Zr and the hydride phases [4], [36], [49]

	α -Zr	γ -hydride	δ -hydride	ϵ -hydride
Typical stoichiometry ^a	Zr	ZrH	ZrH _{1.6}	ZrH ₂
Pure phase region at room temperature ^b	H/Zr = 0-0.00	H/Zr = 1.00	H/Zr = 1.60-1.67	H/Zr = 1.74-2.00
	0-0.01 at%	50.0 at%	61.4-62.5 at%	63.5-66.7 at%
	0-0.00 wt%	1.08 wt%	1.71-1.79 wt%	1.87-2.15 wt%
Lattice structure	hcp	fct	fcc	fct
Space group ^b	<i>P6₃/mmc</i>	<i>P4₂/n</i>	<i>Fm$\bar{3}$m</i>	<i>I4/mmm</i>
a_0 (nm) ^b	0.323	0.460	0.478	0.498
c_0 (nm) ^b	0.515	0.497	0.478	0.444
c_0/a_0	1.59 (< 1.63)	1.08	1	0.89
Volume misfit	0%	+12.7%	+17.1%	+18.4%
Atomic positions of H atoms ^b	Tetrahedral or octahedral sites	Tetrahedral sites in alternate (110)	Tetrahedral sites, disorder	All tetrahedral sites
ICDD powder diffraction file ^b	00-005-0665	00-34-0690	00-034-0649	00-017-0314

a. The δ - and the ϵ -hydrides can exist over a wide range of hydrogen content (Figure 2.4). Typical stoichiometric values are used in the table. The γ -hydride is truly stoichiometric [45].

b. Room temperature data [4], [36], [50], [51]. See [49] for the form factor and the structural factor.

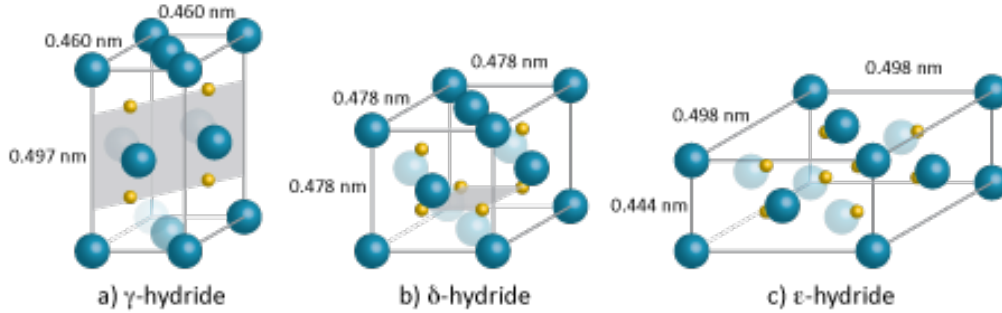


Figure 2.5 Illustration of unit cells of the hydrides. Blue and yellow spheres represent the Zr atoms and the H atoms respectively. These figures are not in scale. a) γ -hydride: fct ($c/a > 1$); four H atoms lay in the (110) plane. b) δ -hydride: fcc ($c/a = 1$); H atoms distribute at the tetrahedral sites. c) ϵ -hydride: fct ($c/a < 1$); eight H atoms occupy all tetrahedral sites.

The crystallographic relationships between the hcp α -Zr and the fcc δ -hydride have been identified with the use of metallography, EBSD and TEM. The most commonly reported relationship is $(0001)_\alpha || (111)_\delta$ and $[11\bar{2}0]_\alpha || [1\bar{1}0]_\delta$ [37], [50]–[58]; in which the two

phases have coincident close packed plane and direction and they share the same lattice arrangement with a small lattice mismatch. Experiments have been carried out to observe the habit plane, which is the crystallographic plane of the α -Zr crystal with which the broad face of the δ -hydride plate coincides [59]. The general understanding is that the δ -hydride precipitates or platelets align along $[\bar{1}\bar{1}20]_{\alpha}$ on the basal plane $(0001)_{\alpha}$ [37], [53]–[56], [60] and these precipitates pile up to form a packet or cluster that lies on the plane $(10\bar{1}7)_{\alpha}$ [55]–[57], [60], [61]. Therefore $(10\bar{1}7)_{\alpha}$ is usually considered as the habit plane but $(0001)_{\alpha}$ has also been reported for a different definition. The same crystallographic relationship and habit plane are likely independent of the alloying elements and they are commonly observed for both intergranular and intragranular hydrides. Hydride/hydride twin boundaries have been observed in samples prepared under different conditions [15], [37], [54], [56]–[58].

2.2.4 Microstructure and Morphology of Hydrides

Hydride precipitates have been considered to be responsible for embrittlement in Zr since the early 1950s [3]. The microstructure and morphology of hydrides are important because the degree of embrittlement depends on factors such as their concentration, distribution and orientation relative to the stress system [4]. Hydrides can be distinguished from the Zr matrix under polarised light. Figure 2.6 shows two Zircaloy-4 samples prepared at different cooling rate after hydrogen homogenisation at 400°C from the work of Birch et al. [62]. By comparing the micrographs, the example shows that the morphology and distribution of hydrides is dependent on the cooling rate. Figure 2.7 shows a Zircaloy-4 sample with over 8 times higher hydrogen content [43]. Thick packets or clusters that consist of fine precipitates form on the surface.

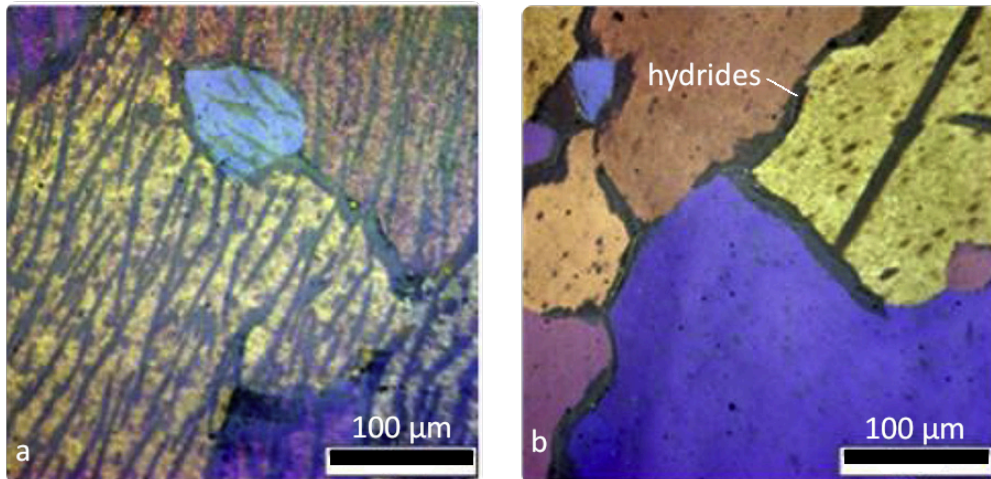


Figure 2.6 Polarised light micrographs show that the morphology of Zr hydrides depends on the cooling rate. The annealed Zircaloy-4 samples were hydrided by electrolytic charging and homogenised at 400°C for 7 hours followed by a) air cool at ~10°C/min (180 ppm wt H) and b) furnace cool at 0.05°C/min (152 ppm wt H) [62].

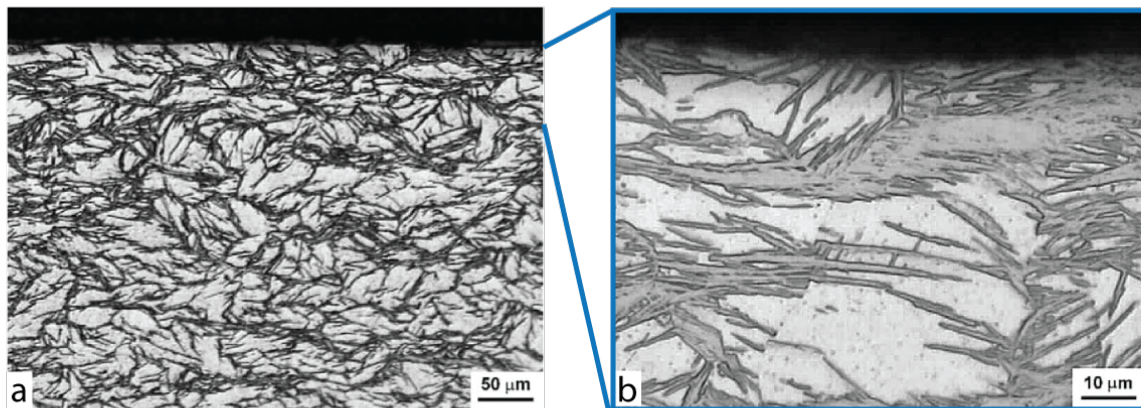


Figure 2.7 Optical micrograph of a Zircaloy-4 sample with a high H content (~1500 ppm wt). a) The dark region consists of hydrides. b) Local image of hydride packets or clusters [43].

TEM is able to show sharp the Zr/hydride phase boundary and the internal structure of a packet (Figure 2.8) [53], [54], [56] while SEM is usually used to characterise the dual-phase microstructure. Figure 2.9 shows the same batch of samples examined under SEM and TEM [63]. Hydrides of ~1 µm in length and ~50 nm in width are seen to align with $\langle 11\bar{2}0 \rangle_{\alpha}$.

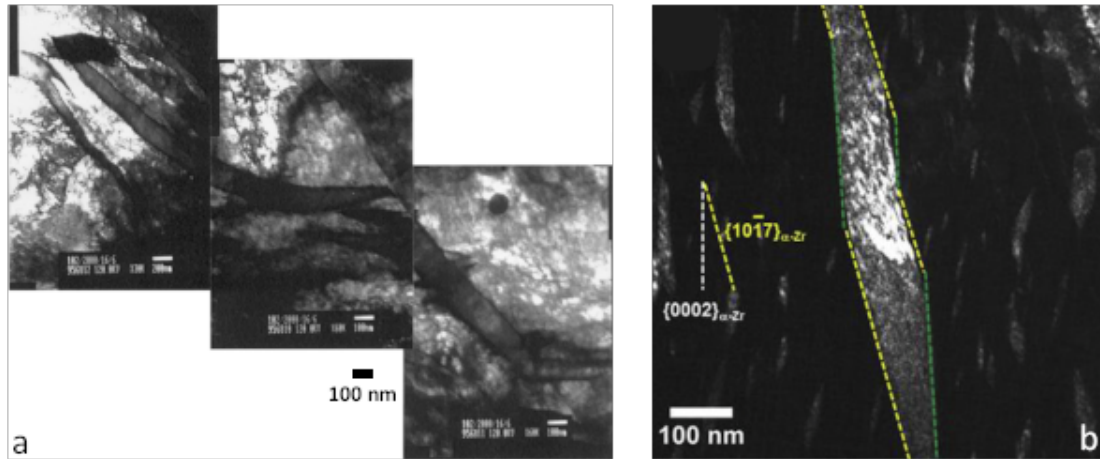


Figure 2.8 TEM examination from two studies. a) A hydride packet in stress-relieved Zircaloy [54]. b) Dark-field TEM image by selecting (111) diffraction spot for the δ -hydride. The hydride packet aligns with $(10\bar{1}7)_\alpha$ [56].

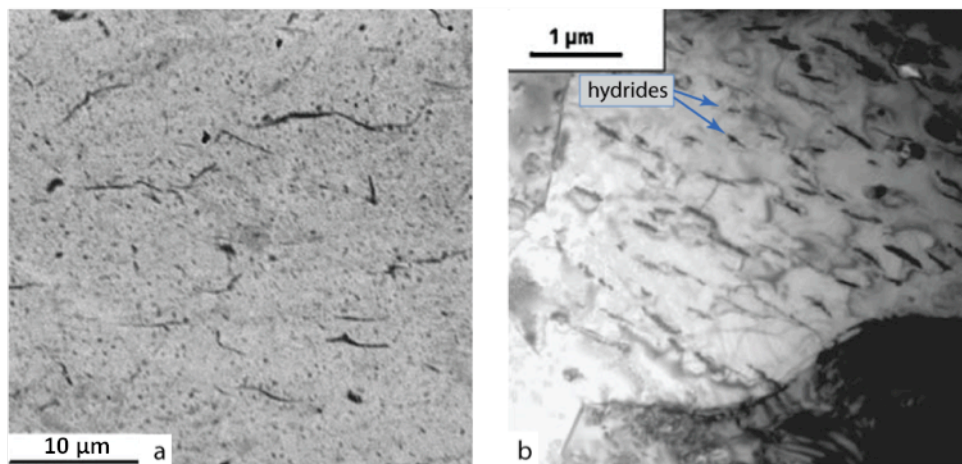


Figure 2.9 The morphology of a Zircaloy-4 sample containing ~200 ppm wt H as examined in a) SEM and b) TEM. Intragranular hydrides show clear crystallographic alignment [63].

Dislocations around individual hydride precipitates have been observed in the work of Bailey in the 1960s [64] (Figure 2.10). The number of dislocations was reported to increase with the thickness of precipitates. This suggests the strain resulting from the non-uniform thickness growth of hydrides is accommodated by long segments of dislocations that punched out into the matrix. Carpenter et al. later showed that these dislocations possess a Burger's vector of $\frac{1}{3}\langle 11\bar{2}0 \rangle_\alpha$ [65] and a significant proportion of them would not annihilate in dissolution [66].

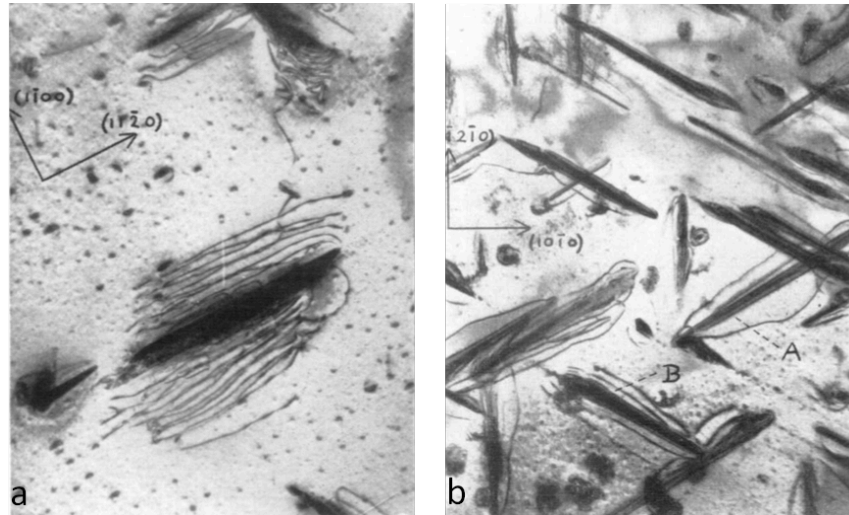


Figure 2.10 a and b) Dislocations are observed to be around individual hydride precipitates in rapidly cooled pure Zr. These needle-shaped hydrides preferentially grew along $\langle 11\bar{2}0 \rangle_{\alpha}$. The length of the precipitates is $\sim 1.5 \mu\text{m}$ and their maximum thickness is $\sim 0.5 \mu\text{m}$ [64].

Hydride growth can generate dislocations in both phases around the Zr/hydride interface. In Figure 2.11a, dislocations are seen attached to the interface in the δ -hydride in order to accommodate the local misfit strain [58]. In Figure 2.11b, dislocations are seen attached to the ends of a precipitate in the α -Zr. They are in the form of completely or partially closed loops running parallel to the long axis of the precipitate [63].

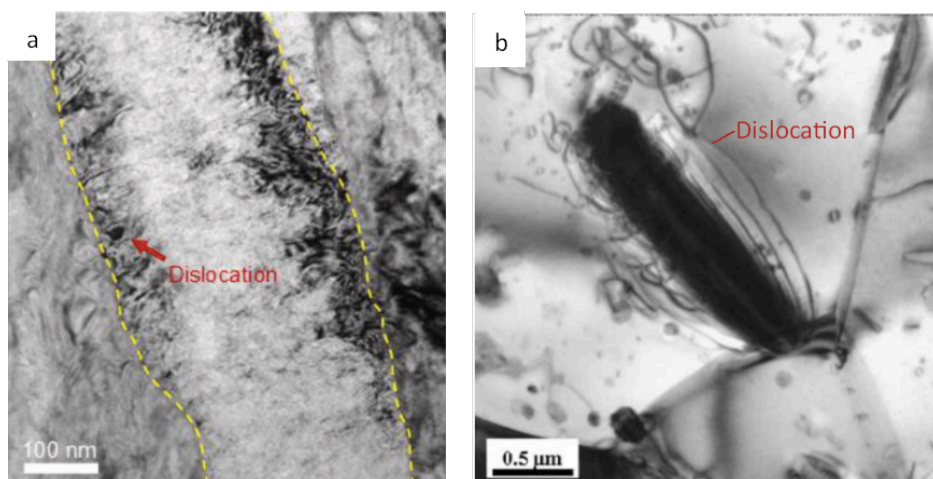


Figure 2.11 TEM examination of hydrides from two individual studies. a) Dislocations are seen attached to the Zr/hydride interface inside the precipitate in a Zr-Sn-Nb sample [58]. b) Dislocations are seen outside the precipitate in a furnace cooled Zircaloy-4 sample [63].

The distribution of hydrides depends on many factors such as texture of the parent material, hydriding condition and stress condition [49], [55], [67]–[71]. Figure 2.12 shows the transverse-radial section of a Zircaloy-4 cladding tube specimen that were hydrided under stress-free condition [49]. A stack of dense circumferential hydride platelets can be seen on the outer edge. The hydride rim thickness increased with the hydrogen content.

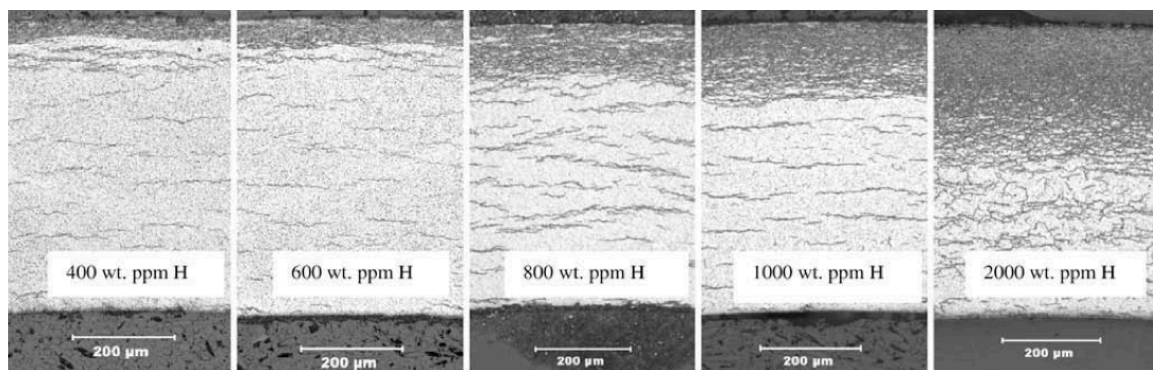


Figure 2.12 Hydride rim on the transverse-radial section plane of a Zircaloy-4 cladding specimen shown in optical micrographs. Hydrides precipitated preferentially along the transverse direction [49]. The indicated hydrogen contents are overall average values.

The effect of stress on the preferential orientation of hydrides is demonstrated in the work of Louthan and Marshall [70]. In Figure 2.13a, the sample was loaded in bending prior to hydriding. Hydride plates precipitate preferentially in an orientation with their planes being perpendicular to the direction of the applied tensile stresses. In Figure 2.13b, the gauge mark was punched into a tensile specimen prior to hydriding under tension. The hydride plates orientated parallel to the walls of the indentations subsequent to autoclaving at 400°C. When a hydrided sample is heated to allow hydride dissolution and loaded during cooling, hydride reorientation occurs in response to the applied stress. A recent work by Weekes et al. shows that the degree of reorientation is higher when a hot rolled Zircaloy-4 sample is loaded in transverse direction compared to rolling direction by using in situ X-ray diffraction [72].

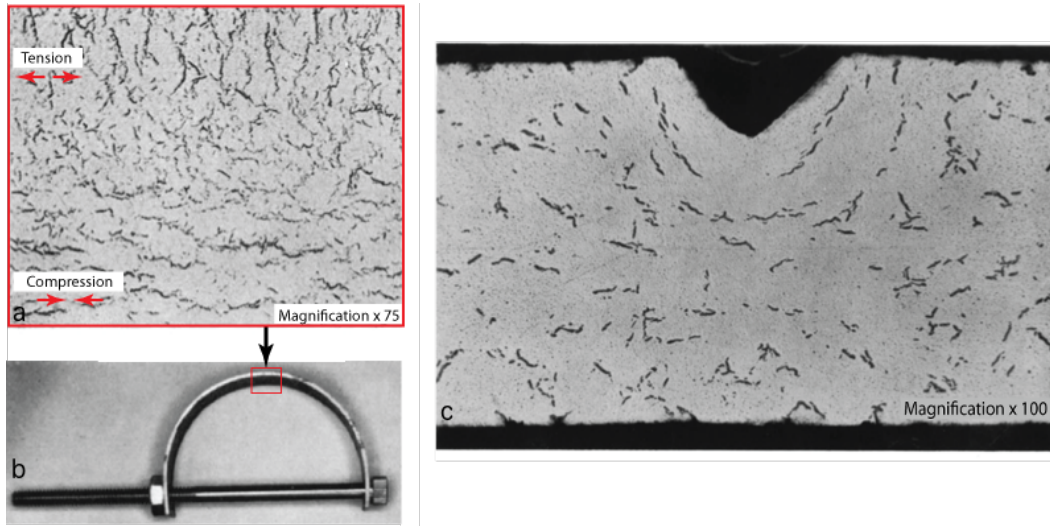


Figure 2.13 Effect of stress during precipitation on hydride orientation. a and b) The Zircaloy sample was bent before being hydrided with < 200 ppm wt H. c) The gauge mark was punched into the sample before hydriding under tension. See the original paper for scale [70].

High resolution EBSD has been used for mapping crystallographic orientations of individual hydride packets and their relationship with the neighbouring Zr grains. In Figure 2.14b, a higher degree of misorientation was observed in the hydrides than that in the matrix, indicating higher dislocation density in the hydrides [57].

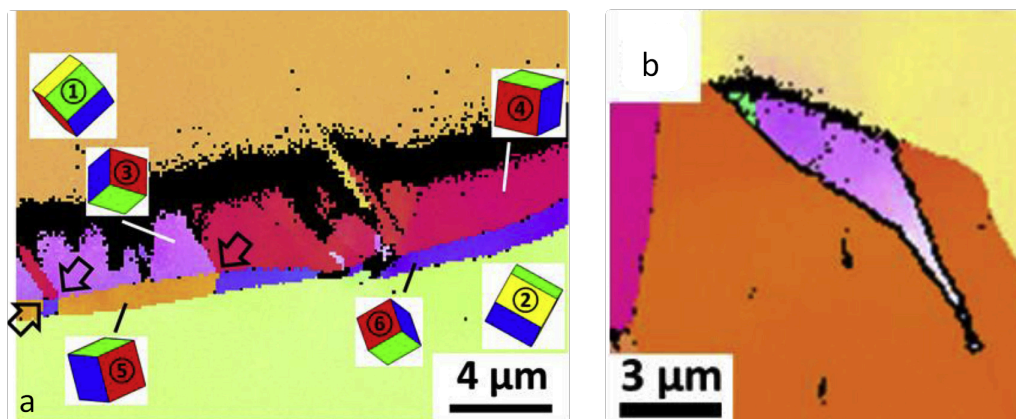


Figure 2.14 a) EBSD map shows an intergranular hydride packet that contains twin boundaries. b) High internal orientation gradient was observed within a hydride grain [57].

2.3 Mechanical Properties of Zirconium Hydrides

2.3.1 Microhardness, Nanohardness and Elastic Properties

Microhardness of Zr hydrides obtained from different studies are in general agreement [16], [17], [73]–[75]. In Figure 2.15, the microhardness increases with the fraction of the δ -hydride as the bulk hydrogen content increases until $H/Zr \sim 1.5$. Then the sharp reduction at $H/Zr > 1.6$ is associated with the $\delta \rightarrow \epsilon$ hydride phase transformation [74]. The maximum microhardness is ~ 2.8 GPa, therefore the diagonals of the Vickers indent mark would be over $36 \mu m$ as the indent load is over 2 N. Since the typical size of hydride precipitates is $\sim 1 \mu m$ (See Section 2.2.4), the indented area must contain a mixture of hydride precipitates and the Zr matrix. The difference in local volume fraction of hydrides that present in the indented materials might influence the measured values reported in the literature.

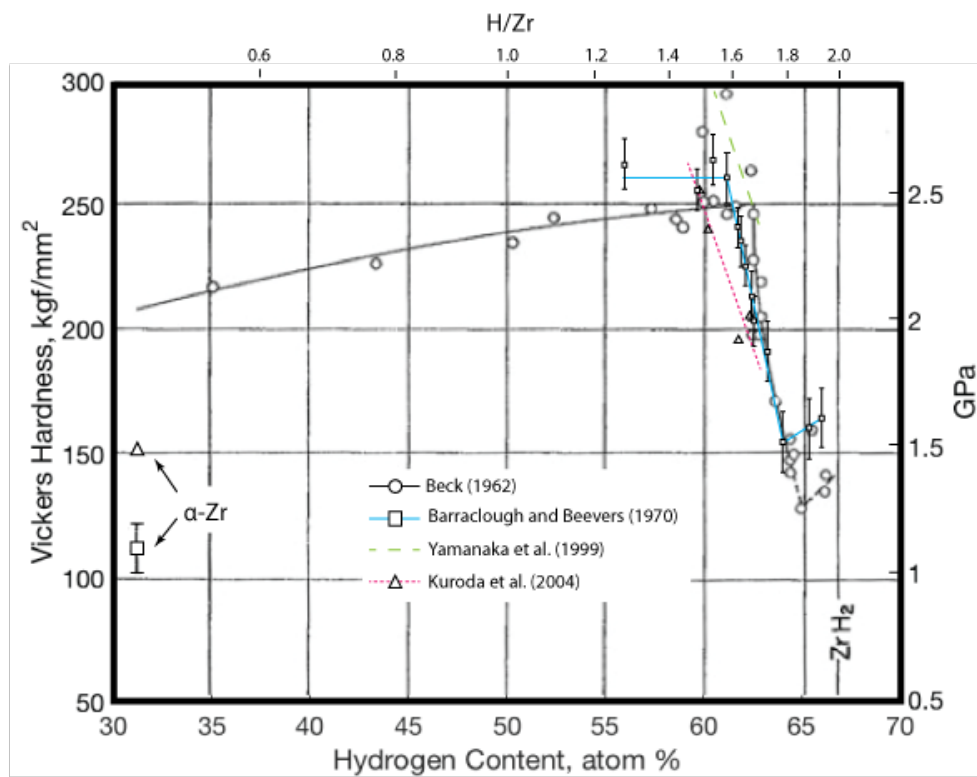


Figure 2.15 Microhardness of bulk Zr hydrides at various hydrogen contents. The hardness increases with the proportion of the δ -hydride when $H/Zr < 1.6$. The measured value starts to drop when the proportion of the ϵ -hydride increases [17], [19], [73], [74].

Nanohardness tests provide hardness measurement over a small area of few square microns. The results reported for nanohardness are compared with the microhardness measurements in Figure 2.16. [17] The hardness of all Zr hydrides is markedly higher than that of pure Zr at all indentation loads. The difference in nanohardness between the $\text{ZrH}_{1.487}$ and the $\text{ZrH}_{1.662}$ samples is smaller than that of the microhardness; it is however inconclusive to show that the influence of hydrogen content is inconsequential at a smaller indentation load. The hardness tends to increase with the decrease in indentation load. This indentation size effect (ISE) is described in Section 2.4.1 and Section 6.3 in conjunction with the interpretation of the nanoindentation results reported in this thesis.

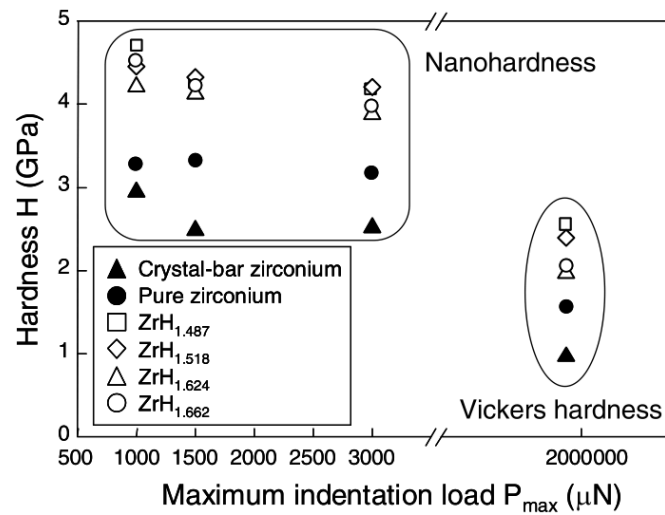


Figure 2.16 Comparison of nanohardness and Vickers hardness measurements obtained in unhydrided and hydrided Zr samples [17].

The elastic moduli of Zr hydride have been determined through many methods [16], [18], [73], [76]–[78]. In Figure 2.17, the dynamic moduli obtained by using the ultrasonic pulse-echo technique are clearly higher than other mechanical test results. The Young's modulus appears to remain constant in the $(\alpha+\delta)$ region when $\text{H/Zr} < 1.6$, indicating the two phases might have a very similar modulus. The stiffness starts to drop until $\text{H/Zr} \sim 1.8$ where the ϵ -hydride becomes the major phase.

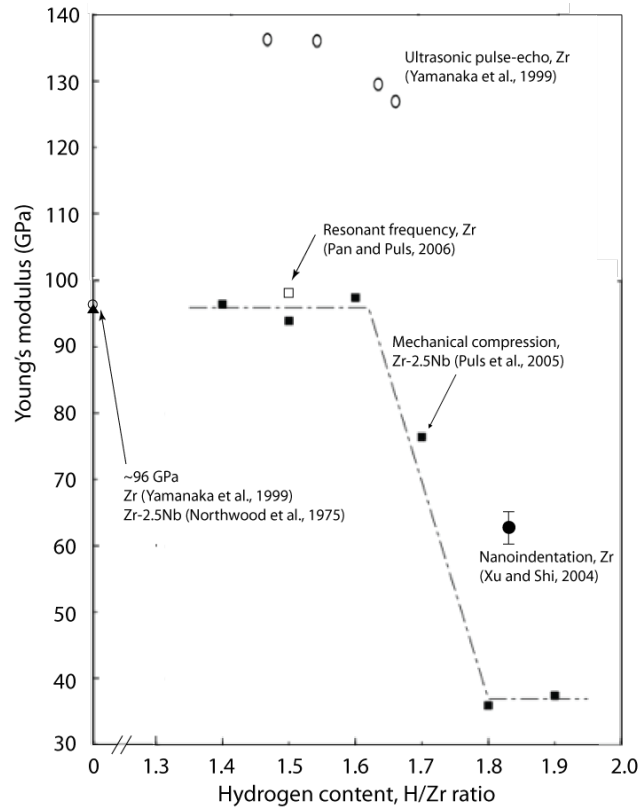


Figure 2.17 Young's modulus versus hydrogen content for various Zr alloys at room temperature [16], [23], [73], [77], [78].

2.3.2 Ductility, Yield and Hydrogen Embrittlement

The presence of hydride precipitates in Zr and its alloys can lead to hydrogen embrittlement. The ductility and fracture toughness are reduced such that small strain failure may occur [3], [4]. In DHC, the tensile strain field near a crack tip favours precipitation of brittle hydrides when Zr is exposed to a hydrogen source. Microcracks extend by a distance in the scale of hydride length when the sub-critical condition involving the stress intensity factor of the local dual-phase microstructure is attained. The microcrack propagation ceases in the ductile Zr matrix followed by hydrides precipitation at the new crack tip. This stepwise microcrack growth process repeats and lead to a substantial large-scale crack growth [5], [34], [79]. The local stress which initiates the brittle fracture of hydride precipitates is therefore a key input parameter to models of DHC [79]–[81]. Studies have shown that the degradation of

mechanical properties is influenced by factors such as: hydrogen content [14], [78], [82], temperature [75], [78], [83], heat treatment [3], [11], cooling rate [83], thermal history [33] and residual stresses [4].

Effect of Hydrogen Content

The effect of hydrogen content on the mechanical properties is illustrated in Figure 2.18. A drop in ductility is indicated by the monotonic decrease of elongation and the reduction of area with increasing hydrogen content. The increase in the ultimate tensile strength (UTS) below 600 ppm wt H is likely caused by dispersion hardening in which dislocations are impeded by hydride precipitates. The mechanical strengthening has been consistently observed in samples with hydrogen content up to 2000 ppm wt H [11], [13], [82]. Gill, Bailey and Cotterill [48] observed that brittle failures were associated with the continuous hydride networks and the progressive reduction in failure strain with the increasing precipitate concentration is a result from the reduction of load-bearing area of the metal matrix.

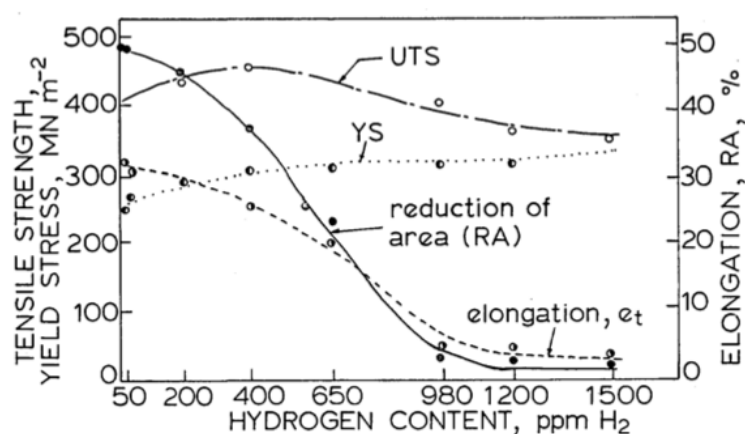


Figure 2.18 Effect of hydrogen content on mechanical properties. The results were obtained from macroscopic tensile tests on Zircaloy-4 at room temperature [14].

Figure 2.19a shows the stress-strain relations for compression specimens with relatively high hydrogen contents ($H/Zr > 1.4$) [78]. The material exhibits the most brittle behaviour when the δ -hydride is the dominant phase ($H/Zr \sim 1.4$ -1.6). In comparison, the specimens having the ϵ -hydride composition ($H/Zr \geq 1.7$) are more ductile but they are still relatively brittle compared to the unhydrided material. Figure 2.19b shows the yield strengths of the same batch of specimens. A notably drop can be seen from $H/Zr \sim 1.6$ to 1.8 where the major phase changes from the δ - to the ϵ -hydride.

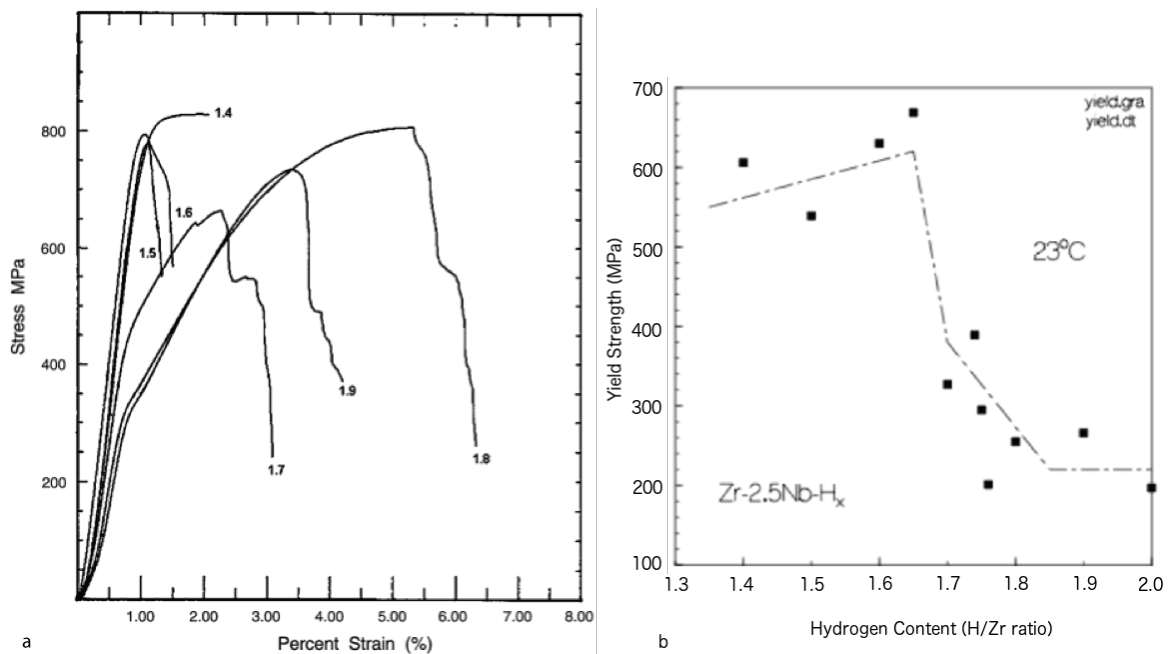


Figure 2.19 Deformation properties of bulk Zr hydrides. The samples were tested under compression at a strain rate of $2 \times 10^{-4} \text{ s}^{-1}$ at room temperature. a) Stress-strain curves of samples having a range of H/Zr ratios from 1.4 to 1.9. b) The yield strength measurements of the same batch of compression samples [78].

Microscale pillar specimens were used to investigate the properties of the δ -hydride in the work of Weekes et al. [15]. The yield strength of unhydrided Zircaloy-4 was determined to be $\sim 530 \text{ MPa}$, which is 15-43% higher than that for the bulk alloy [12] and 32% lower than the nanoindentation results [16]. In comparison, a notably higher value of $\sim 1600 \text{ MPa}$ was obtained for a hydride micropillar. More results are reviewed in Section 2.3.3.

Effect of Temperature

A range of brittle-ductile transition temperature from 50 to 400°C has been reported for Zr alloys having various hydrogen contents [82], [84], [85]. Figure 2.20a shows the stress-strain curves of bulk Zr hydride compression specimens tested by Barraclough and Beevers [75]. The specimens were completely brittle without apparent plasticity below ~100°C. Small plastic strains up to ~3% were observed between 100-120°C. The proportional limit decreases rapidly with increasing temperature from 20°C to 200°C as shown in Figure 2.20b. A similar drop of yield strength at elevated temperature was observed in the work of Puls et al. [78], although their compression test results that obtained were systematically higher than those of Barraclough and Beevers [75]. Shi and Puls [83] carried out tensile tests for Zr-2.5Nb samples having a low hydrogen content of ~100 ppm wt. Their results indicate that the yield strength and the hydride fracture strength decrease as the temperature increases (Table 2.4).

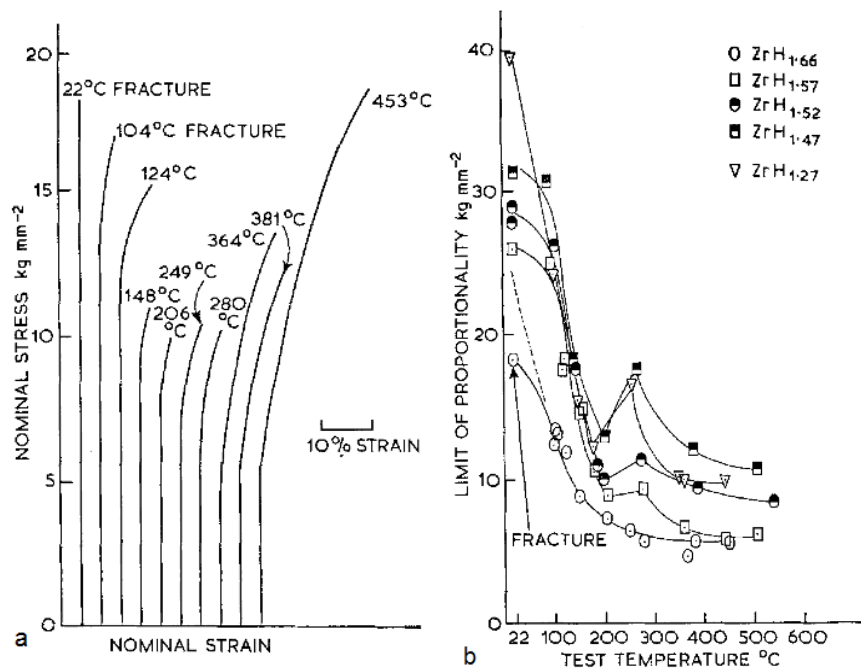


Figure 2.20 The deformation properties of bulk Zr hydrides at various temperatures. The results were obtained in a compression test at a strain rate of $3.3 \times 10^{-4} \text{ s}^{-1}$ a) Nominal stress-strain curves of ZrH_{1.66} samples. The specimens exhibited no measurable plastic deformation below ~100°C. b) Temperature dependence of the limit of proportionality [75].

Table 2.4 Effects of temperature on the mechanical properties of hydrided Zr-2.5Nb samples. The results were obtained from acoustic emission measurements in a tensile test at a strain rate of about $4 \times 10^{-4} \text{ s}^{-1}$ [83]

T (°C)	Type of specimens	σ_f (MPa)	σ_y (0.2%)(MPa)	σ_u (MPa)	Break at σ_u
23	As-received	-	772	797	No
23	As-received	-	748	772	No
23	Hydrided	650	Failed before 0.2% yield	704	Yes
50	Hydrided	644	752	752	Yes
75	Hydrided	643	720	725	Yes
100	Hydrided	643	660	663	Yes
105	Hydrided	644	Failed before 0.2% yield	664	Yes
125	Hydrided	638	650	654	No
150	Hydrided	-	632	635	No
180	Hydrided	-	577	581	No
180	Hydrided	-	586	589	No
250	As-received	-	536	568	No
250	Hydrided	-	541	546	No
* σ_f is the macroscopic fracture stress at which cracking of hydrides was first detected. σ_y is the yield strength and σ_u is the ultimate tensile strength.					
** As-received specimens contained <10 ppm wt H. Hydrided specimens contained ~100 ppm wt H					

Effect of Heat Treatment and Grain Size

Heat treatment correlates with the grain size, the microstructure and the hydride morphology. Two sets of heat treatments, recrystallisation (1.5 hours at 565°C) and stress-relieving (3.5 hours at 488°C), were used to prepare Zircaloy tensile samples followed by hydriding at 460°C in the work of Arsene et al. [11] (Figure 2.21). The average grain size was larger in the recrystallised material; a continuous network of brittle hydrides formed primarily along the grain boundaries at a low hydrogen content. In comparison, the same magnitude of ductility reduced at a higher hydrogen content in the stress-relieved material; in which neighbouring cracks were connected to form larger cracks. A similar effect of grain size on embrittlement was observed in slow-bend tests [85]. The degree of brittleness depends on the proportion of the cross-sectional area locally covered by brittle hydrides [3].

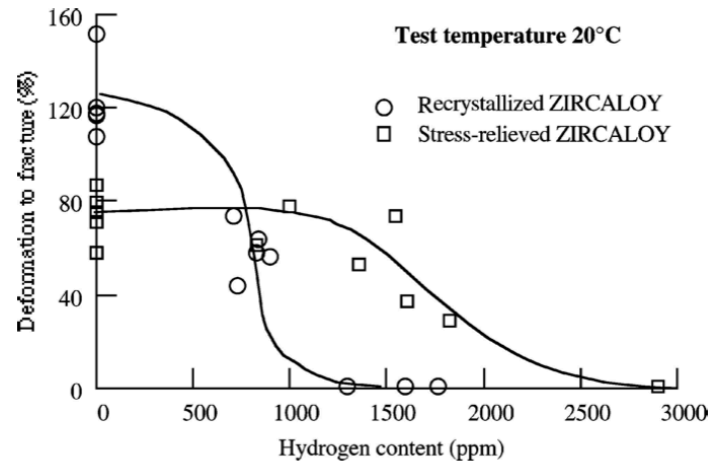


Figure 2.21 Fracture strains of Zircaloy samples with different heat treatments [11]

Effect of Cooling Rate, Thermal History and Stress System

Cooling rate affects the grain size of the α -Zr and the distribution, size and phase of the hydrides [8], [62], [86]. In the work of Shi and Puls [83], a range of cooling rates was used to grow hydrides to various sizes. The hydride fracture stress decreases with increasing hydride length. A different parameter, the ratio of hydride length to specimen thickness, was used by Coleman and Hardie [3] to characterise the elongation. The brittle δ -hydride tends to form at slow cooling as described in Section 2.2.3 and the fracture stress decreases as the proportion of the δ -hydride increases (Figure 2.22a) [75]. This can be related to the reduced resistance to the propagation of cleavage cracks in the δ -hydride (Figure 2.22b). The thermal history can influence the volume fraction of hydrides [33]. Its effect on the TSS hysteresis is described in Section 2.2.1. Texture can affect the distribution of hydrides because of their preferential precipitation along certain directions (See Section 2.2.3). The texture is therefore important because the effect of ductility is likely more deleterious when the plane of the hydride platelets is perpendicular to the tensile stress axis [4], [13]. The failure strains can be reduced by the presence of a tri-axial stress system near a notch [48], [87].

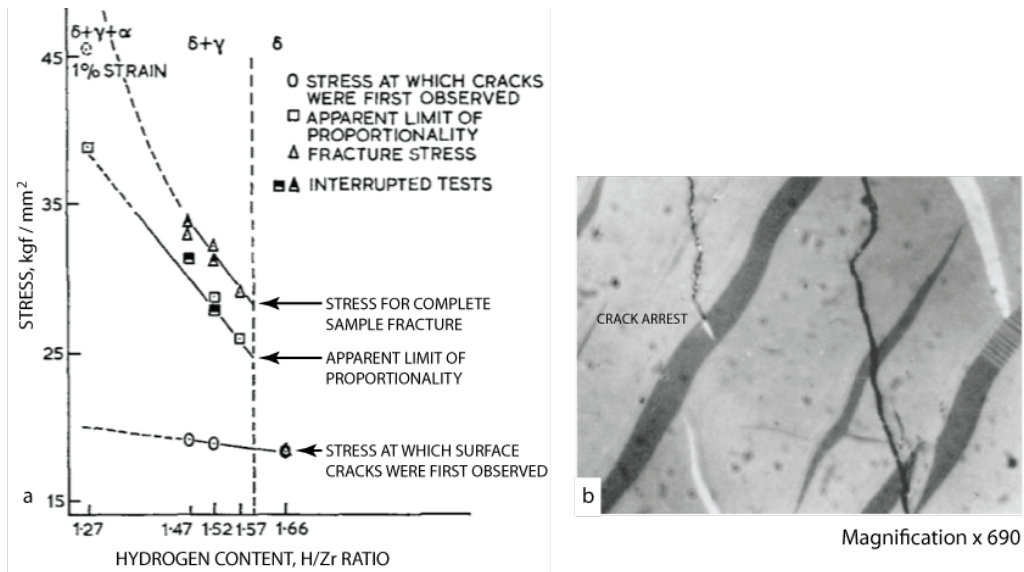


Figure 2.22 Effect of hydride contents on fracture. a) The dependence of characteristic stresses on the proportion of different phases of hydrides. Zr hydride becomes more brittle with a higher content of δ -hydride, as indicated by the decrease in fracture stress and the limit of proportionality. b) A $\text{ZrH}_{1.52}$ specimen after 0.5% strain at room temperature [75].

2.3.3 Deformation Behaviour and Fracture

The deformation behaviour of Zr hydride has been analysed through metallographic examination by Coleman and Hardie [3], [85]. The authors observed that fractures appeared to propagate through linking up cracks in cleaved hydrides by ductile parting of the intervening Zr and brittle fractures takes place below a certain inter-hydride spacing. In the work of Arsene et al. [11], [88], tensile specimens were tested *in situ* in an SEM. Cracks appeared to open in the δ -hydrides without propagating into the matrix (Figure 2.23); no cavity initiation or fracture of the Zr/hydride interface was observed. Cleavage features can be seen on the fracture surfaces after brittle failure as shown in Figure 2.24.

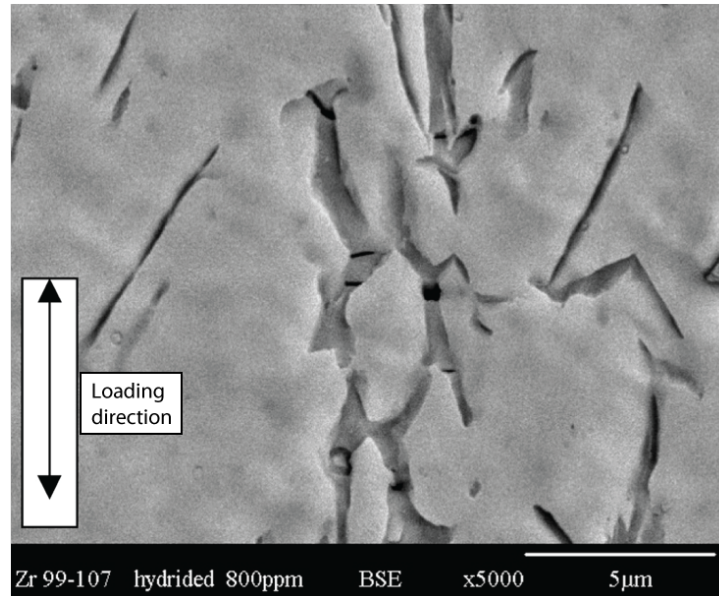


Figure 2.23 Cracks opened within hydrides during an *in-situ* SEM tensile test. The arrows indicate the loading direction in the back-scattered electron image [88].

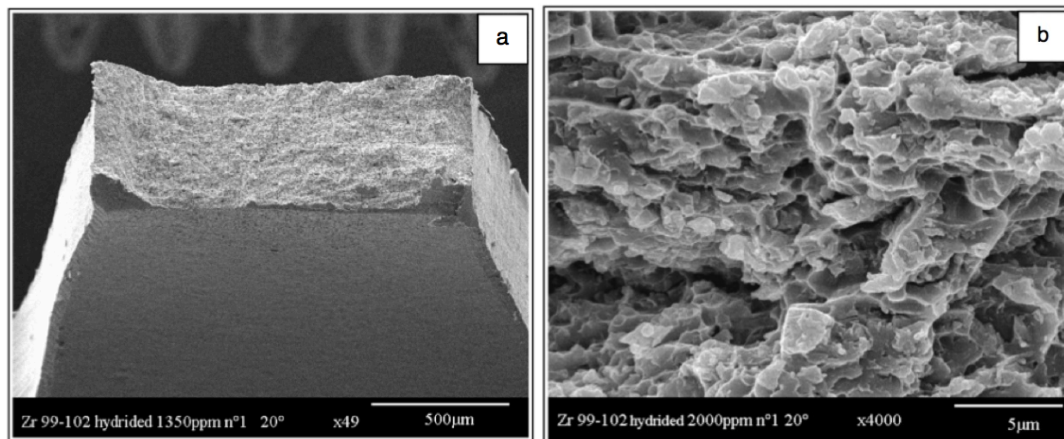


Figure 2.24 Fracture surfaces of hydrided Zircaloy samples. a) Brittle fracture surface of a sample with 1350 ppm wt H. b) Cleavage feature on the fracture surface of a sample with 2000 ppm wt H [11].

The $\{111\}_{\delta}$ operative slip plane in δ -hydride was observed above 100°C in the mechanical test carried out by Barraclough and Beevers [75] (Figure 2.25). However slip plane was not determined at room temperature since the samples were extremely brittle.

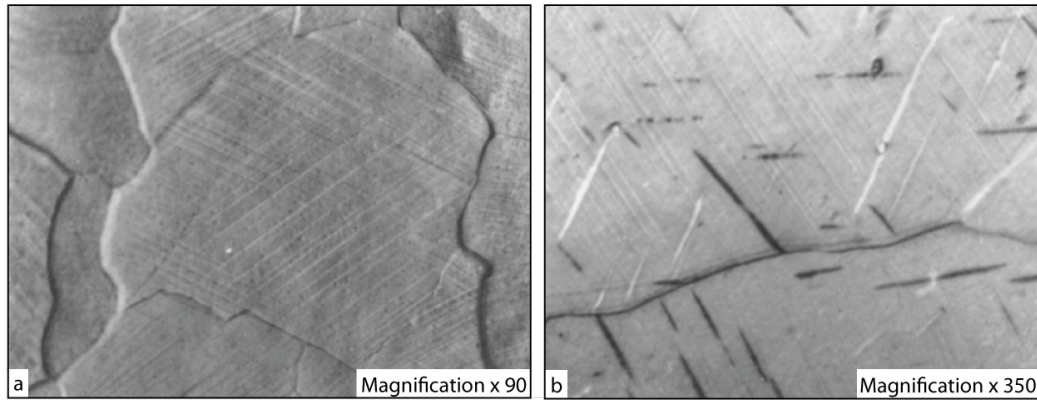


Figure 2.25 Slip lines observed on the surface of hydrided Zr samples at elevated temperature. a) Surface slips on a $\text{ZrH}_{1.66}$ sample after 2% plastic strain at 148°C . b) Planar slip lines in the δ -phase of a $\text{ZrH}_{1.57}$ sample after 2.5% plastic strain at 117°C [75].

TEM examination carried out by Veleva et al. [54] shows that dislocations seemed to exist inside deformed microscale hydrides at room temperature; however it was difficult to identify the slip planes. In an *in situ* SEM tensile test by Grange, Besson and Andrieu [13], slip bands that formed in the matrix appeared to transmit through transgranular hydrides. Both observations suggested that the δ -hydride exhibits certain degree of elongation at room temperature. The microscale plastic behaviour of hydrides was investigated by Weekes et al. [15]. The deformation responses of micropillar specimens were compared in an *in situ* SEM compression test. Figure 2.26a and b show an unhydrided Zircaloy micropillar. Shear bands were observed with a rotation about the c-axis; indicative of the $\langle a \rangle$ type slip in the Zr matrix. In comparison, shear bands that formed in the α -Zr matrix of a dual-phase micropillar appeared to arrest at the phase boundary without penetrating the hydride packet (Figure 2.26c and d). Dislocations and internal twinning of $(1\bar{1}1)_{\text{parent}} || (\bar{1}1\bar{1})_{\text{twin}}$ were observed in the hydride packet (Figure 2.26e and f).

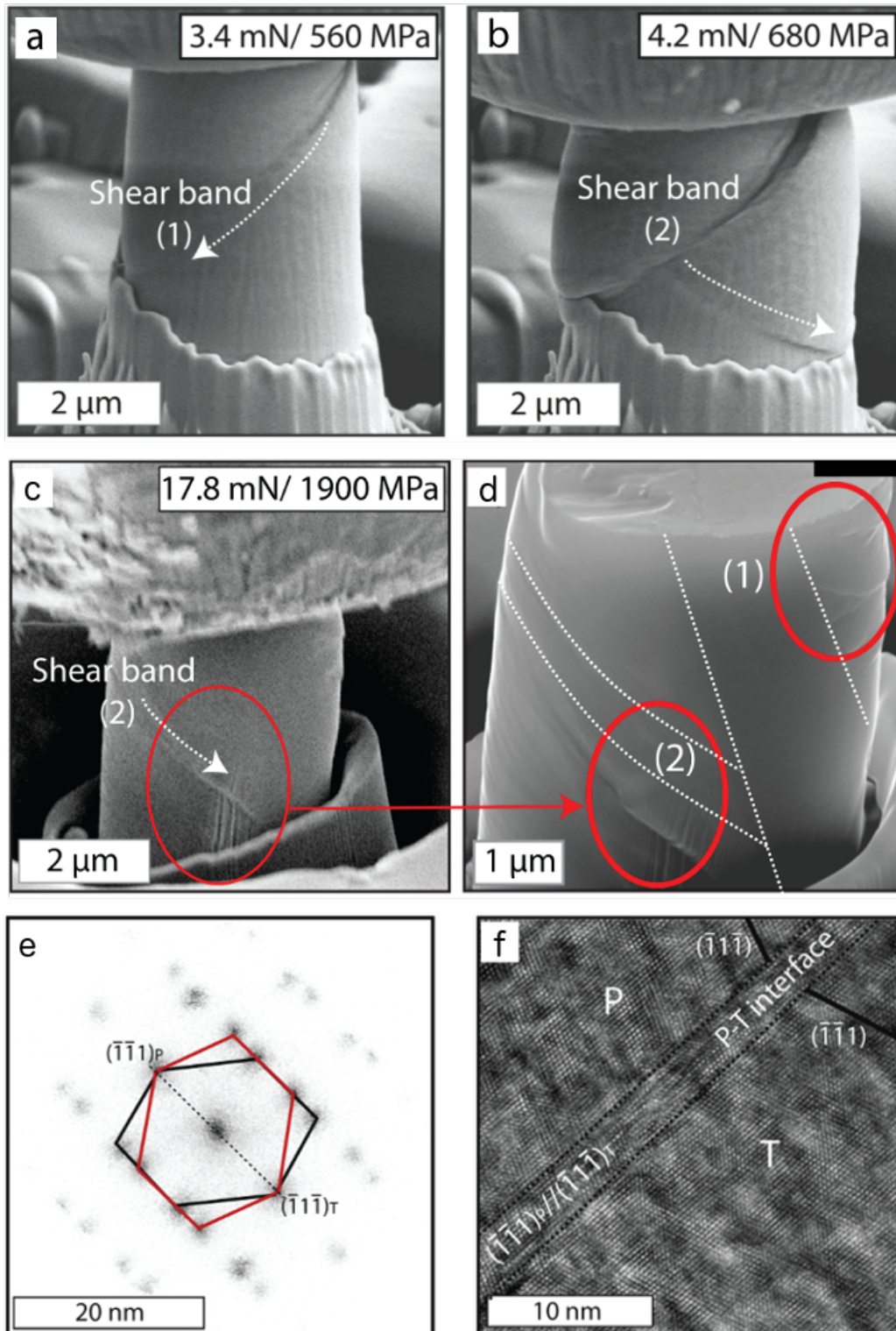


Figure 2.26 Micropillars loaded under compression [15]. a and b) Unhydrided Zircaloy specimen. Shear bands were observed shortly after yielding. c and d) Hydrided Zircaloy micropillar. White lines outline the hydride packets. Red circles indicate shear bands formed in the Zr matrix. e) Diffraction pattern shows the presence of the hydride and twin in a TEM foil extracted from a hydride-containing micropillar. f) High resolution phase contrast image of defects within a hydride platelet at the parent/twin interface (P: Parent, T: Twin).

Voids and steps were observed in the ductile fracture surface of Zircaloy-2 samples with low hydrogen content by Kerr et al. (Figure 2.27) [89]. They were likely related to fractures of acicular hydride clusters. Similar features were observed in notched tensile specimens by Huang and Huang (Figure 2.28) [82]. Voids or microcracks mainly nucleated in the hydride precipitate regions below the ductile fracture surface. These irregular features became more spherical as the temperature increased from 25°C to 300°C. Void coalescence was observed subsequent to hydride fragmentation and growth of cavities [13].

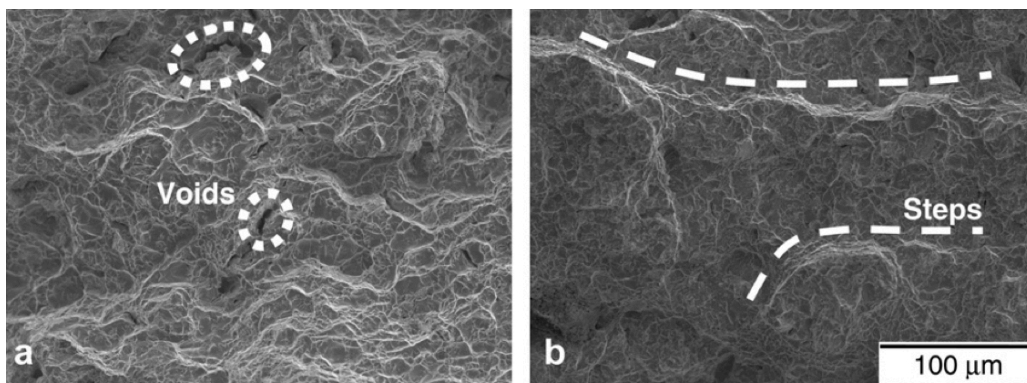


Figure 2.27 Fracture surfaces of a tensile Zircaloy sample with low hydrogen content (~90 ppm wt H). a) Voids were observed in the SEM micrograph. b) Steps formation was likely a result of the fracture of hydride plates [89].

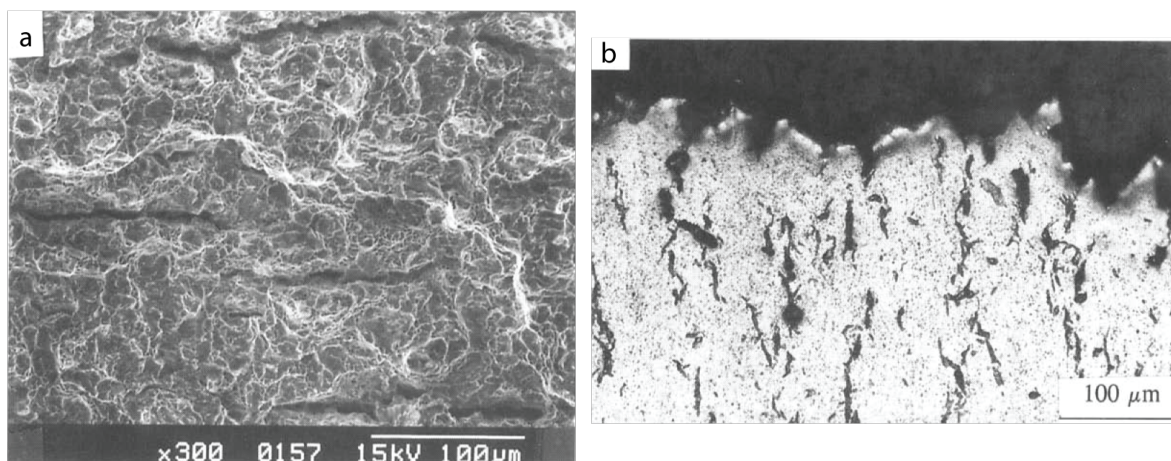


Figure 2.28 Microcracks observed after tensile test of a notched Zircaloy-4 sample containing 140 ppm H. SEM fractograph of a) the fracture surface b) the transverse section [82].

High resolution digital image correlation and EBSD have been applied to compare the localised strain introduced in the two phases by Thomas et al. [90]. Figure 2.29 shows the orientation map of an intergranular hydride packet that contains a number of hydride grains and the map of effective shear strain after tensile loading. Higher strain was observed in the α -Zr; likely attributed to the lower yield strength of the matrix in comparison with the hydrides. Shear bands initiated in the matrix were observed to terminate at the phase boundary and this result is consistent with the work of Weekes et al. [15].

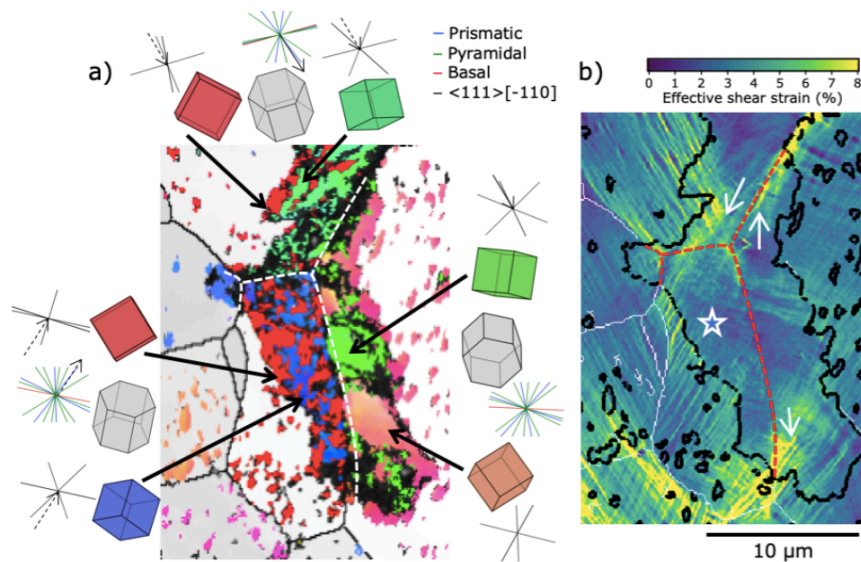


Figure 2.29 a) EBSD orientation map shows the crystallographic relationship between hydride grains in an intergranular packet in a Zircaloy-4 sample. b) The localised shear strain was measured with the use of digital image correlation [90].

2.3.4 Fracture Toughness and Crack Growth

The fracture toughness of bulk hydrided Zr has been measured from 3.5 mm thick conventional compact tension specimens by Simpson and Cann [91]. Figure 2.30 shows that the fracture toughness decreases as the hydrogen content rises due to the increased proportion of the brittle δ -hydride. In the SEM examination, transgranular cleavage and subsidiary cracks were seen in the samples having H/Zr > 1.0. Compact tension tests were also carried

out for hydrided Zircaloy-4 [12]. Most samples having low to medium hydrogen contents failed in ductile mode at room temperature.

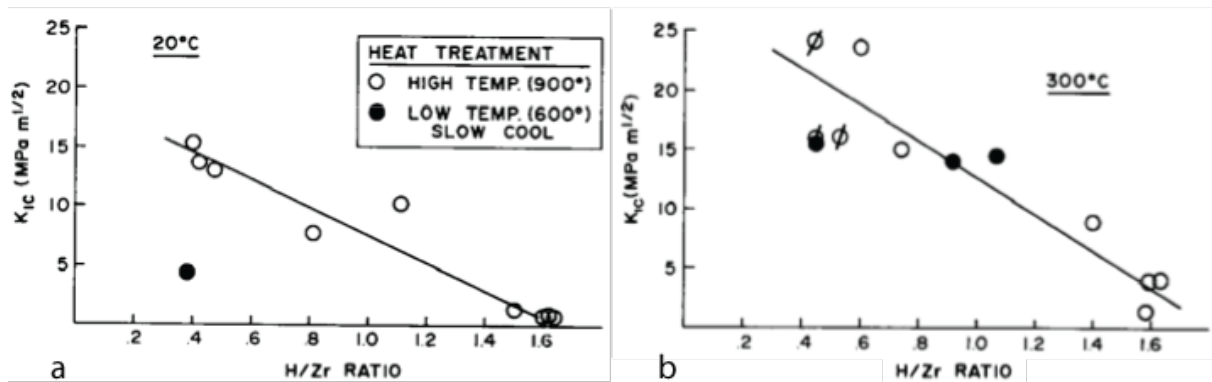


Figure 2.30 Influence of hydrogen contents on fracture toughness at a) 20°C and b) 300°C. A stroke through circles indicates that the specimens failed by through thickness necking [91].

The influences of hydride orientation and hydrogen content on the fracture toughness were studied by Bertolino, Meyer and Ipiña [92] using small single-edge band Zircaloy-4 specimens in an *in situ* SEM test. Higher fracture toughness values were obtained when the hydride precipitates were normal to the crack path than being parallel to it. The crack growth behaviour was investigated for samples with various hydrogen contents. Ductile failure was observed in unhydrided Zircaloy-4 (Figure 2.31a) as well as notched samples containing low hydrogen content (~170 ppm wt) (Figure 2.31b). A repetitive process involving crack blunting followed by development of a new crack tip occurred during the stable crack growth. Less plastic deformation and less blunting occurred for samples with medium hydrogen content (~600 ppm wt) (Figure 2.31c). Hydride precipitates located ahead the crack tip fractured in most of the tests. For samples with relatively high hydrogen content (~1300 ppm wt) (Figure 2.31d), a damage zone resulting from fractured hydrides was observed around the crack path.

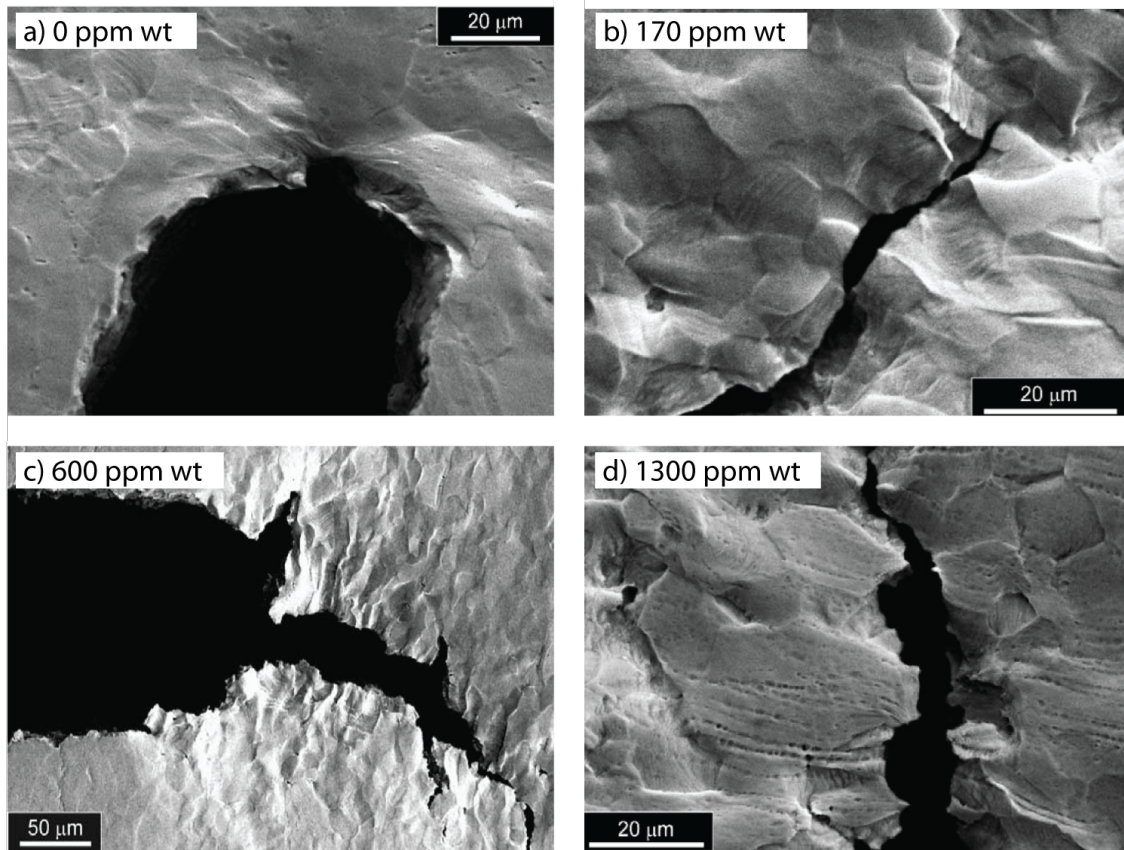


Figure 2.31 Crack growth in notched Zircaloy-4 samples with a range of hydrogen contents. a) Ductile failure in an unhydrided sample. b) A damage zone ahead the crack tip in a hydride rich area. c) Microcracks formation near the main crack tip. d) Crack growth following an intergranular path [92].

The effect of hydride reorientation on fatigue crack growth has been recently examined by Li et al [58]. Figure 2.32a shows an SEM image of the typical dual-phase structure after 15,000 fatigue cycles. Slip traces initiated in the Zr matrix are clearly seen to attach to fractured hydrides due to their distinct deformation response to stresses. A foil that contains Zr/hydride interface was lifted out across a hydride crack (Figure 2.32b). Lattice rotation and increased dislocations were observed in the hydride; indicating that plastic deformation has occurred. Figure 2.32c shows that the fatigue crack apparently propagated along the hydride/hydride interface. The analysis for diffraction patterns shows that the Zr/hydride crystallographic relationship has been deviated with a change of misorientation angle.

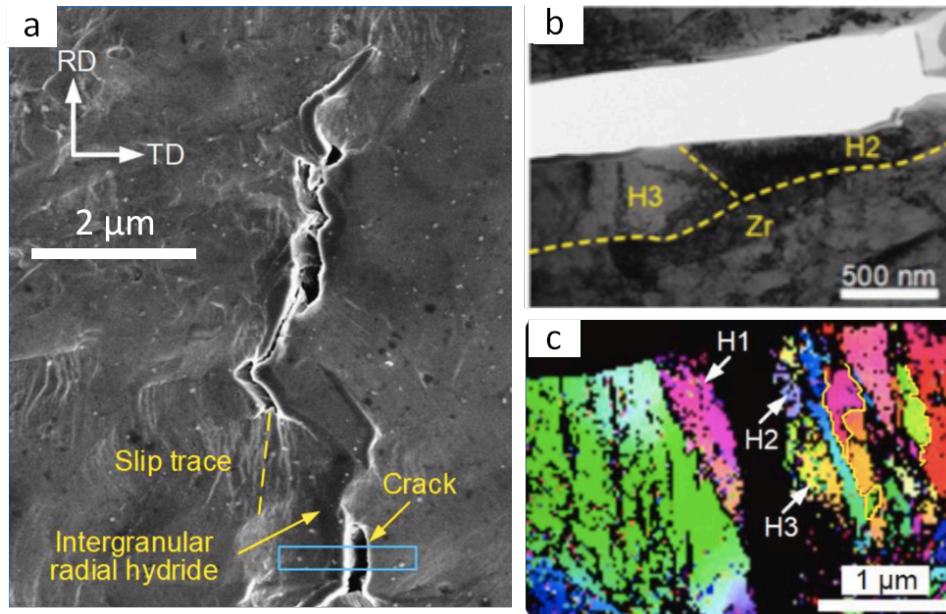


Figure 2.32 Examination of fatigue crack growth. Hoop stress is applied horizontally to the hydrided Zr–1.0Sn–1.0Nb–0.1Fe sample. a) SEM image shows that the Zr matrix underwent plastic deformation as indicated by slip traces that are attached to some fractured hydrides. b) Local dual-phase region in which the diffraction pattern analysis shows lattice rotation. c) The fatigue crack apparently extended along the hydride/hydride interface [58].

2.4 Micromechanical Testing Methods

2.4.1 Nanoindentation

Nanoindentation is a common micromechanical testing method for a wide range of materials [93]–[95]. It relies on measurement of the surface residual impression introduced by using an indenter tip under a controlled load. Advanced instrumental systems enable precise control of the stage position and continuous stiffness measurement (CSM) when an indentation is made [93], [96], [97]. These capabilities combined with technological development in imaging and characterisation techniques, such as SEM and AFM, allow material responses to be examined below sub-micron length scale [95], [98]. The indentation load-displacement data can be used to determine a variety of micromechanical properties; among which hardness and Young's modulus are most frequently measured [98], [99]. The interpretation of these measurements is however not necessarily straightforward; in particular hardness is dependent on indent depth.

Indentation Size Effect

A number of studies observed a pronounced increase in hardness and flow strength when the indent depth of a crystalline material is reduced to micron scale [100]. This physical phenomenon of enhanced hardening is usually referred to as indentation size effect (ISE). In a more general sense, Fleck and Hutchinson [101] proposed a plasticity theory to include an internal material length scale. The underlying idea is that material hardening is controlled by the total density of dislocations which have been stored, part of which being a storage of geometrically necessary dislocations (GNDs) resulting from the spatial gradient of plastic strain. This extra storage of GNDs appears because of the geometry of loading or because the material itself is plastically inhomogeneous. The concept of GND was applied to account for ISE in the mechanistically based model developed by Nix and Gao [102], [103]. Figure 2.33 illustrates that the material originally occupying in the indent region has been pushed into the underneath. GNDs must be present to accommodate the volume of material displaced by the indenter [100]. These extra storage GNDs could act as obstacles to dislocation motion causing enhanced hardening.

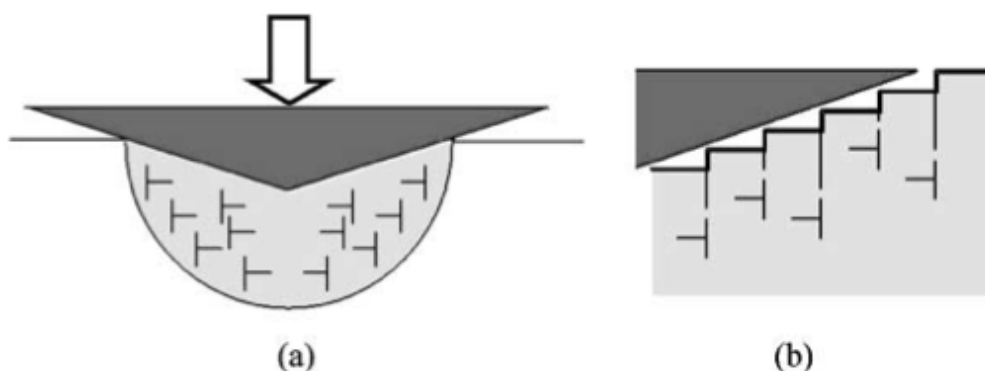


Figure 2.33 Illustration of geometrically necessary dislocations (GNDs) underneath an indenter. a) The material originally occupying the region is pushed into the substrate as an extra storage of defects. b) Non-uniform plastic deformation associated with GNDs [103].

Determination of Elastic Modulus, Yield Strength and Fracture Toughness

Indentation unloading curves are commonly employed to determine the Young's modulus of a sample using a widely adopted method proposed by Oliver and Pharr [99] (See Section 3.4.1). Nonetheless the effect of elastic anisotropy on the indentation modulus may not be large even for highly anisotropic materials [104], [105]. The indentation modulus involves non-trivial averaging over the stiffness in all directions. The size and shape of the elastic zone around the indenter are complex since the stress state is not uniaxial [106]. Herbert, Oliver and Pharr tested some models that were developed for yield strength measurement [107]. The evaluation shows poor prediction with overestimated values since all models assume a perfect contact between a spherical tip and a flat homogeneous sample. However in experiments a small surface roughness of ~15 nm would cause an appreciable discrepancy.

Nanoindentation can be applied to determine fracture toughness by measuring crack lengths emerged from the corners of an indent [108]. Schiffman tested the method by taking measurements on a number of bulk and thin film materials [109]. The main discrepancy arises from the dissimilarity between the true crack geometries and the assumptions of the empirical models, i.e. the configurations of the cracks present around the indenter deviated from any ideal crack type (Figure 2.34). The poor accuracy of fracture toughness determined from these complex three dimensional crack systems with substantial deformation residual stresses was also discussed by Quinn and Bradt [110]. The viable maximum indentation load may be insufficient to generate any fracture in the testing of small precipitates; it could be below the critical load P^* identified by Lawn and Evans [111], [112], typically a few tens of mN for hard and brittle materials.

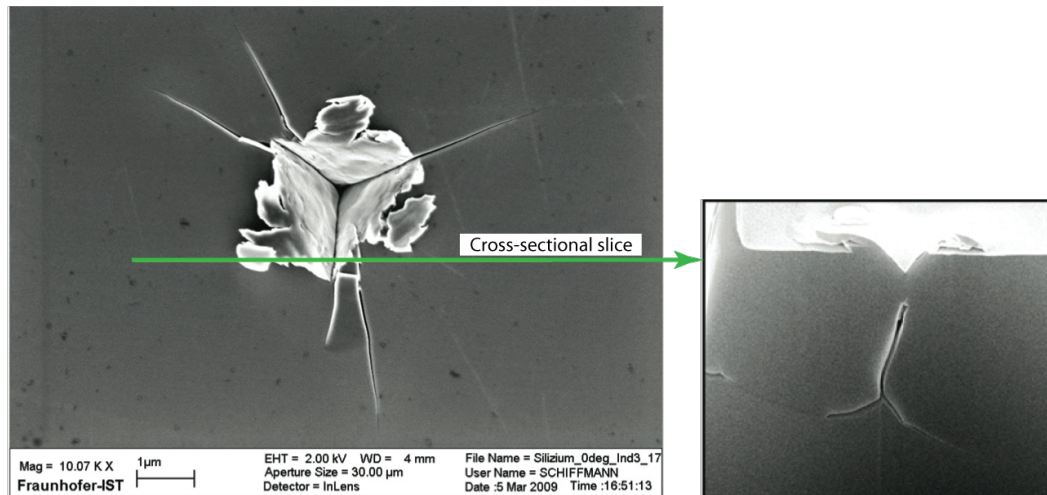


Figure 2.34 Cracks generated around an indent in Si. a) Cracks that are not emerged from corners of the indent deviate from model assumption. b) The cross-sectional slice of the indent shows that a vertical crack splits into two horizontal cracks [109].

2.4.2 Direct Loading Tests of FIB-Machined Specimens

Micromechanical loading tests are increasingly being used to extract characteristic properties of materials, such as elastic modulus, yield strength and fracture toughness, owing to the growing interest in miniaturized microelectromechanical systems (MEMS) and thin film technology [108], [113]–[118]. Recent advance in precision FIB technique combined with improved load resolution of nanoindentation apparatus has allowed manufacture and testing of microscale specimens. Geometries including pillars [119]–[122], clamped beams [123], cantilevers [6], [22], [106], [124]–[129], pre-notched cantilevers [7], [115], [130]–[137], double cantilevers [138] and tension specimens [139] have been used to carry out micromechanical tests (Figure 2.35). In all mentioned FIB-machined geometries, direct loads are typically applied on the specimens by a nanoindenter to introduce displacement. Jaya, Kirchlechner and Dehm [140] reviewed the advantages and the limitations of some geometries by comparing microfracture testing results for Si(100). The study demonstrates both geometries are capable of providing consistently accurate fracture toughness; while individually they have limitations in terms of alignment, friction effect and flexibility.

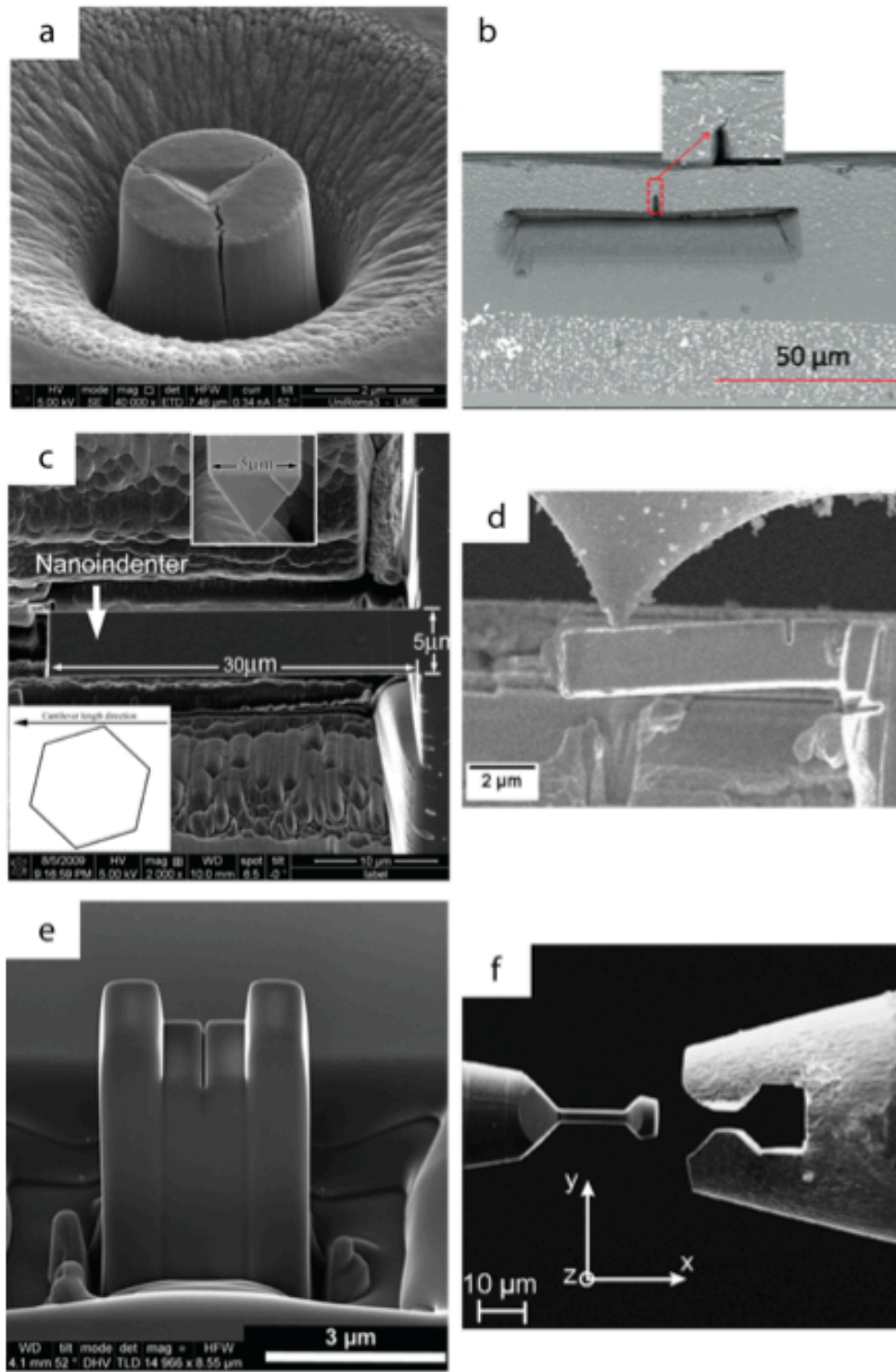


Figure 2.35 Various geometries of FIB-machined specimens designed for micromechanical testing. a) Pillar [121], b) clamped beam [123], c) cantilever [126], d) pre-notched cantilever [131], e) double cantilever [138] and f) tension specimen [139].

Gallium FIB Damage

Ion implantation damage is inevitable in all FIB-machined specimens regardless of the geometry. FIB damage caused by Ga^+ ion implantation may lead to formation of defects and surface roughening on the scale of few tens of nm [141], [142]. TEM examination shows that a high milling current of 2 nA at 30 kV can result in formation of an amorphous Ga containing surface layer up to 50 nm in Cu [142]. In the case of a low to medium current, the concentration of Ga ranged from 1 to 15 at% at a depth of 10 nm for TiAl alloys, duplex stainless steel and Cu [142], [143]. Monte Carlo simulation and TEM examination indicate that the radiation damage on the side-wall of a FIB milled trench is about 10 to 30 nm at 30 kV for Si [141], [144]. The implantation damage can be reduced by decreasing the accelerating voltage [142]. For instance, the concentration of Ga reduces from 15 to 5 at% at a depth of 5 nm in Cu/Co multilayer films when 10 kV is used instead of 30 kV [143].

2.4.3 Microcantilever Testing

Microcantilever testing method is suitable for measuring the local anisotropic plastic properties as well as providing surface examination for deformation analysis. The loading position can be accurately located during an *in-situ* SEM test or with the use of a topographic map produced by scanning mode in a conventional nanoindentation system. Early work includes the study of Young's moduli and yield strengths for Au and SiO_2 by Weihs et al. [6]. Throughout the years, microcantilever testing has been employed to study metal alloys such as Cu, Ti alloys and stainless steel [106], [124]–[127]. In a recent work of Wang et al. [128], high resolution EBSD was used to quantify stress and GND density during bending tests of hydride containing Zircaloy-4 microcantilevers. Microcantilever testing has also been employed to study the slip systems of Zr at microscale by Gong et al. [22] (Figure 2.36).

Microcantilevers of various sizes were fabricated along specific crystallographic directions such that single slip system was activated in a specimen during the bending test. The results show strong dependence of Young's modulus on crystallographic orientation and large difference in CRSS for various slip systems (The results are compared with those obtained from this thesis in Figure 7.35 and 7.36). The study also discusses the specimen size effect on CRSS in all slip systems.

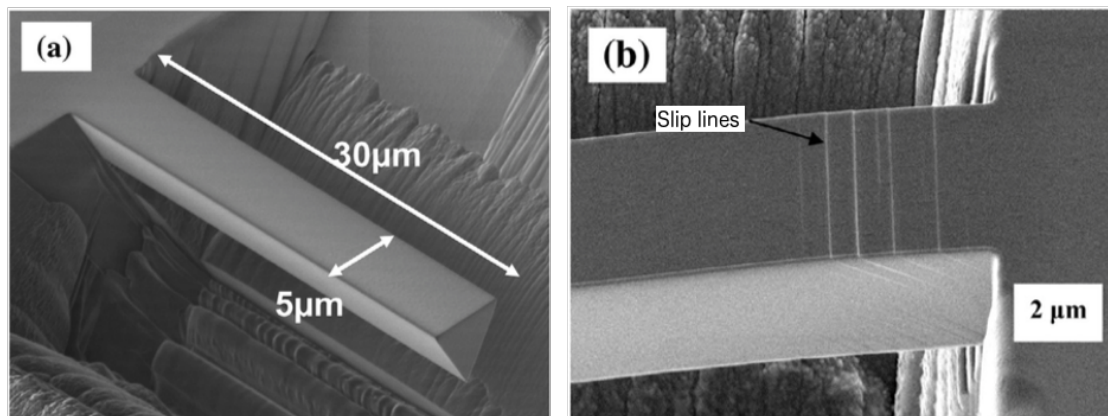


Figure 2.36 α -Zr microcantilevers. a) 5 μm wide by 30 μm long specimen. b) $\langle a \rangle$ prismatic slip bands are observed on the surfaces near the fixed end of a deflected specimen. [22]

Size Effect of Microcantilevers

Microcantilever testing shows a strong size dependence of flow stresses [145], [146]. The concept of strain gradient plasticity in conjunction with GND has been used as an attempt to explain the size effect [103]. In a plastically bent metal beam, GNDs that accommodate the lattice curvature may act as obstacles to the motion of dislocations and hence contribute to work hardening. However experiments carried out for Cu specimens with thickness $1 \mu\text{m} \leq t \leq 8 \mu\text{m}$ show that the flow stress is proportional to t^{-1} , which is different from $t^{-0.5}$ as predicted by some GND models [129], [145]. TEM foils extracted from polycrystalline Ti-6Al-4V specimens at various deformation extents suggest that dislocations moved from top and bottom to the neutral line [126]. This result is comparable with the simulations computed

from a 3-D discrete dislocation dynamics model; in which it shows pronounced dislocation pile-ups around the neutral plane [147]. Microcantilever bending was also simulated by a planar model of discrete dislocation plasticity [148]. It shows that soft pile-ups occur at isolines of zero resolved shear stress. Back stress created from these pile-ups combined with the limitation of available space for dislocation source operation may explain the size effect.

Pre-notched Microcantilevers

Pre-notched microcantilever testing allows post-examination of the fracture surfaces (Figure 2.37) and fracture properties measurement at a chosen location. The method has been demonstrated to be effective in studying a range of crystalline materials such as Si, Au, NiP and NiAl [115], [130], [131] as well as thin films in TiAl, TiN, Ni-W and Si-based materials [132], [133], [135], [136], [149]. In some *in-situ* experiments, the loading device was installed inside the SEM chamber for observing materials deformation behaviour [7], [131], [133]. The testing method has also been employed to study hydrogen embrittlement in FeAl intermetallic alloy in the work of Deng and Barnoush [137]; in which pre-notched microcantilevers were loaded under water vapour pressure to promote hydrogen uptake. Microcantilevers fabricated with straight notches are inherently unstable owing to the monotonically increasing shape factor [140], [150]. Since the stress intensity factor increases at a high rate as the crack advances (Eq.7.1), the crack spontaneously extends for materials with a constant crack resistance. Stable crack growth can be achieved by the use of chevron notch in testing brittle materials [151]. Chevron notched microcantilevers have been demonstrated to be useful in studying high temperature behaviour of tungsten in the work of Li et al. [152]. More literature review on pre-notched microcantilever testing for Zr hydrides is presented in Chapter 7.1.

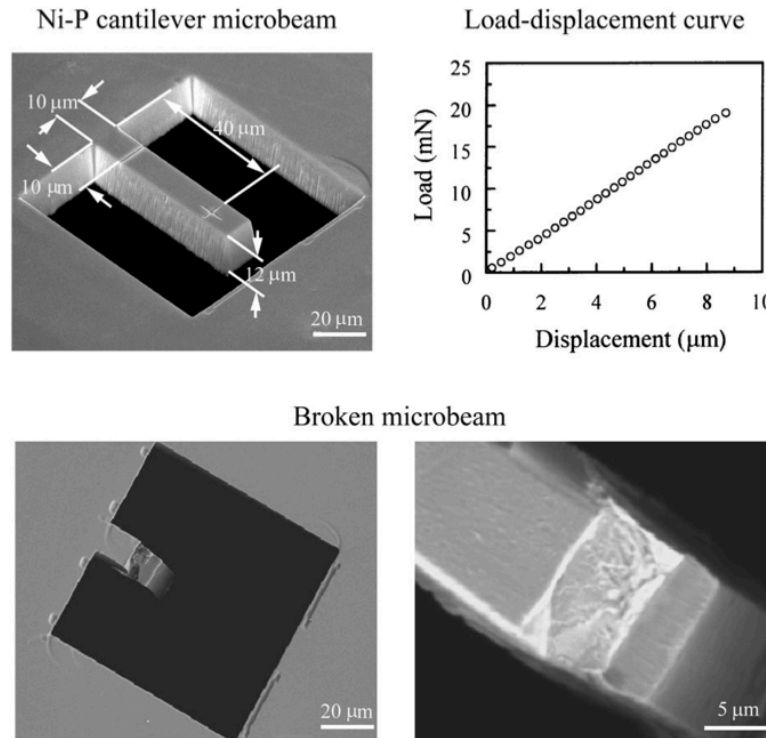


Figure 2.37 Testing of a pre-notched microcantilever. a) The specimen was milled by FIB. b) Load-displacement curve. c) and d) Post examination of the fracture surface [115].

2.5 Summary

The formation of microscale δ -hydride precipitates in Zr considerably reduces the ductility and the fracture toughness. This effect of hydrogen embrittlement is deleterious at room temperature because of the low TSS of hydrogen in Zr. The degradation of mechanical properties is dependent on factors such as hydrogen content, temperature and stress system. These factors influence the microstructure and the hydride morphology. Many experimental studies investigate the overall properties of macroscopic scale Zr hydrides; rather than the intrinsic properties of microscale hydrides that involved in DHC. The development of micromechanical testing methods combined with the advance in surface examination techniques provides insights into mechanical characterisation of hydrides at microscale. Nanoindentation and microcantilever testing methods are appropriate to measure the localised properties of a specific Zr-hydride microstructure.

3 MATERIALS AND EXPERIMENTAL METHODS

3.1 Materials and Sample Preparation

A commercial grade unalloyed Zr rod purchased from Goodfellow, Cambridge Ltd, UK was used to prepare samples. The composition provided by the supplier is listed in Table 3.1.

Table 3.1 Typical composition of commercial grade unalloyed Zr from Goodfellow, UK

	Typical purity	Zr bal.	C	Hf	Fe	Cr	N	O	H
Industrial standard composition (%wt)	99.2	99.57	0.025	0.25	0.02	0.02	0.01	0.1	0.001

The rod was annealed for 72 hours at 750°C in an argon atmosphere and slowly cooled for 96 hours to room temperature. The annealed rod was cut into 10 mm x 7.5 mm x 1 mm samples with a low speed saw. The samples were then ground with 120-4000 grit SiC papers, followed by mechanical polishing with colloidal silica at 60 rpm for more than 24 hours. The aqueous polishing would neither generate a considerable amount of oxide nor hydride. Zr has a very good corrosion resistance to slightly alkaline solution mixed with colloidal silica [8], [153], [154]. The reaction kinetics for oxide formation and hydrogen evolution are very low at room temperature: the estimated mass fraction of oxide in a Zr sample is less than 0.001 ppm wt [155], [156]. The chemical reaction for Zr oxidation theoretically restricts the hydrogen uptake to a even smaller order of magnitude [156]. Since the hydrogen produced is below the terminal solid solubility at room temperature (0.05 ppm wt) (Section 2.2.1), hydride precipitates were very unlikely to form during aqueous medium polishing. The calculated oxide and the hydride film, if any, would occupy an incomplete atomic layer.

The sample surfaces used for materials analysis were slightly etched by 1% HF, 10% HNO₃ and 89% H₂O (v/v) solution in order to enhance topographic contrast for observation [15], [157], [158]. The etching typically takes a few seconds, depending on the polishing condition of an individual sample. Ion beam polishing was also used to produce fine flat surfaces sufficiently low in deformation for EBSD patterning [158]. The technique involves bombardment of energetic ion beam on the surface in vacuum. The samples were typically polished with Ar ion at 7.5 keV with the dual-beam gun angle set at 5° for 15 to 30 minutes in a Gatan Precision Ion Polishing System (PIPS-II). These parameters are similar to that in the work of Abdolvand and Wilkinson [159] in which it demonstrates good quality Kikuchi pattern acquisition on Zircaloy-2.

3.2 Electrolytic Hydriding

An electrochemical technique developed for hydriding Zr was adapted to produce a hydride film [4], [160]. A large surface of a 10 mm x 7.5 mm x 1 mm sample was polished as described in Section 3.1. The sample was then spot welded to a Zr wire (0.5 mm in diameter) and immersed in a 0.5% (v/v) sulphuric acid electrolyte to form a cathode (Figure 3.1). Sulphuric acid was selected because of its high electrical conductivity and low corrosion effect on Zr (~0.5 mm per year for 15 % wt acid concentration at room temperature [8]). The back and side surfaces were covered with lacquer while the 10 mm x 7.5 mm polished surface was positioned parallel to a 25 mm x 25 mm Pt mesh anode at a distance of about 30 mm. The hydriding process operated under a constant current density of 1.5 kA/m² at a voltage of about 1.5 V at 65°C for durations ranging from 0.5 to 130 hours. Hydrogen evolution was indicated by steady gas bubbles formation and identified by pop tests. The analysis for the hydride formation and the diffusion process is presented in Section 5.5.

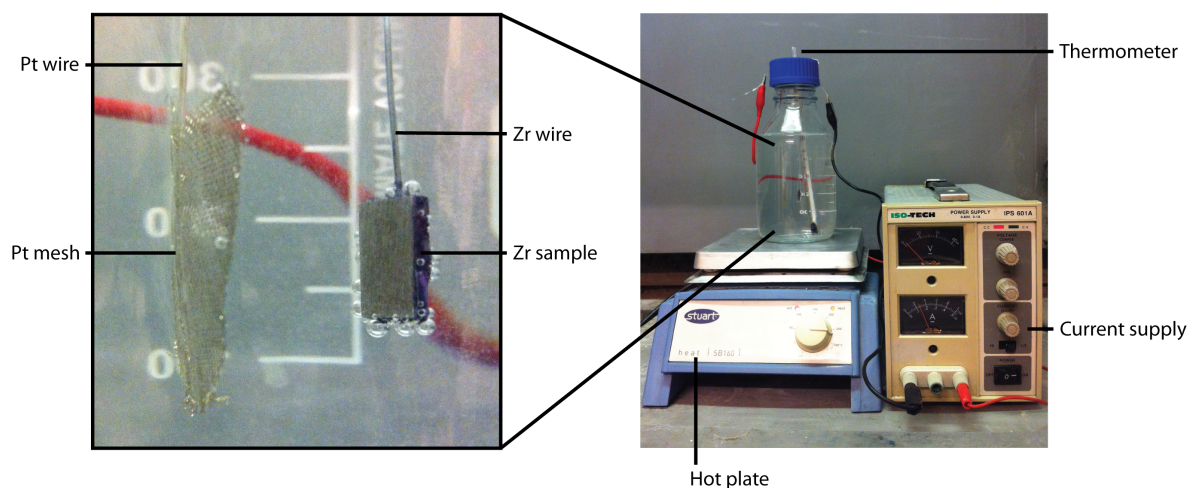


Figure 3.1 Electrolytic hydriding experimental arrangement. a) Reduction occurred on the Zr sample surface. Bubbles formed on the sample were identified as hydrogen gas by simple pop tests. b) Constant current was supplied to produce a hydrided sample at a steady temperature.

The hydrided surface was examined directly following the electrolytic hydriding experiment (Figure 3.2a) but more work was needed before examining the cross-sectional surface. First the hydrided coupons were cut into 7.5 mm x 1 mm x 1 mm samples using a low speed saw. Only samples located more than 3 mm away from the welding spot were used. The sample were then embedded in resin before further grinding and polishing (Figure 3.2b and c). This avoided a round hydriding edge since the cross-sectional surface was flush with the surface of the resin during polishing. At the initial attempt, epoxy resin was selected because of the standard SEM sample mould size. Although a thin layer of silver conductive paint was applied on the epoxy surface, electron charge-up was frequently observed during the SEM examination. The preparation method was then modified by the use of phenolic carbon conductive resin. The hydrided sample was covered with a layer of silver conductive paint before being embedded in the conductive resin. The dried paint provided adhesion and protection to the sample edges. The cross-sectional surface was then ground and polished using the procedure as described in Section 3.1.

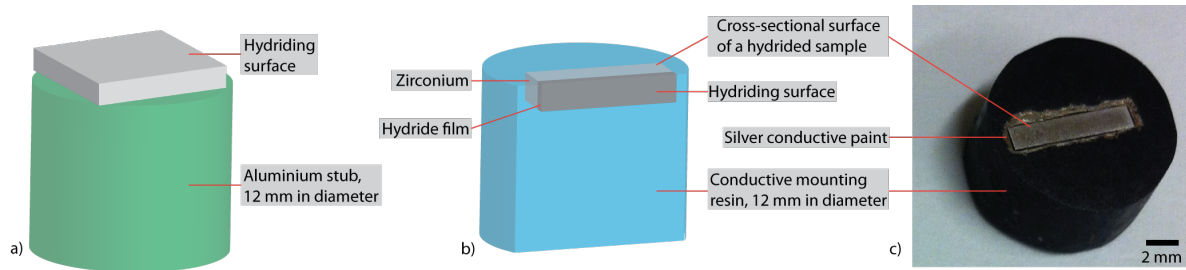


Figure 3.2 Two types of hydrided Zr samples used for microstructural characterisation and testing. a) The first type is used for examination of the hydride surface. b and c) The second type is used for examination of the cross-sectional surface. The hydrided Zr was covered with a layer of silver conductive paint before being embedded in the conductive resin.

3.3 Characterisation of Materials

Scanning Electron Microscopy

Both Zr and hydrided Zr samples were examined by using SEM at various experimental stages. First the imaging technique was combined with EBSD to determine the crystallographic properties of the regions of interest. The SEM examination was also carried out throughout the FIB manufacture of specimens. Finally the deformed specimens were re-imaged in SEM after the micromechanical tests. In an SEM examination, secondary electron signals produced by the interaction between the high-energy focused electron beam and the sample were collected to generate greyscale images. The length scale of a scanned area ranged from tens of microns to sub-micron. Small features such as grain boundaries and hydride precipitates ($< 1 \mu\text{m}$) were imaged with the use of high resolution SEM. The high resolution allowed determination of accurate locations of the Zr/hydride phase boundary.

X-Ray Diffraction

XRD was used as a rapid analytical technique to identify the phases of the polycrystalline samples immediately after electrolytic hydriding. However due to the large beam size, it is not suitable for microstructural characterisation. In an XRD examination, monochromatic X-rays that scattered from atoms in a crystalline sample produce diffraction patterns. Constructive interference occurs when the condition satisfies Bragg's Law,

$$n\lambda = 2d \sin \theta \quad 3.1$$

where n is a positive integer, λ is the wavelength of Cu K_α x-ray which is 0.15 nm, d is the interplanar spacing and 2θ is the diffraction angle. The lattice parameters reported in literature were used to calculate the positions of diffraction peaks for each family of planes [18], [36]. The calculations were verified against data from the International Centre for Diffraction Data (ICDD) that listed in Table 2.3. In addition, the x-ray penetration depth can be estimated for Zr. In a solid material, the transmitted x-ray intensity, I , decays exponentially with the path length, L , [161]

$$I = I_0 e^{-\rho A L} \quad 3.2$$

where I_0 is the incident x-ray intensity, ρ is the density of the material and A is the mass attenuation coefficient. Therefore a specific penetration depth at which the intensity has decreased to $1/e$ or $\sim 37\%$ of I_0 is

$$L_{37\%} = \frac{-\ln(1/e)}{\rho A} = \frac{1}{\rho A} \quad 3.3$$

The density of Zr is 6.51 g/cm^3 and its mass attenuation coefficient is $135.6 \text{ cm}^2/\text{g}$ [162]; therefore the specific penetration depth is $11.4 \text{ }\mu\text{m}$ for an incident normal x-ray beam.

Energy Dispersive Spectroscopy

EDS was applied to determine the elemental composition of some microscale impurity particles that was present in the initial material. The technique is based on the interaction between a focused electron beam and a sample in which it produces characteristic x-rays from existing elements. The energy spectrum was then analysed to determine the abundance of specific elements and their distribution on the surface.

Electron Backscatter Diffraction

EBSD was employed for phase identification and crystal orientation mapping in selected regions of interest. Information such as grain sizes and locations of interface was used for microstructure characterisation. EBSD mapping data provided a basis to determine the milling location of a microcantilever. The technique was used in conjunction with SEM to analyse the Zr/hydride interfacial properties such as the crystallographic relationship between the two compositional phases. The analysis results are presented in Section 4.1.1 and 4.4.

3.4 Micromechanical Testing

3.4.1 Nanoindentation

Instrumentation and Data Analysis

Nanoindentation was carried out in an Agilent Nano Indenter G200 [163]. Figure 3.3 shows a schematic diagram of the instrument hardware. Force is imposed on the indenter shaft by electromagnetic actuation and displacement is measured by capacitance gauges [164].

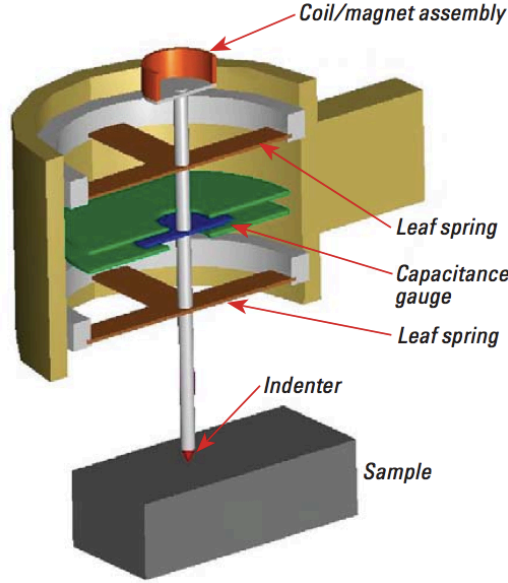


Figure 3.3 Illustration of the actuation and sensing system of a G200 nanoindenter [164].

Oliver and Pharr [96], [99] modified the linear unloading assumption as suggested by Doerner and Nix [165] to a power law relation. The improved method has been adopted for testing a wide range of materials [93]–[95], [166], [167]. The unloading curve is

$$P = \alpha(h - h_f)^m \quad 3.4$$

where P is the load on sample, α and m are fitting constants. h is the displacement and h_f is the final displacement as shown in Figure 3.4. The elastic deformation of the non-rigid indenter is accounted for by defining a reduced modulus, E_r , using the equation,

$$E_r = \left(\frac{1 - \nu^2}{E} + \frac{1 - \nu_i^2}{E_i} \right)^{-1} \quad 3.5$$

where E and E_i are the Young's moduli for the testing material and the indenter. ν and ν_i are the Poisson's ratio for the testing material and the indenter. The reduced modulus is related to the initial unloading stiffness, S , and the projected area of contact, A , by

$$S = \frac{dP}{dh} = 2\beta E_r \frac{\sqrt{A}}{\sqrt{\pi}} \quad 3.6$$

where the empirical parameter $\beta = 1.05$ for a Berkovich tip [96][166]. The Young's modulus is calculated from Eq.3.5 and Eq.3.6; while the hardness at peak load is determined as

$$H = \frac{P_{max}}{A} \quad 3.7$$

where P_{max} is the peak indentation load. The projected area of contact was computed from an area function $A = f(h_c)$, where h_c is the contact depth of the indent (Figure 3.4). For a perfect Berkovich tip, $A = 24.56 h_c^2$. The deviation from the ideal geometry due to tip blunting were accounted for by a calibration procedure as proposed by Oliver and Pharr [96]. This calibration of area function was carried out by making indents on fused silica with known elastic modulus (73 GPa) and Poisson's ratio (0.17).

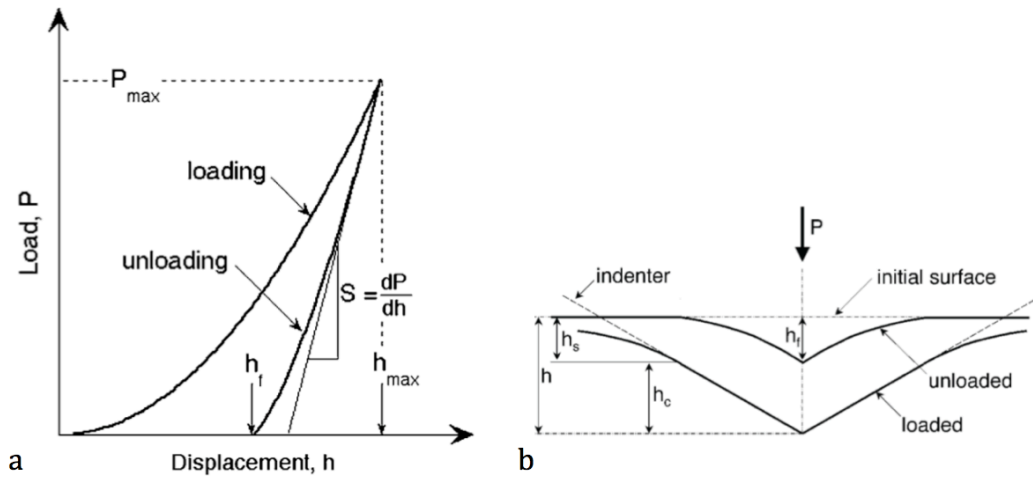


Figure 3.4 A schematic representation of a) nanoindentation load-displacement and b) contact section through an indentation [96]. h_{max} is the indenter displacement at the peak load, P_{max} , and h_s is the displacement of the surface at the perimeter of the contact.

Continuous Stiffness Measurement

The G200 indenter is capable of providing continuous stiffness measurement (CSM) in order to facilitate depth-sensing measurement. It is different from the quasi-static indentation testing in which the stiffness of contact is determined during the final unloading. CSM is a technique in which stiffness is measured continuously during the loading by imposing a small dynamic oscillation on the force. The amplitude and phase of the corresponding displacement are measured by a frequency-specific amplifier [96], [97]. All nanoindentation tests were carried out with CSM in this study. The nanohardness values at varying depths were measured for comparing the ISE on the two compositional phases of the hydrided Zr samples.

3.4.2 Microhardness Measurement of Thin Films

Vickers hardness tests were carried out on the hydrided surface to measure the microhardness. The $\sim 20\ \mu\text{m}$ thick continuous hydride layer was considered as a thin film. (See Section 3.1 and 4.3.2) A simple geometrical model proposed by Jönsson and Hogmark [168] was used to account for the influence of the Zr substrate. The authors suggested the composite hardness, H_c , can be expressed in an area law of mixture [169]:

$$H_c = \frac{A_f H_f + A_s H_s}{A_f + A_s} \quad 3.8$$

where A_f and A_s are the load bearing area of the film and the substrate; H_f and H_s are the hardness of the film and the substrate. The model assumes the film is plastically strained to match the geometry of an ideal Vickers indenter tip with a face angle of 136° . Then the relationship between the fractions of the load bearing area and the film thickness, t_f , is:

$$\frac{A_f}{A_0} = 1 - \frac{A_s}{A_0} = \frac{2C_0 t_f}{h_v} - \left(\frac{C_0 t_f}{h_v} \right)^2 \quad 3.9$$

$$C_0 = \sin^2 \left(\frac{180^\circ - 136^\circ}{2} \right) \approx 0.140 \quad 3.10$$

where h_v is the penetration depth of the indent and it is about 1/7 of the diagonal of the impression. In order to calculate the microhardness of the hydride film, H_f , the microhardness of the unhydrided α -Zr, H_s , was measured at a range of loads (See Section 6.4)

3.4.3 FIB Fabrication of Microcantilevers

FIB was used as the micro-machining technique to prepare pre-notched cantilevers. The technique involves scanning a raster beam of Ga^+ ions across a sample surface for site specific sputtering or milling [170]. The capability of milling complex geometries and FIB induced implantation damage are reviewed in Section 2.4.2. In this study, the pentagonal cross-section was used because it allows flexible testing locations and uniform notch width. The rectangular cross-section was not used because the undercut of a cantilever is only possible if the specimen is located on a sample edge. The triangular cross-section was not used because the stress-state of the notch depends on the width and it complicates the measurement of fracture toughness.

The fabrication was carried out at 30 kV in an FEI FIB 200 or in a Zeiss Auriga. In the FIB 200, emitted electrons generated by initial ion collisions produce an image. In the Auriga, the FIB/SEM dual beam enables imaging. The first step of the fabrication is to determine the pre-notch location. In the case of making a notch along a Zr/hydride phase boundary, a high resolution SEM image was needed to accurately locate the interface.

Location marks were then made at 10 μm away from each side of the planned position using single passes of the Ga beam at a low current of 50 pA. The notch would finally be located at 0.5 μm away from the fixed end of the cantilever.

The second step creates the shape of the cantilever by a series of coarse cut at 1 nA. In order to fabricate a 4 μm x 10 μm cantilever, an 8 μm x 11 μm rectangle was milled on each side of the planned position, followed by making a rectangle at the centre that created the tip of the specimen (Figure 3.5a). The dimensions of the rectangles were designed such that a Berkovich indenter tip would not touch the U-shaped trench when the cantilever was loaded to a maximum deflection of 2 μm (dotted lines in Figure 3.5a). The third step undercuts the pentagonal cross-section at 300 pA beam. The sample was rotated by 45° around the longitudinal axis of the cantilever (Figure 3.5b). The operation was repeated on the opposite side of the cantilever. Then a series of fine polish was carried out to produce sharp edges and corners at 100 pA (Figure 3.5c). The final step makes the pre-notch with the use of 10 pA and 1 pA (See Figure 7.2 in Section 7.2 for details). Subsequent to precision milling, the sample was tilted at 0°, 30° and 45° for dimensional measurement.

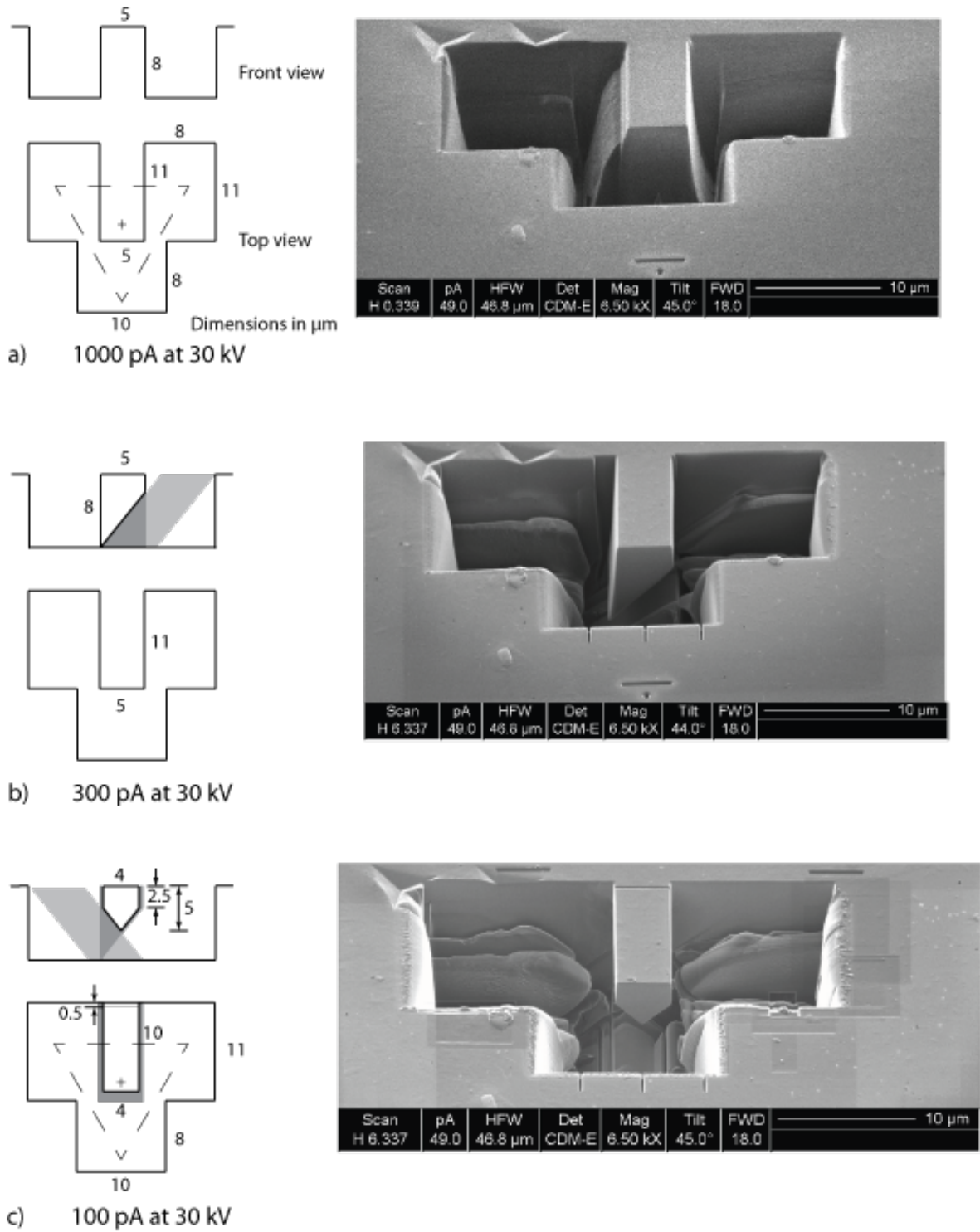


Figure 3.5 FIB milling procedure for manufacture of a 4 μm x 10 μm cantilever. The sample is tilted at 45° in the SEM images.

3.4.4 Microcantilever Testing

The FIB-machined microcantilevers were deflected by a nanoindenter tip to generate load-displacement data [130], [163]. The testing region was first brought into focus by adjusting the height of the stage (Figure 3.6). The G200 indenter was then switched to the contact mode in which it could function as an AFM style imaging device. A topographical map of the T-shaped position mark was produced for the purpose of setting up a reference position and surface height (Figure 3.6a). The free end of the cantilever was then parked at 5 μm below the indenter tip before the loading test. More experimental details for testing the cantilevers are described in Section 7.2. Simple beam theory is not suitable for calculating the elastic properties because the notch considerably alters the internal stress distribution. The FE model used for load-displacement simulation is presented in Section 7.4.3.

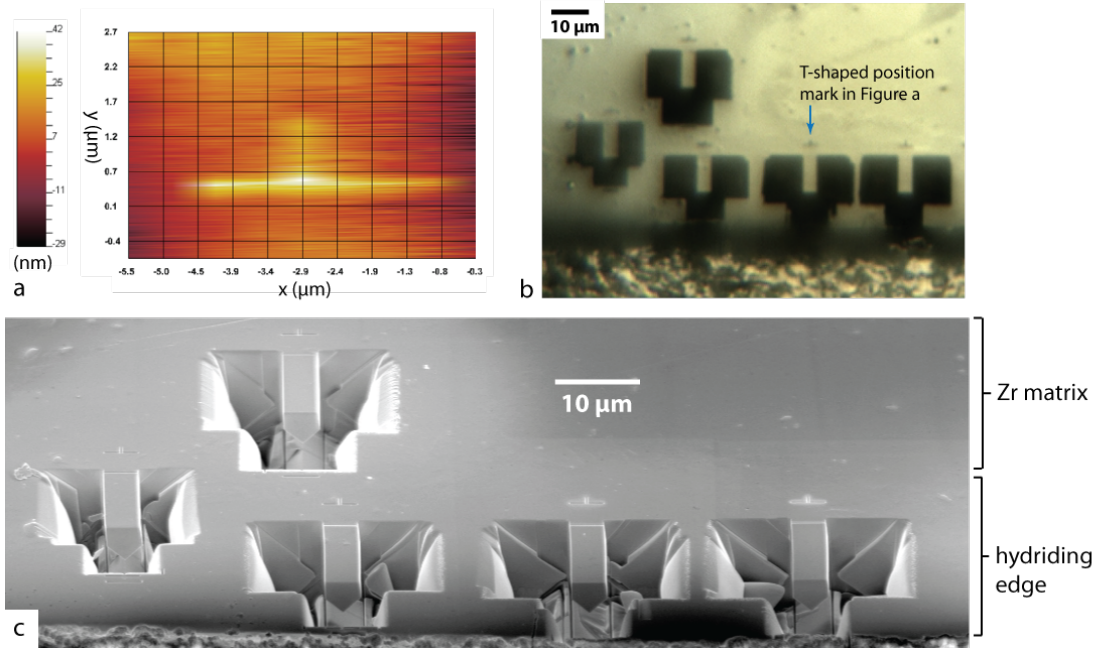


Figure 3.6 Microcantilever specimens before testing. a) Contact scan of a T-shaped position mark. The mark is located 3 μm away from the fixed end of a microcantilever. This sets up a reference position for the indenter tip. b) Optical image of a testing region near the hydrided edge. c) SEM micrograph of the same region at the tilt angle of 45°.

4 MICROSTRUCTURE AND CHARACTERISATION OF MATERIALS

4.1 Characterisation of Unhydrided Material

4.1.1 Microstructure

The initial unhydrided material was examined under polarised light in a Zeiss Axiophot microscope. In Figure 4.1, dark traces were progressively removed from the polycrystalline grain structure. Since these traces are parallel across grains and morphologically different from surface hydride nuclei (Figure 4.11), the observed traces correspond to remains of grinding scratches. Figure 4.2 shows the surface condition subsequent to 1% HF etching. An appreciable fraction of grains had a diameter over 50 μm ; which allowed microcantilevers being made within individual grains.

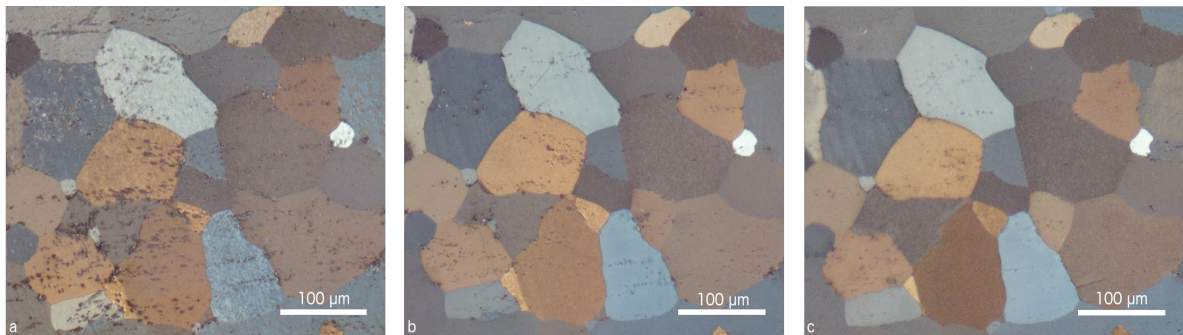


Figure 4.1 Initial material observed under a polarised light microscope a) polished for 8 hours and etched with 1 % HF for 10 sec. b) polished for a total of 12 hours and c) for 24 hours.

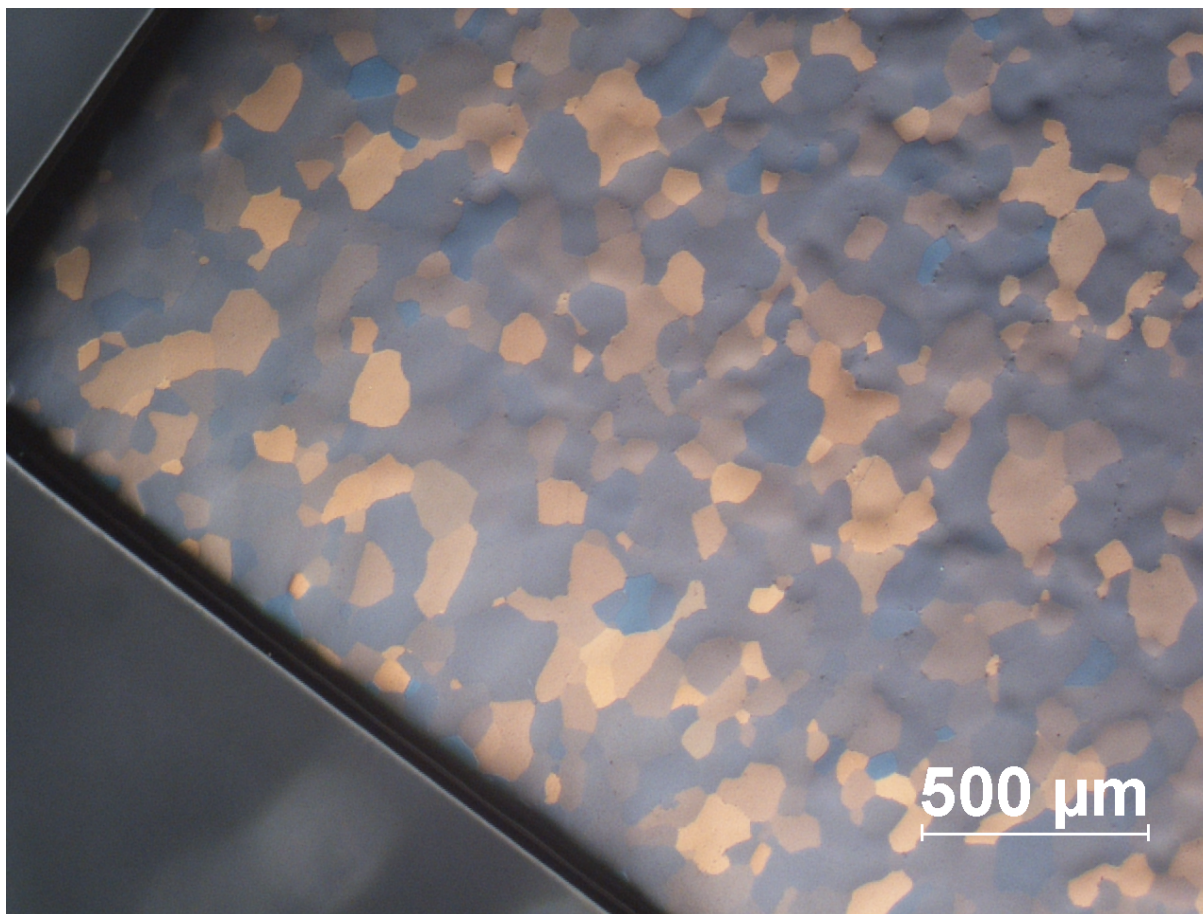


Figure 4.2 Polarised light micrograph of a Zr sample finished with chemical etching.

The SEM examination was carried out in an Zeiss Auriga. Figure 4.3a shows that individual grains can be distinguished with sufficient contrast. In Figure 4.3b, the higher magnification image shows some loose traces and grooves of width $< 2\ \mu\text{m}$. These features are not hydrides since the aqueous medium polishing at room temperature would not generate sufficient hydrogen to form hydrides (See Section 3.1). These features were then examined at the tilt angles of 45° and 60° (Figure 4.4). The examination suggests that these morphological features are extrinsic and they correspond to surface roughness. They are $< 0.5\ \mu\text{m}$ in depth as measured from the images, likely resulting from the physical polishing with colloidal silica of $\sim 50\ \text{nm}$ in size. In comparison with hydrided samples in which bulging edges were observed (Figure 4.14), this unhydrided Zr sample has straight edges.

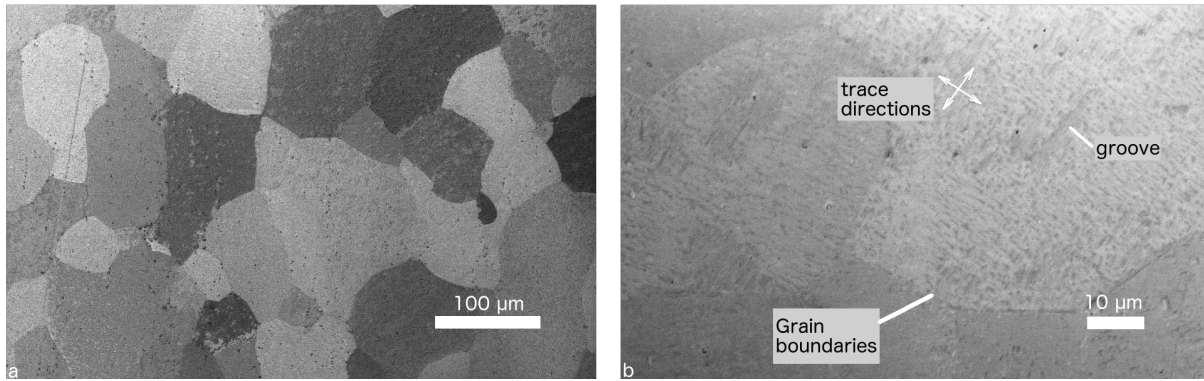


Figure 4.3 SEM examination of a polycrystalline Zr sample.

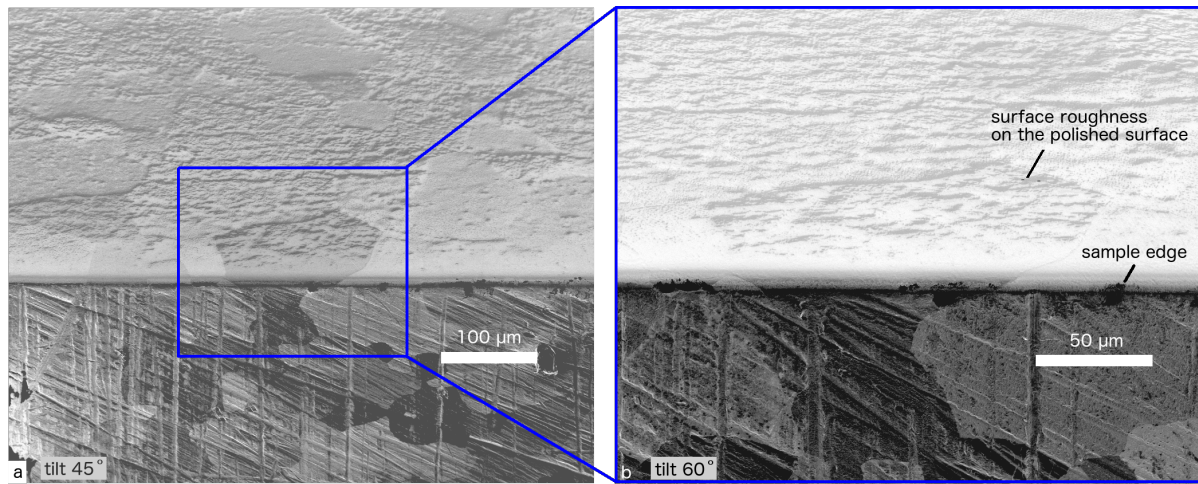


Figure 4.4 The edge region of a Zr sample at the tilt angle of a) 45° and b) 60°. The sample has a straight edge after cutting and polishing.

4.1.2 EBSD Analysis

An EBSD analysis was carried out for the initial material prepared with Ar ion polishing as described in Section 3.1. A Carl Zeiss Merlin equipped with FESEM and Bruker EBSD system was used for pattern acquisition in the first scan. In Figure 4.5, the EBSD map of the single-phase Zr shows a homogeneous equiaxed polycrystalline structure. The data were collected with 20 keV beam energy, 5 nA current at a working distance of 18 mm.

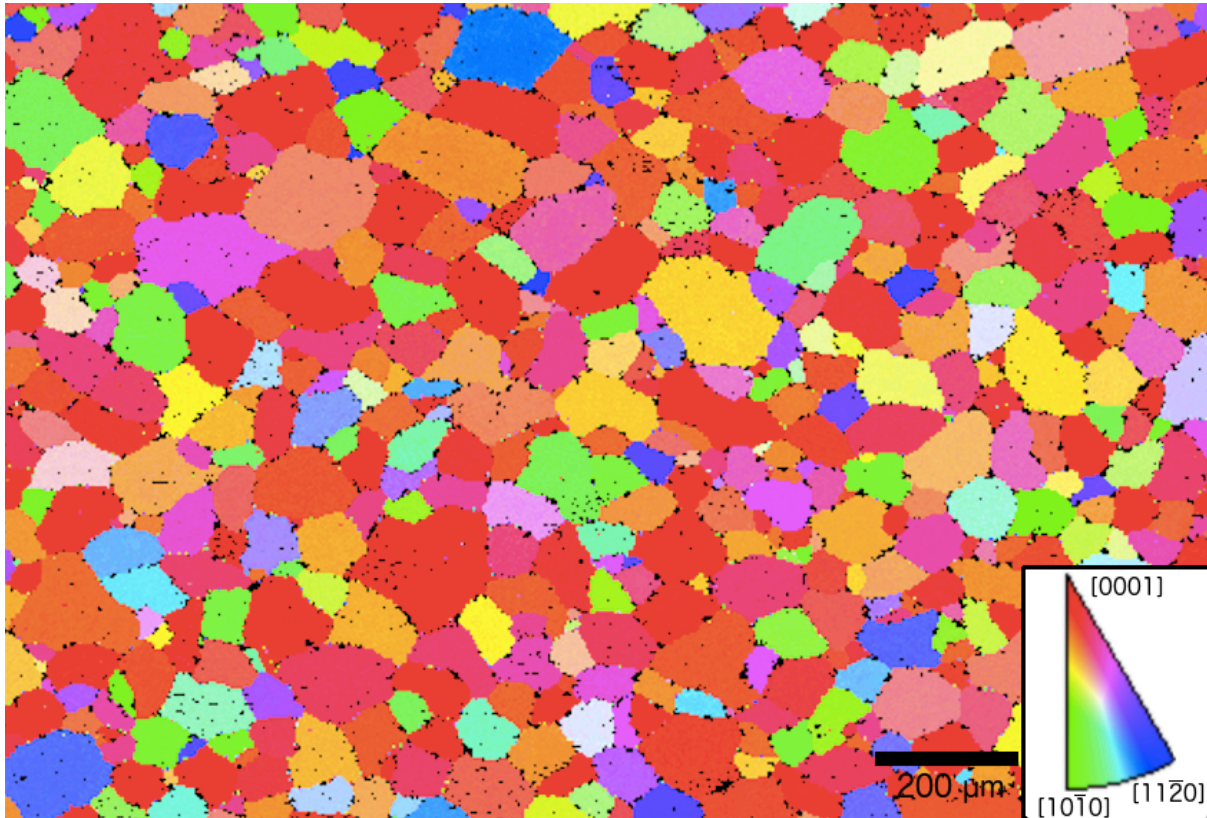


Figure 4.5 Single-phase Zr EBSD map indexed for the surface of the initial material.

The region has a preferential texture in which the density of grains having $[0001]$ direction along the sample normal is the highest (Figure 4.6a). This result is consistent with the texture analysis presented for the same batch of initial material [21]. In Figure 4.6b, grain sizes were obtained from over 400 sample grains with each grain contained at least 100 indexed pixels. The misorientation tolerance is 5° and the calculation excludes the edge grains. The average grain diameter is $94\ \mu\text{m}$, which is adequately large for a $4\ \mu\text{m} \times 10\ \mu\text{m}$ microcantilever to be milled within an individual grain such that the influence of the vicinity of grain boundaries is eliminated [171].

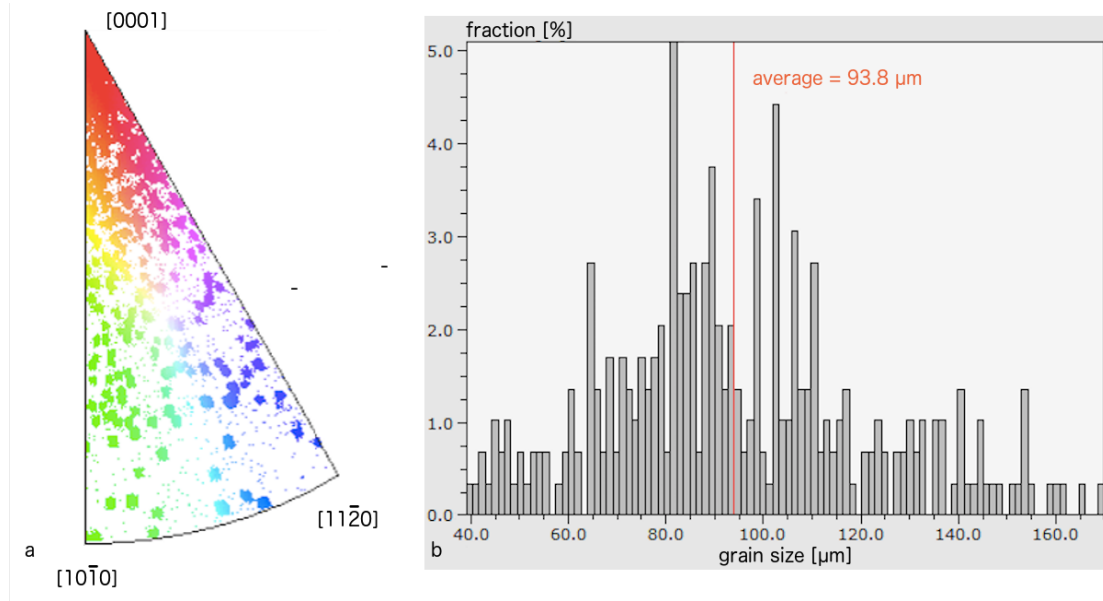


Figure 4.6 EBSD analysis of the Zr region as shown in Figure 4.5. a) The inverse pole figure indicates the preferred orientation along [0001] direction. b) Grain size distribution.

The second EBSD scan was carried out on a relatively small amount of grains in a JEOL JSM-840A with 30 nA probe current and 20 keV energy at a working distance of 14 mm. The sample surface was finished with HF etching as described in Section 3.1. The signals were converted to crystallographic information with EDAX-TSL EBSD analysis system and Oxford Instruments INCA system. In Figure 4.7, the result shows a similar equiaxed grain structure in comparison with the first experiment. In Figure 4.7b, the pattern quality map provides a metric for the pattern sharpness by generating contrast between the intensity peaks of probed bands and the average brightness of the background [172], [173]. The noise in terms of the ratio of the misindexed points to all scan points is low (0.01%). This demonstrates the thermionic emission microscope JSM-840A accompanied by slight chemical etching finish is capable of providing quality crystallographic orientation maps.

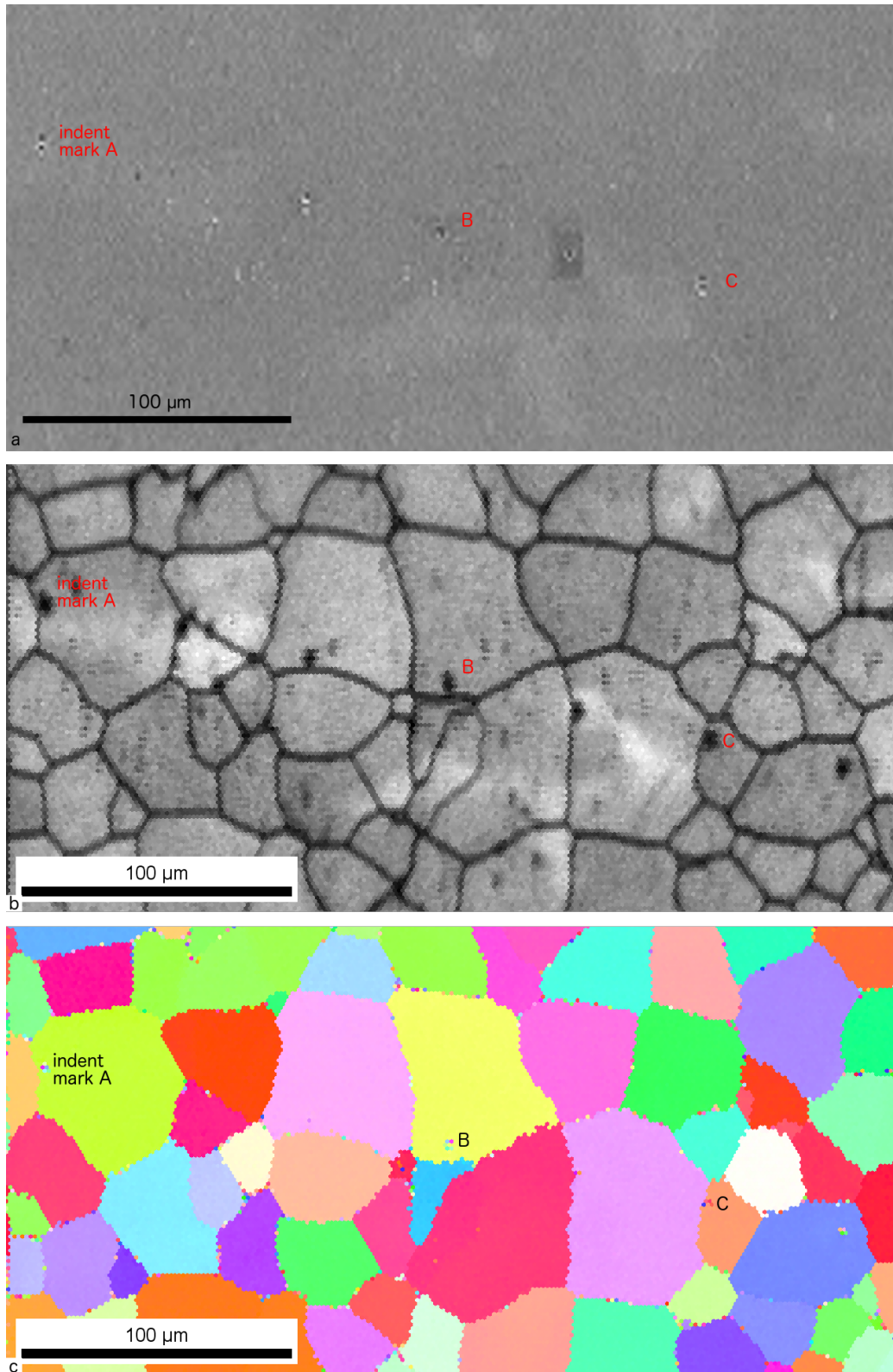


Figure 4.7 EBSD experiment for a Zr sample region obtained in a thermionic emission microscope. a) SEM image. The indent marks were made by nanoindentation prior to the scan in order to mark reference locations. b) Pattern quality map. The low pattern quality regions (dark colour) are mainly grain boundaries. c) EBSD map. The grain orientations can be clearly identified.

4.1.3 XRD Analysis

An X-ray diffraction analysis was carried out to identify the phase of the initial material in a macroscopic scale. The θ - 2θ measurement was taken with the use of monochromatic Cu K- α radiation generated in a Philips PW1729 diffractometer at 35 keV and 50 mA. The step size was 0.02° over the range of diffraction angles, 2θ , from 30° to 70° . The specific penetration depth, at which the intensity of the x-rays drops to 37% of the normal incident intensity, was estimated to be $11\text{ }\mu\text{m}$ based on the mass attenuation properties of Zr (Eq.3.2 and 3.3). The scanned pattern was transferred to the software X'Pert HighScore for analysis. Figure 4.8 shows the measurement for an initial unhydrided sample. All the diffraction peaks match the α -Zr indexed positions (PDF 00-005-0665). Since the sample was not in powder form, the grain orientations were not necessarily random. Therefore the relative intensities of the detected peaks deviate from the standard powder diffraction files. All available standard files for Zr oxides or hydrides of different stoichiometric ratio were compared to the experimental diffraction peaks; there is no match that indicates the presence of oxide or hydride.

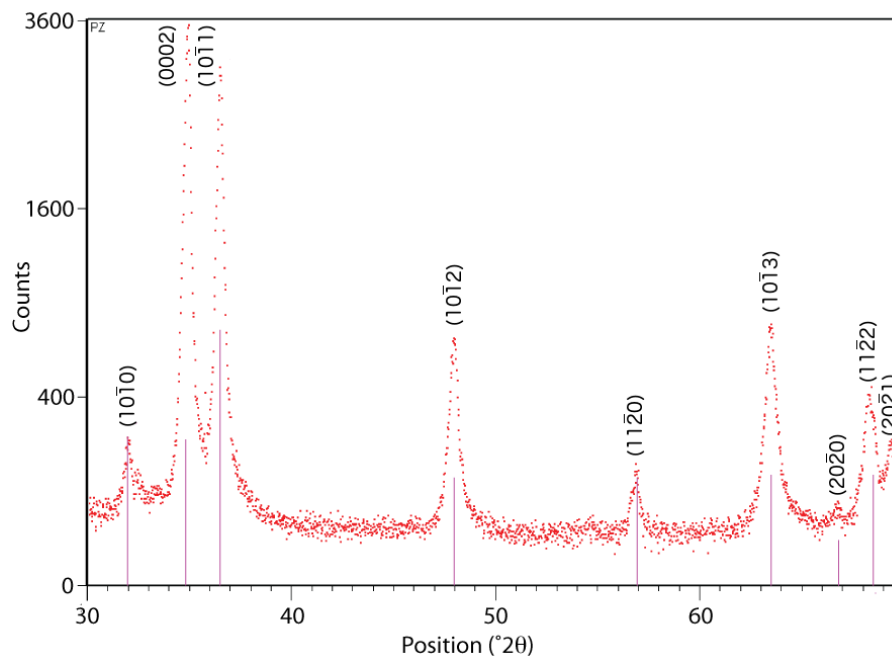


Figure 4.8 XRD result of the initial material shows matching with the Zr indexed positions.

4.1.4 EDS Analysis

An EDS analysis was performed to identify some impurity particles that were seen during the SEM examination of the initial material (Figure 4.9a). A Carl Zeiss Merlin equipped with FESEM was used with Oxford Instruments EDS software for analysis. The experiment was carried out with the help of Prof Sergio Lozano-Perez of the University of Oxford. Microscale impurity particles with a diameter of approximately 0.6-2.0 μm can be seen in the zirconium matrix (Figure 4.9a and b). The EDS analysis indicates that the particles contain iron and nickel (Figure 4.9c and d). These elements are surrounded by an oxygen-containing shell with a diameter of roughly 1.4-8.5 μm as shown in Figure 4.9e. The local composition of a sample impurity particle and its shell contains 9.5%wt iron, 7.3%wt nickel, 1.0%wt oxygen and a traceable amount of fluorine. The presence of fluorine would be a result from the use of 1% (v/v) hydrofluoric acid in the etching process.

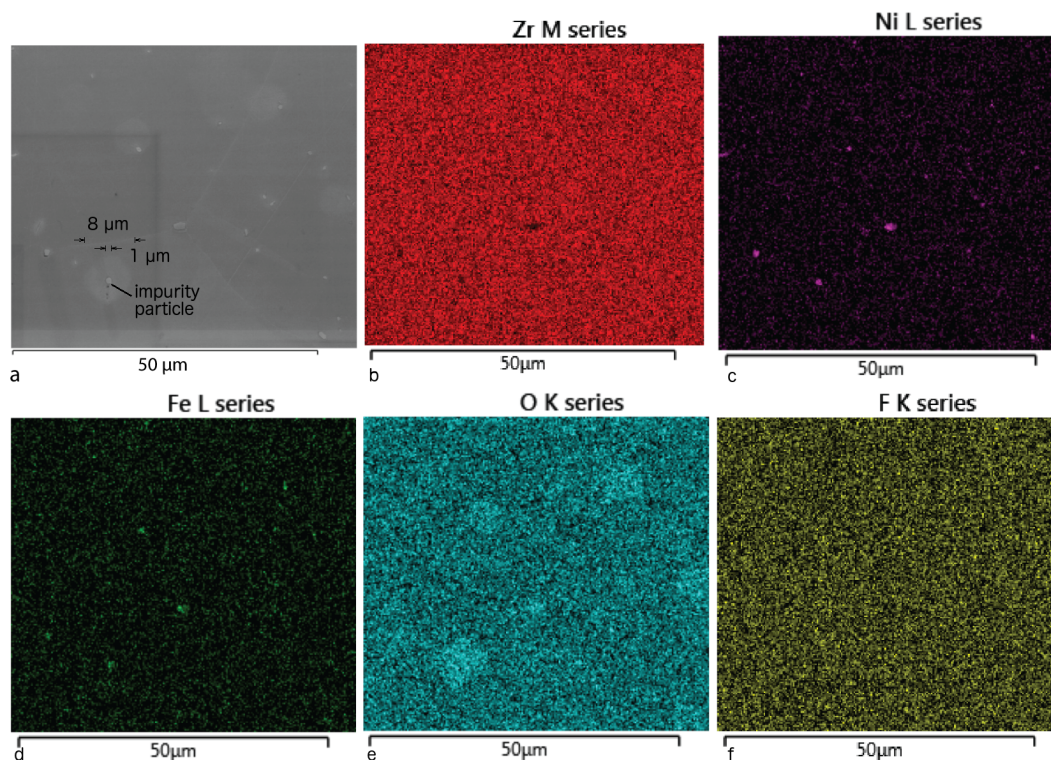


Figure 4.9 EDS analysis of the initial unhydrided material. a) Electron image. Elemental map of b) zirconium, c) nickel, d) iron and e) oxygen and f) fluorine.

4.2 XRD Analysis of Hydrided Material

An XRD analysis was carried out on the 7.5 mm x 10 mm hydrided surface with a similar experimental setting as for the initial material (Section 4.1.3). The sample was placed in a PW1729 diffractometer immediately after electrolytic hydriding without further preparation. The step size was 0.01° over the range of diffraction angles from 30° to 75° . Figure 4.10 shows the measurement for a 96-hour hydrided sample. All diffraction peaks were identified with the standard indexed positions of the δ -hydride except a deviation was observed at 37.2° where the peak was 0.4° away from the $(200)_\delta$ position. Some relevant reference patterns such as oxides and the ϵ -hydride had been checked to ensure no overlapping peaks were present. It should be noted that for a powder mixture, the ratio of peak intensities is approximately proportional to the weight fraction of phases [161]. However since the weight fraction varies with the diffraction angle in this thin film sample, the relative intensities between the two identified phases do not necessarily correlate with their relative abundances.

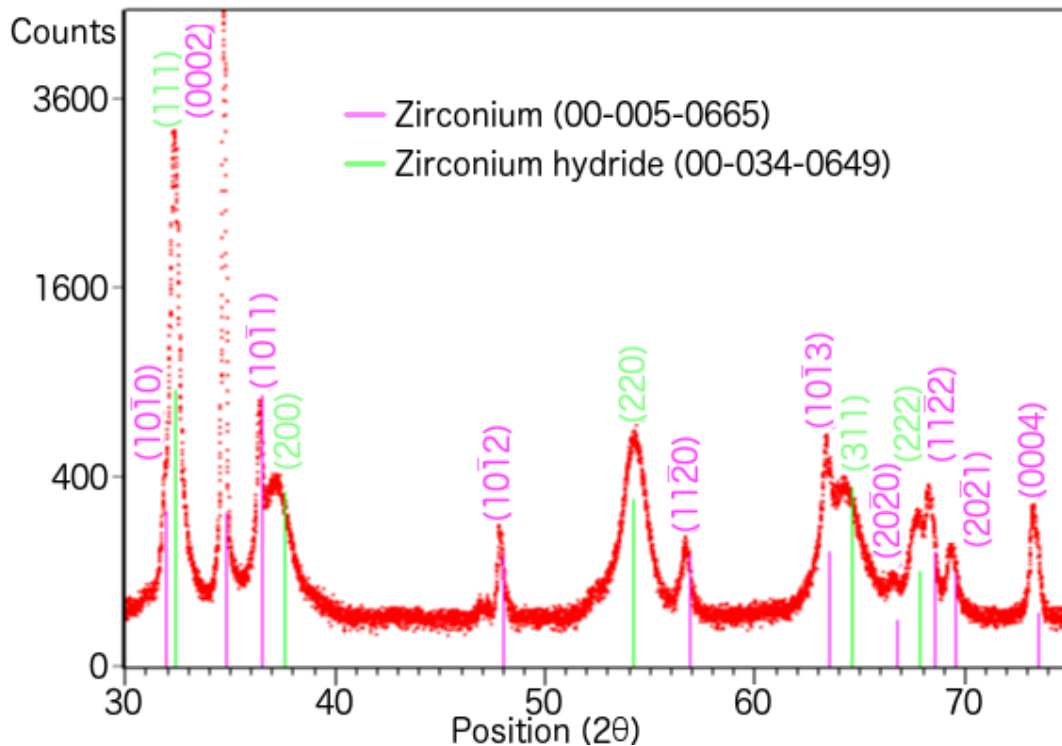


Figure 4.10 XRD identified the presence of the α -Zr and the δ -hydride in hydrided material.

4.3 Microstructure and Morphology of Hydrided Material

4.3.1 Hydrided Surface

The hydrided surfaces were examined in a Zeiss Axiophot polarised light microscope. Samples hydrided for various durations are compared in Figure 4.11. In Figure 4.11a and b, hydride nodules of 2-10 μm in diameter formed and no clear preferential nucleation sites were observed. A considerable amount of hydride grain impingement sites were observed after 12 hours of hydriding (Figure 4.11c and d). The nuclei density increased and the transformed area covered almost the whole surface after 96 hours (Figure 4.11e and f). The quantitative analysis for the rate of transformed coverage area is presented in Section 5.1.

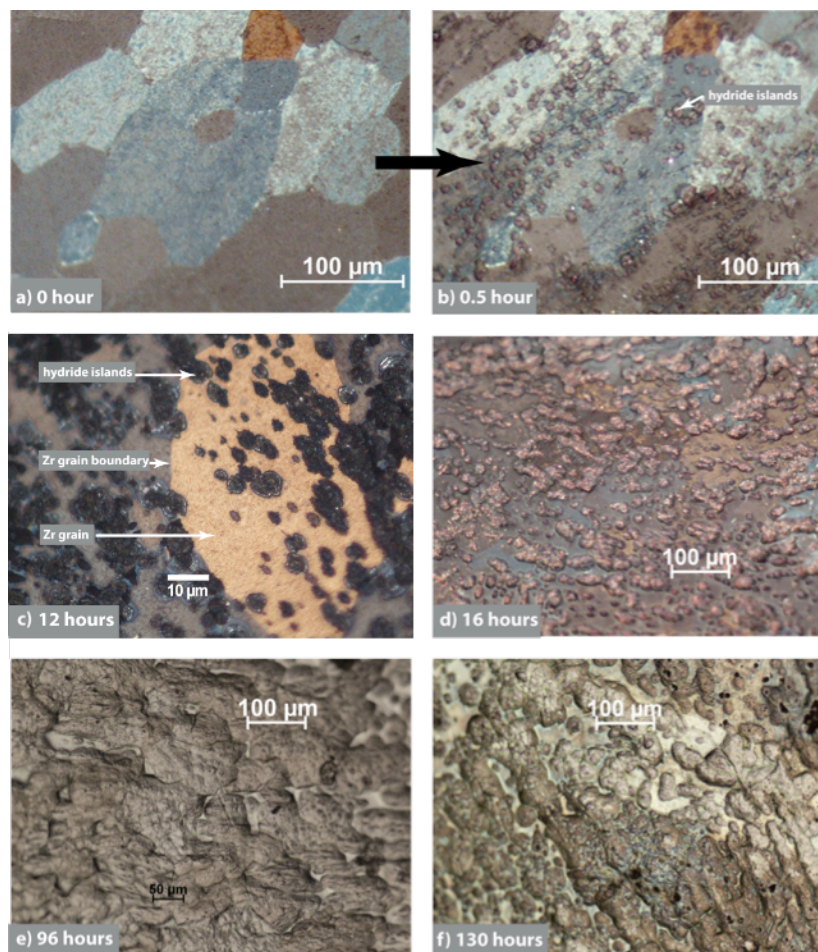


Figure 4.11 Hydrided surfaces after various hydriding durations. a) and b) The same area was imaged after hydriding. c) and d) No obvious preferential nucleation sites for precipitation was seen. e) and f) Overlapped islands covered almost the whole surface of the sample.

SEM was used to examine the morphology of the hydride nodules. Figure 4.12a and b shows a 96-hour hydrided sample at the tilt angles of 0° and 60° . Hydride islands having a diameter of about 5-35 μm and a height of about 1-2 μm covered most of the surface. Microscale cracks can be clearly seen on the surface of a 34-hour hydrided sample (Figure 4.12c). The crack formation is unlikely result from handling since sub-surface cracks of similar dimensions can be seen inside the film after low current FIB milling (Figure 4.12d). Impingement and overlapping of island nuclei can be seen at a tilt angle in Figure 4.13.

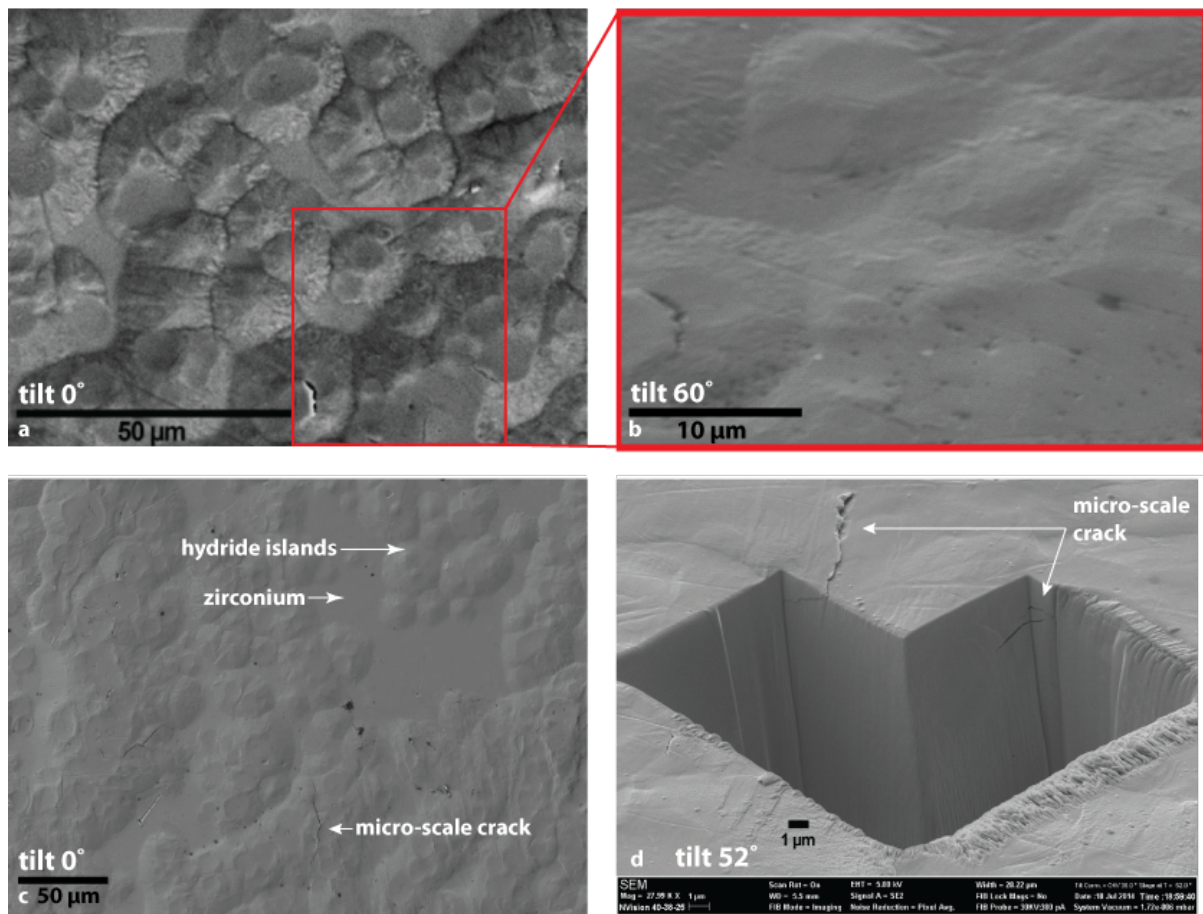


Figure 4.12 The morphology of hydride clusters was examined by comparing SEM micrographs imaged at different tilt angles. a and b) A sample hydrided for 96 hours was observed at 0° and 60° . c) Microcracks extended across hydride nodules on the surface of a 34-hour hydrided sample. d) Microcracks were also seen at a depth of several microns into the hydride layer in the same 34-hour hydrided sample.

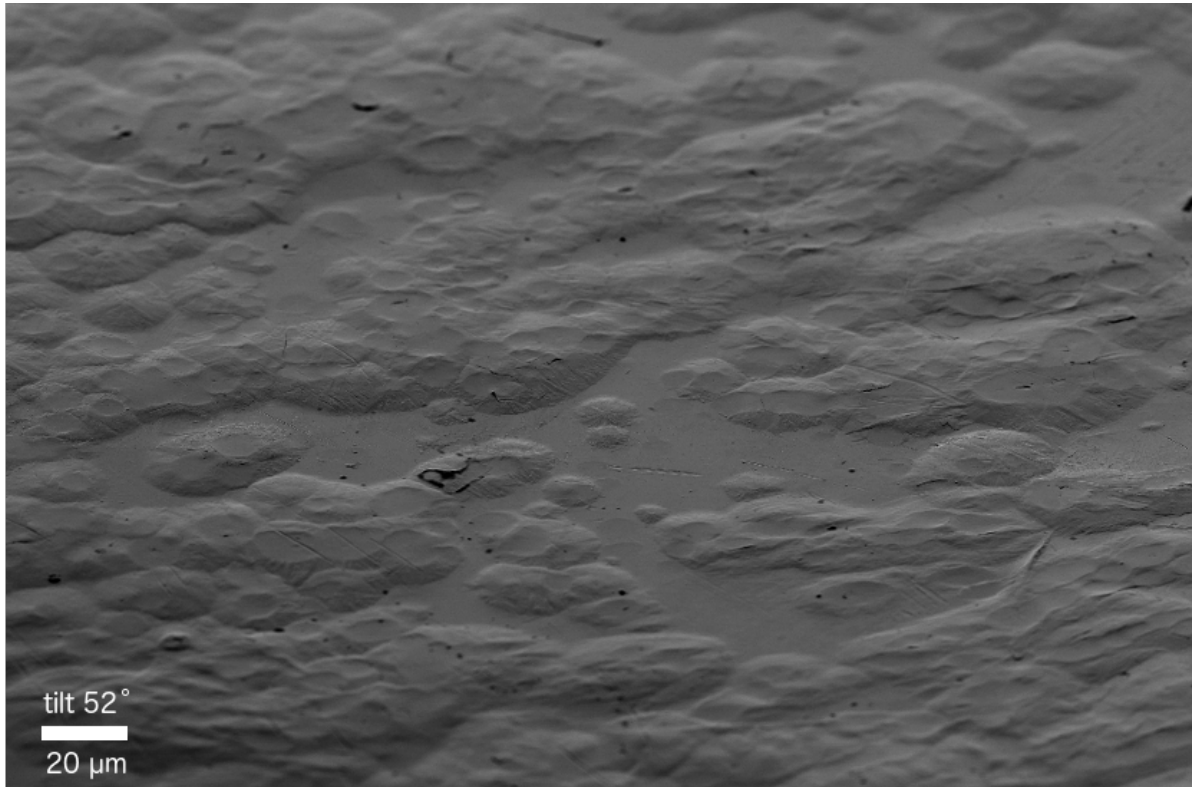


Figure 4.13 The SEM micrograph shows a large number of hydride islands impinging on one another after 34 hours of hydriding. The Zr sample was polished to form a flat surface before hydriding.

4.3.2 Cross-Sectional Hydrided Surface

The cross-sectional surfaces of the hydrided samples were polished as described in Section 3.2. High resolution SEM was used to examine the Zr/hydride dual-phase microstructure. In Figure 4.14a, the hydride clusters protruding from the edge are caused by expansion of local volume during phase transformation. Microscale cracks were frequently observed around edges and corners (Figure 4.14b to d). These naturally formed cracks indicate the intrinsic brittle nature of the δ -hydride.

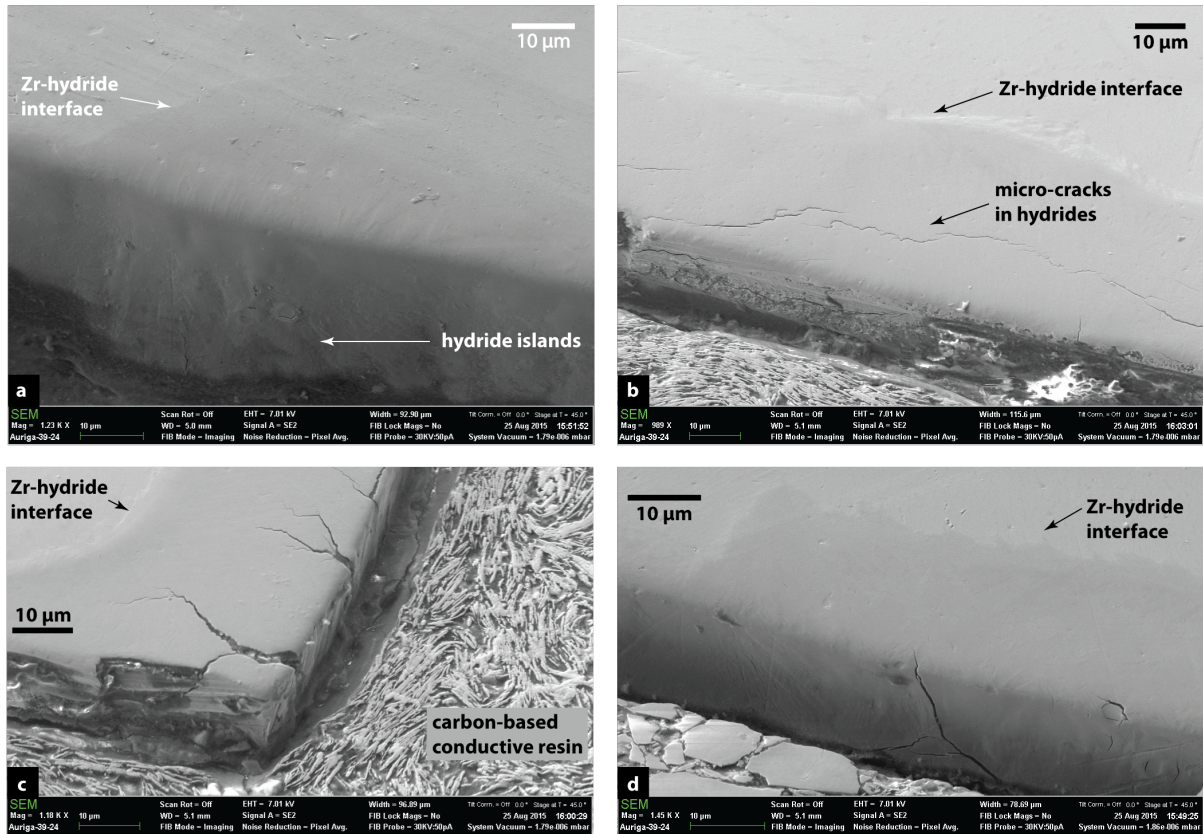


Figure 4.14 The SEM micrographs show the regions near hydrided edges and corners. a) Local volume expansion during phase transformation led to bulging hydride edge. The edge was straight before hydriding as shown in Figure 4.3. b to d) Microscale cracks were seen on the side and top surfaces of the hydride film. The top surface was polished before hydriding.

Isolated islands were observed in all hydrided samples (Figure 4.15a). The number of islands increased with the hydriding time and eventually coalesced to form a continuous film (Figure 4.15b and c). Sub-surface microscale cracks, roughly parallel to the hydriding surface, were observed within the film in all samples. This observation is consistent with that seen in the hydrided surface examination (Figure 4.12d).

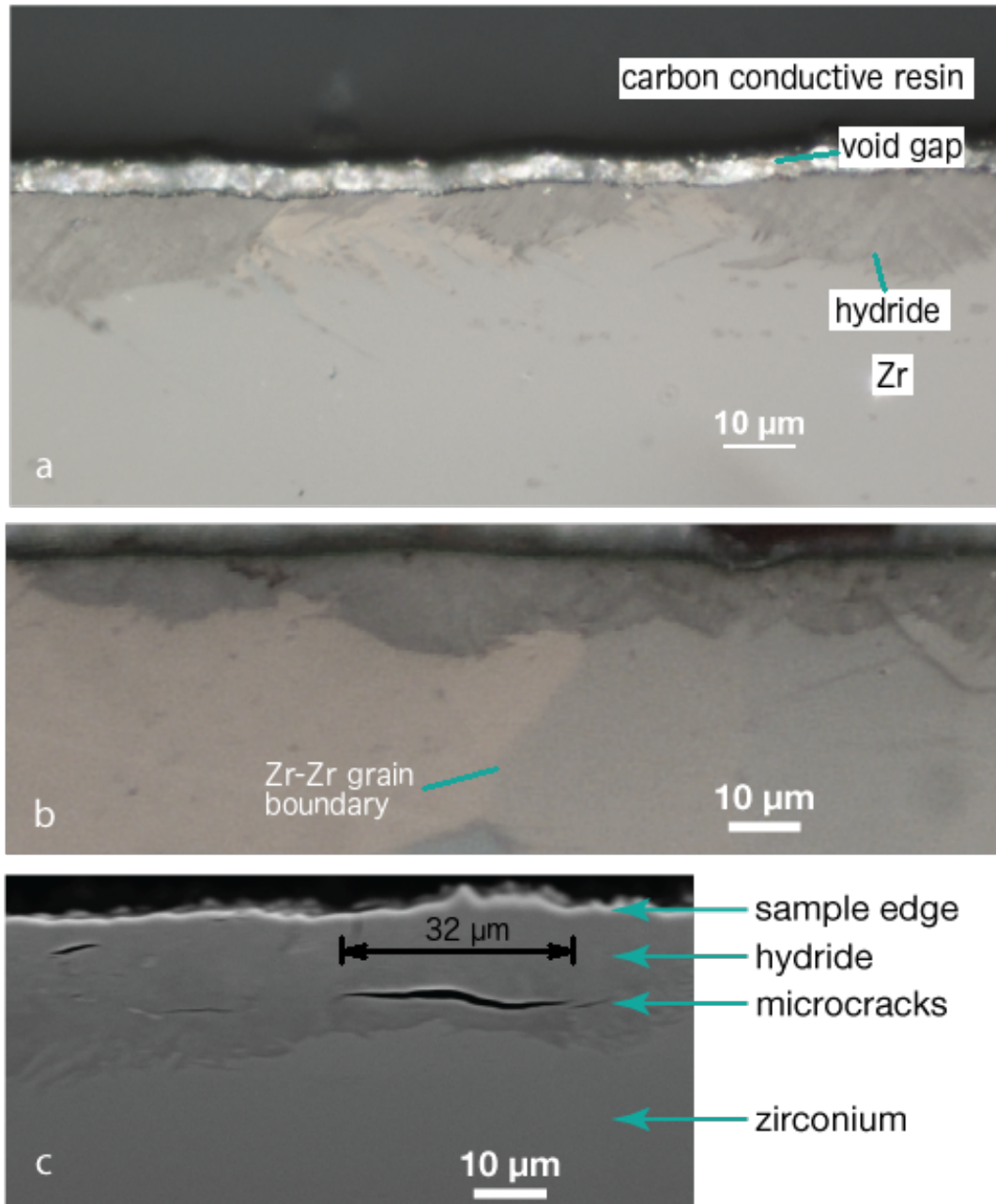


Figure 4.15 The cross-sectional surface of hydrided samples. a) Isolated islands were observed in a 12-hour hydrided sample under polarised light. The apparent bright layer on top of the sample is an empty gap since some conductive paint peeled off during polishing. b) Hydride islands touched one another in a 16-hour hydrided sample. c) SEM image shows microcracks are roughly parallel to the edge in a 96-hour hydrided sample.

Figure 4.16 shows the cross-sectional surface of a hydride island and its interface with the Zr substrate. A spike-shaped phase boundary between the α -Zr and the δ -hydride can be seen.

Figure 4.17 indicates that the spike-shaped feature corresponds to a dense stack of sub-

micron scale hydride platelets. Figure 4.17 shows that the orientation of hydride precipitates changes across a Zr/Zr grain boundary.

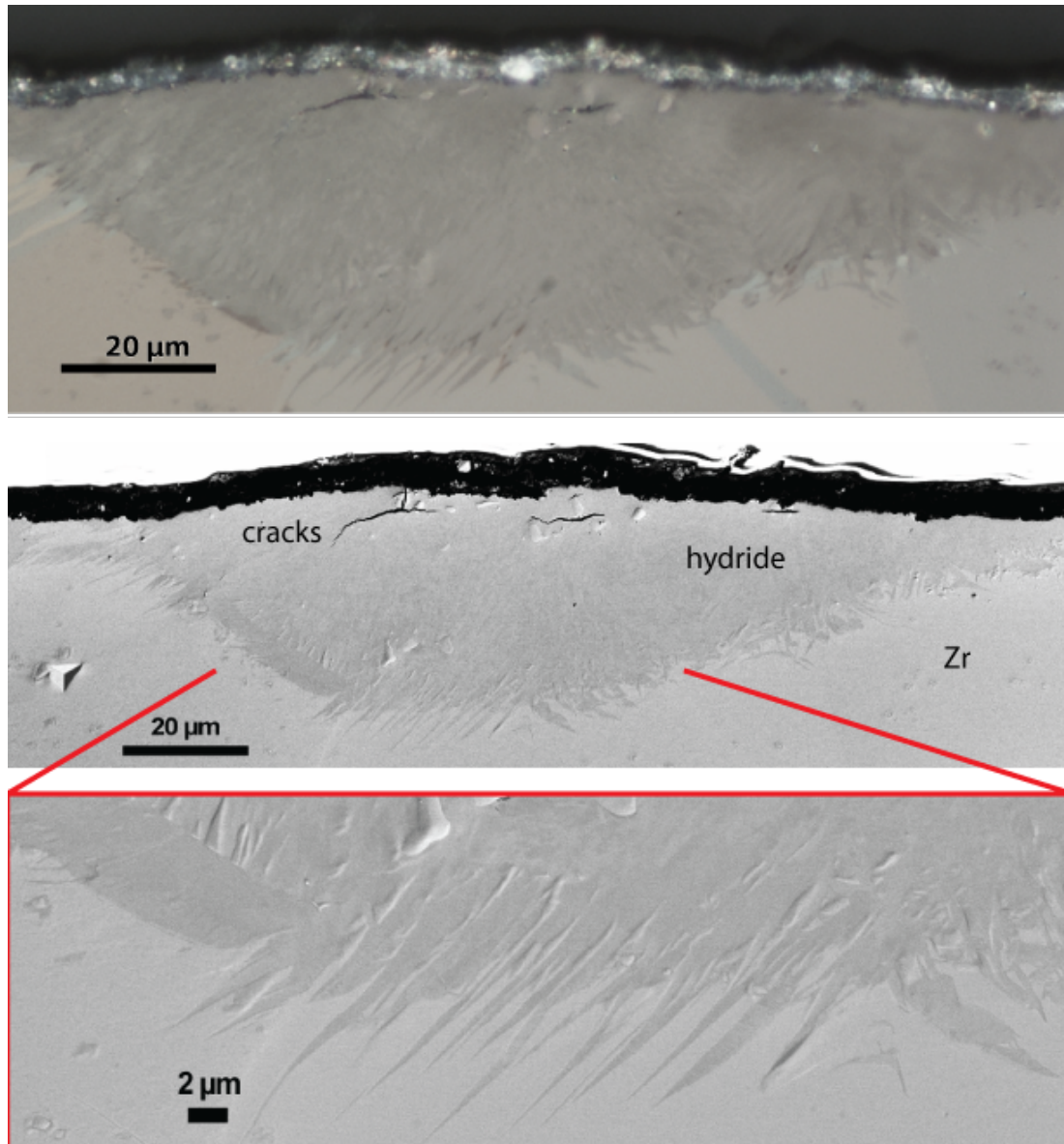


Figure 4.16 A hydride island and its interface with the Zr matrix. a) A preliminary examination was carried out using polarised light OM. The bright layer between the top dark resin region and the bottom hydride edge is a void gap. b) High resolution SEM image of the same area. The microcracks can be observed more clearly in comparison to the optical micrograph in Figure a. c) Spike-shaped features were observed along the interface.

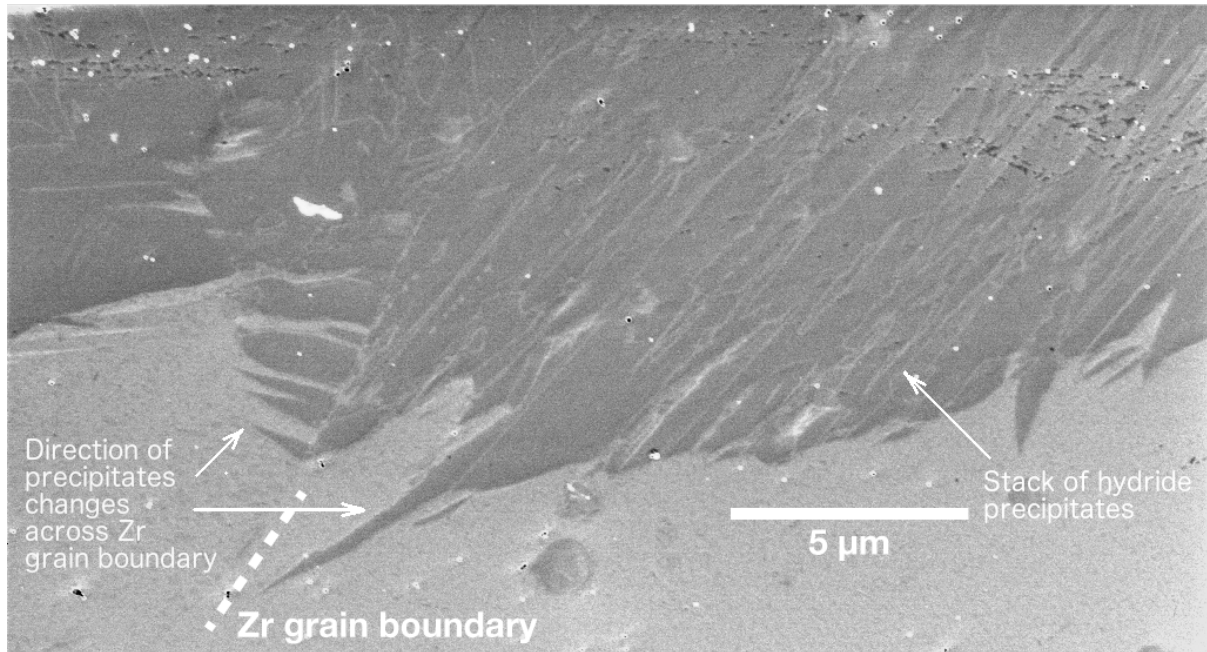


Figure 4.17 The microstructural examination of hydride islands shows packets of smaller platelets. These hydride precipitates pile up to form the Zr/hydride boundary. The orientation of precipitates changes across a Zr/Zr grain boundary.

A foil sample was lifted out from the hydrided surface for microstructural examination (Figure 4.18). The lift-out procedure was similar to the preparation of a conventional TEM sample with the use of FIB.

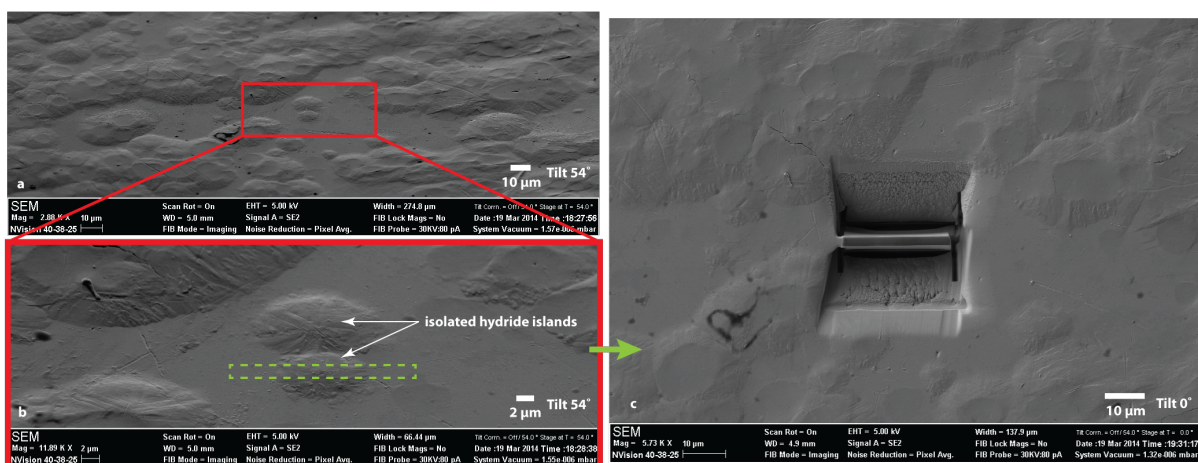


Figure 4.18 Foil sample preparation. a and b) The foil was lifted out along an isolated island on the hydrided surface. The lift-out location is represented by the green rectangle. c) FIB was used to remove the surrounding materials.

Figure 4.19 a and b show the lens-shaped δ -hydride island on the cross-sectional foil. Hydride precipitates are closely stacked and aligned below the island. The typical dimensions of these precipitates are $\sim 0.2\text{-}1\text{ }\mu\text{m}$ in length and $\sim 0.03\text{-}0.1\text{ }\mu\text{m}$ in width as measured directly from the magnified image (Figure 4.19a). The crystallographic relationship between the Zr and the hydride is presented in next section. Aligned hydride precipitates were consistently observed in some FIB-milled trenches on the hydrided surface as shown in Figure 4.20.

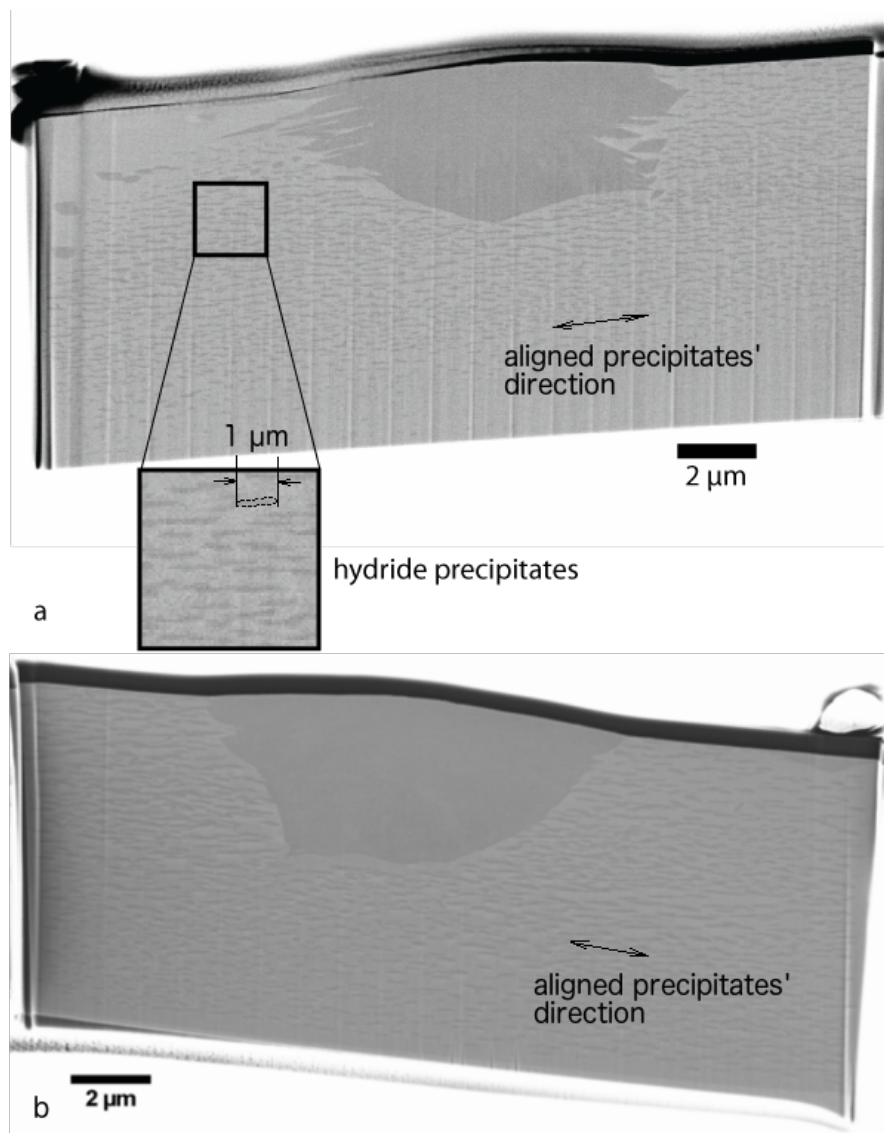


Figure 4.19 Hydrides near the α/δ phase boundaries. a and b) Closely stacked hydride precipitates align below a lens-shaped hydride island in a foil sample.

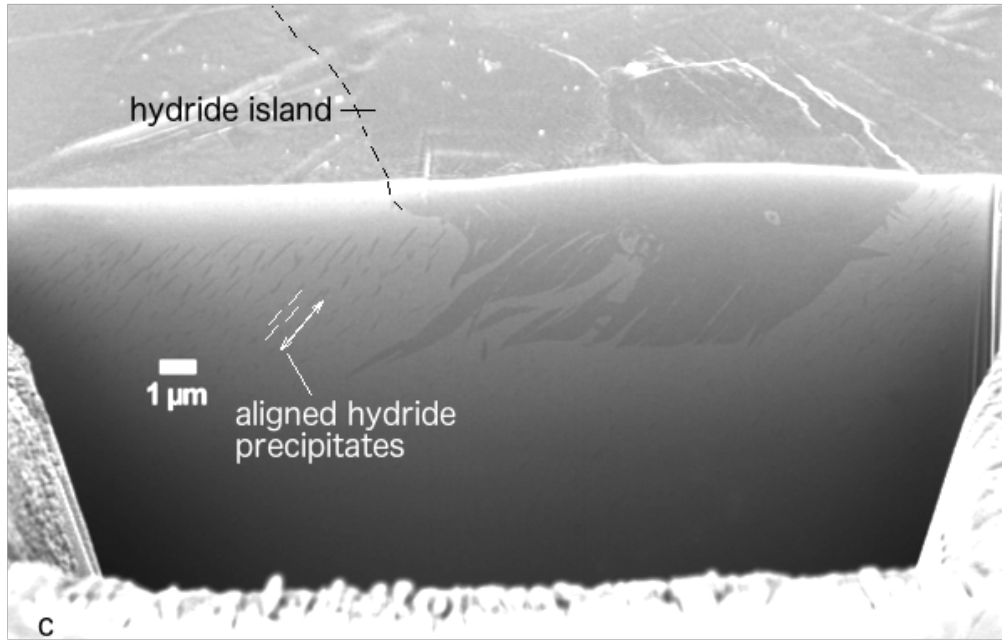


Figure 4.20 Aligned hydride precipitates were observed near an isolated island on the wall of some FIB-milled trenches. The island consists of clusters of hydride platelets.

4.4 EBSD Analysis of Hydrided Material

An EBSD analysis was carried out for the dual-phase region on the cross-sectional hydrided surface. The experimental parameters and setups are summarised in Table 4.1.

Table 4.1 Experimental setup information for the EBSD analysis of the hydrided material.

	Sample type	Instrument	Accelerating voltage	Probe current	Working distance	Step size	Surface preparation
i	Conventional	Carl Zeiss Merlin	20 kV	5 nA	17.8 mm	1.12 μm	Ar ion polish
ii	Conventional	Carl Zeiss Merlin	20 kV	20 nA	17.8 mm	0.17 μm	Ar ion polish
iii	Conventional	JEOL JSM-840A	20 kV	30 nA	14.0 mm	0.53 μm	HF etch
iv	Lift-out foil	Carl Zeiss Merlin	20 kV	20 nA	16.7 mm	0.02 μm	Ga ion polish

In the first experiment, a relatively large area of $210 \times 280 \mu\text{m}^2$ of a 96-hour hydrided sample was examined. A Carl Zeiss Merlin equipped with FESEM and Bruker high resolution EBSD system was used for pattern acquisition. The surface was finished with Ar ion polishing with procedure described in Section 3.1. Figure 4.21a and b show the polarised optical micrographs of the region in which the two phases are distinguishable as annotated. The

region was then imaged at the tilt angle of 60° in a FIB 200 as shown in Figure 4.21c; however the contrast is inadequate to reveal any feature. In Figure 4.21d, the SE micrograph obtained in the Merlin is also unable to provide sufficient contrast for surface examination. The crystal orientations of the Zr grains can be acquired by EBSD however the phase of the film was not identified (Figure 4.21e and f). The causes are discussed in Section 4.5 with more information obtained in the experiments described below.

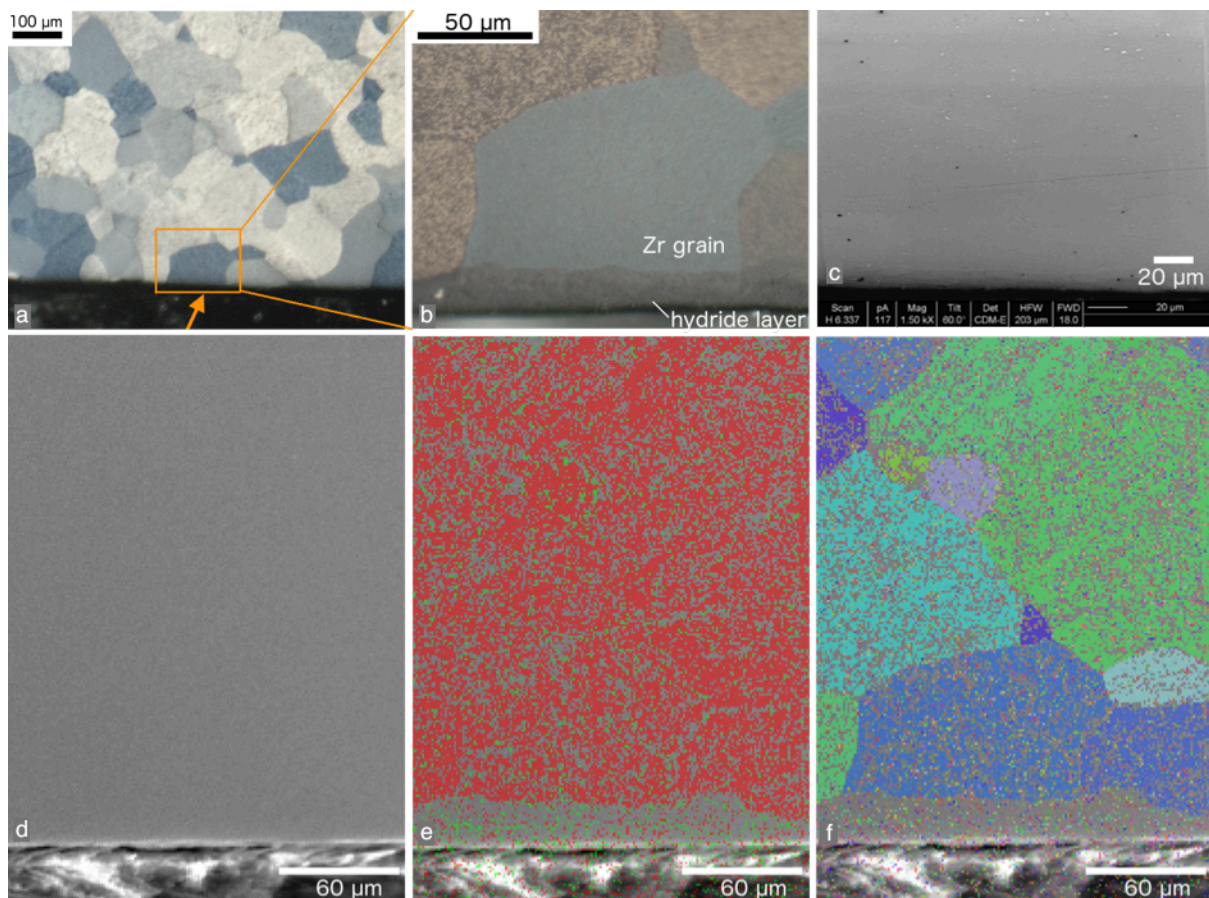


Figure 4.21 EBSD analysis of the dual-phase region. a and b) Polarised optical micrograph. The hydride layer is about $18\ \mu\text{m}$ in thickness. c) SE image obtained in a FIB200 with $100\ \text{pA}$ probe current at the tilt angle of 60° . d) SE image of the same region in a Merlin without tilting. e) Dual-phase map obtained in a Merlin. The identified Zr region is shown in red and the hydride is shown in green. f) The EBSD map shows the Zr grain structure but no information about the edge film.

Figure 4.22 shows the $85 \times 63 \mu\text{m}^2$ region for the second EBSD experiment. The selected region of interest contains main features including Zr/hydride phase boundaries, intragranular hydride precipitates and microcracks as annotated in Figure 4.23a. Intragranular hydride precipitates of similar crystallographic orientations can be clearly seen in one of the Zr grains (Region A). The typical dimensions of the precipitates are $\sim 1\text{-}3 \mu\text{m}$ in length and $\sim 0.3\text{-}1 \mu\text{m}$ in width as measured from the image. In Figure 4.23b, all Zr grains and some of the hydride precipitates were identified in the phase map. However much of the continuous hydride layer, including those regions which are few microns away from a microcrack (e.g. Region B) could not be identified. In Region C, a dense stack of parallel hydride precipitates piles to form the Zr/hydride phase boundary.

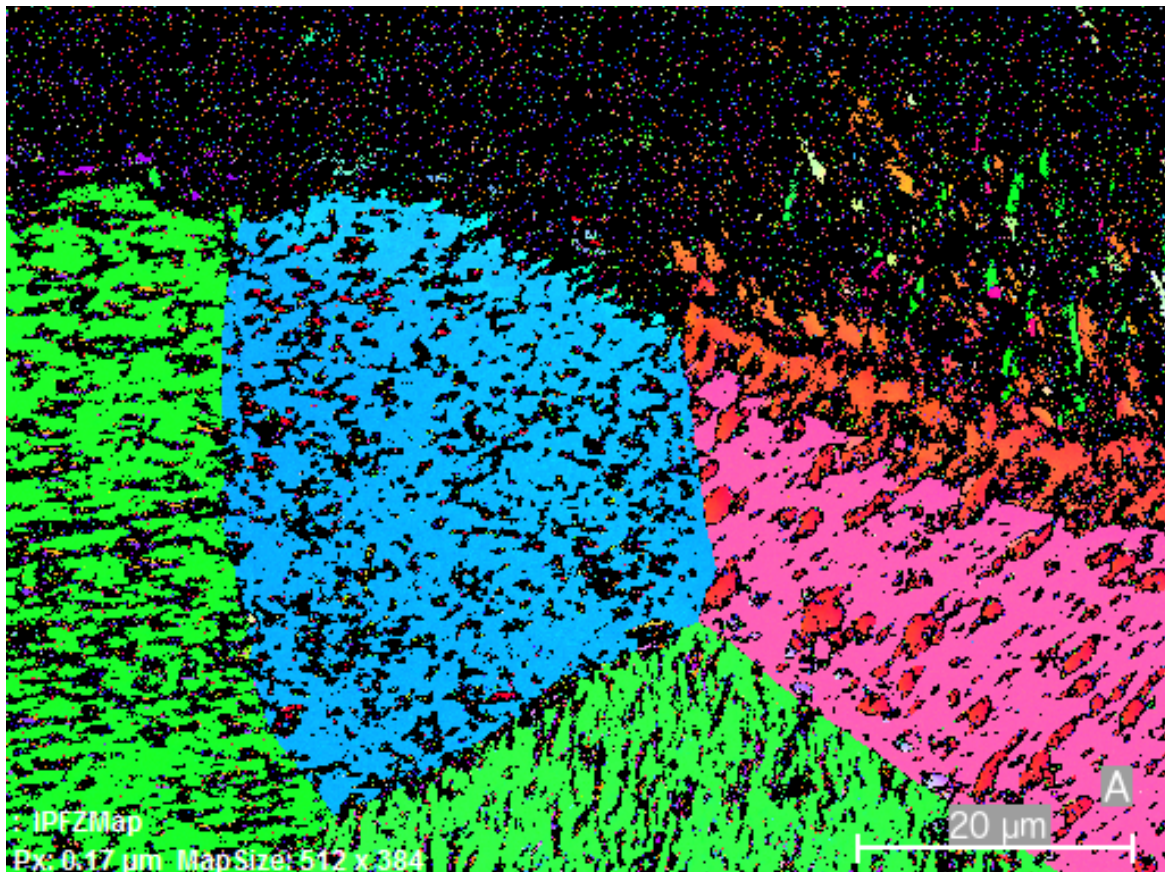


Figure 4.22 EBSD Inverse pole map of the hydrided sample normal to the Z-direction. The unindexed region on top of the figure is the hydride thin film. The SE image is shown in Figure 4.23. In Region A, the aligned precipitates have similar orientations (See Figure 4.25).

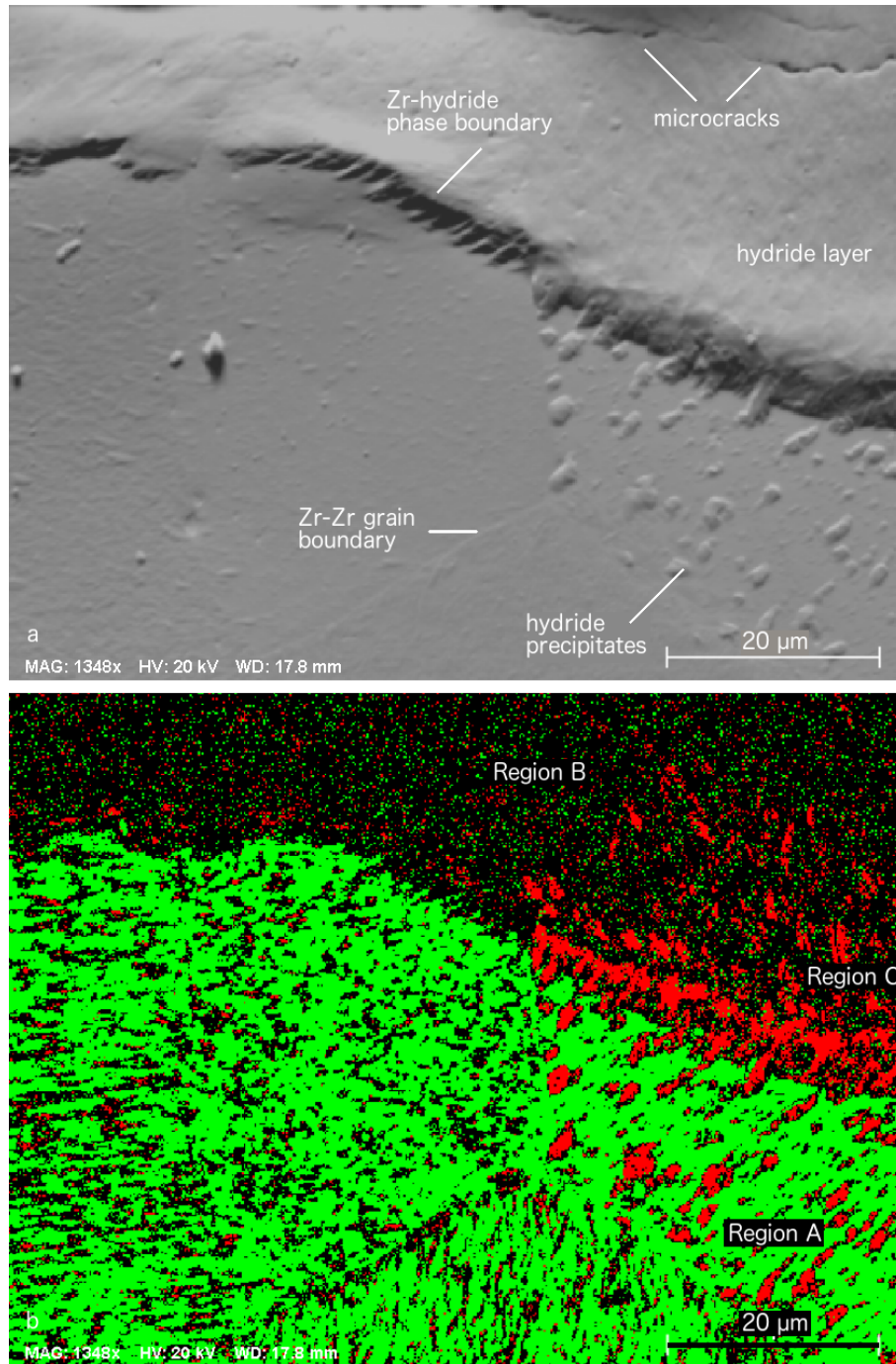


Figure 4.23 Phase identification of a local dual-phase region. a) The SEM image shows some features observed near a Zr/hydride phase boundary of a 96-hour hydrided sample. b) Phase map shows piles of intragranular precipitates formed within a Zr grain (Region A and C).

Figure 4.24 shows the EBSD pattern quality map and some sample diffraction patterns. The automated detection process set the camera to an optimum exposure time of 35 ms for each indexing pixel. In Region B, the sample pattern for the continuous hydride layer is more

diffuse than the others. It can be caused by factors such as lattice strain and ion sputtering. Plastic deformation might occur in the hydride layer during phase transformation. The diffracting volume would then contain a set of crystal lattices of slightly different orientations with dislocations being introduced [172]. In addition, the Ar ion polishing procedure could result in preferential milling and amorphisation. The process could produce an amorphous layer above the crystalline hydride causing poor pattern acquisition [174].

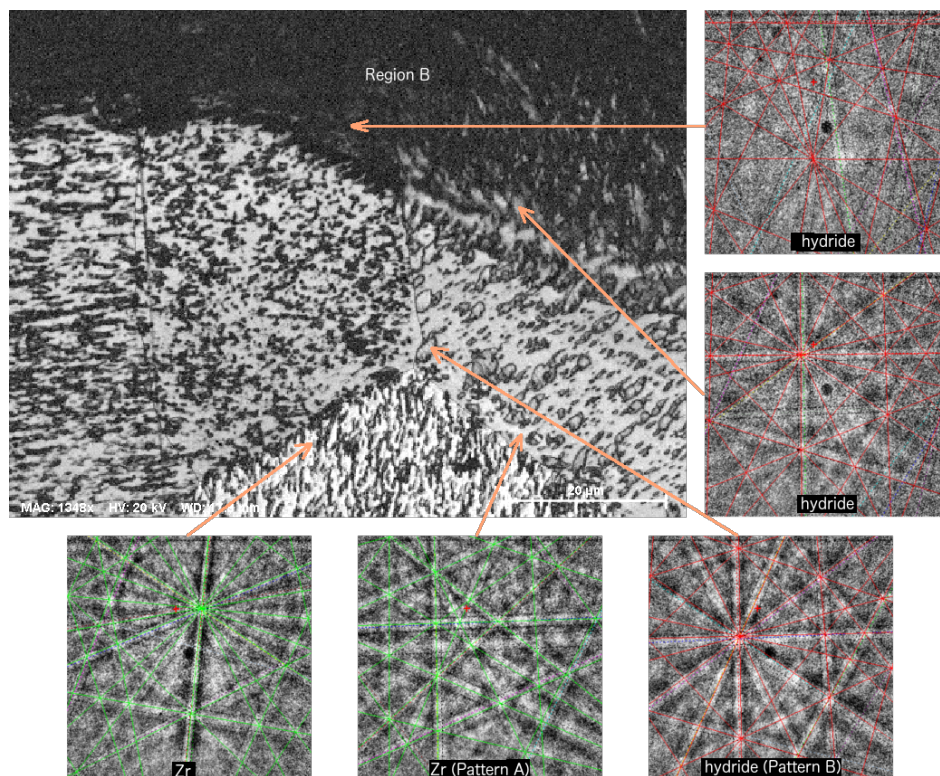


Figure 4.24 EBSD pattern quality map and some sample patterns. The patterns obtained in the hydride film (top right, two figures) are diffuse in comparison to that obtained in the substrate (bottom, three figures).

The crystallographic relationship between a sample Zr grain (Pattern A in Figure 4.24) and an intragranular hydride precipitate (Pattern B) was analysed by using MATLAB toolbox MTEX. In Figure 4.25, the blue dots mark the poles and the red circles represent the stereographic projection of identical points from an imaginary sphere. The overlap of poles

shows that the close packed plane of the α -Zr (hcp) is parallel to that of the δ -hydride (fcc): $(0001)_\alpha || (111)_\delta$ and their close packed directions are also parallel: $[\bar{1}\bar{1}20]_\alpha || [\bar{1}01]_\delta$.

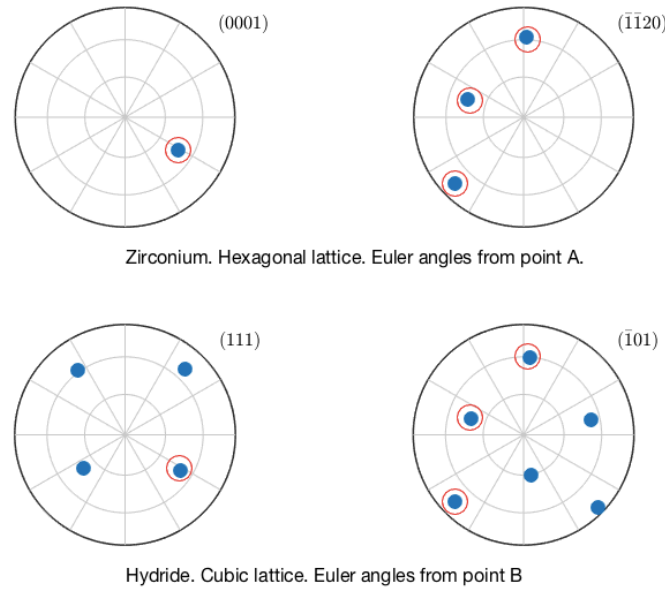


Figure 4.25 Crystallographic relationship between a Zr grain and an intragranular hydride precipitate. The sample points are obtained from patterns A and B as shown in Figure 4.24.

The third EBSD experiment was performed in a thermionic emission SE microscope, JEOL JSM-840A, with a probe current of 30 nA at 20 kV (Table 4.1). The instrument setting was similar to that used in characterization of the unhydrided material (See Section 4.1.1). Figure 4.26 shows the EBSD map and the polarised light micrograph obtained from the dual-phase microstructure near the sample edge. The region consists of a single Zr grain (Figure 4.26a), across which intragranular hydrides are located (central white region), and a $\sim 15 \mu\text{m}$ thick hydride film (Figure 4.26b). The hydride film consists of microscale elongated grains such as grains A_1 and B_1 . Hydride grains of similar orientations, denoted as A or B, are arranged in piles as seen in the figure. The crystallographic orientations of the hydride layer can be obtained with high confidence as suggested by the bright region at the bottom of the pattern quality map (Figure 4.26f). This result is different from the previously described EBSD experiments in which the whole hydrided edge is almost unindexed.

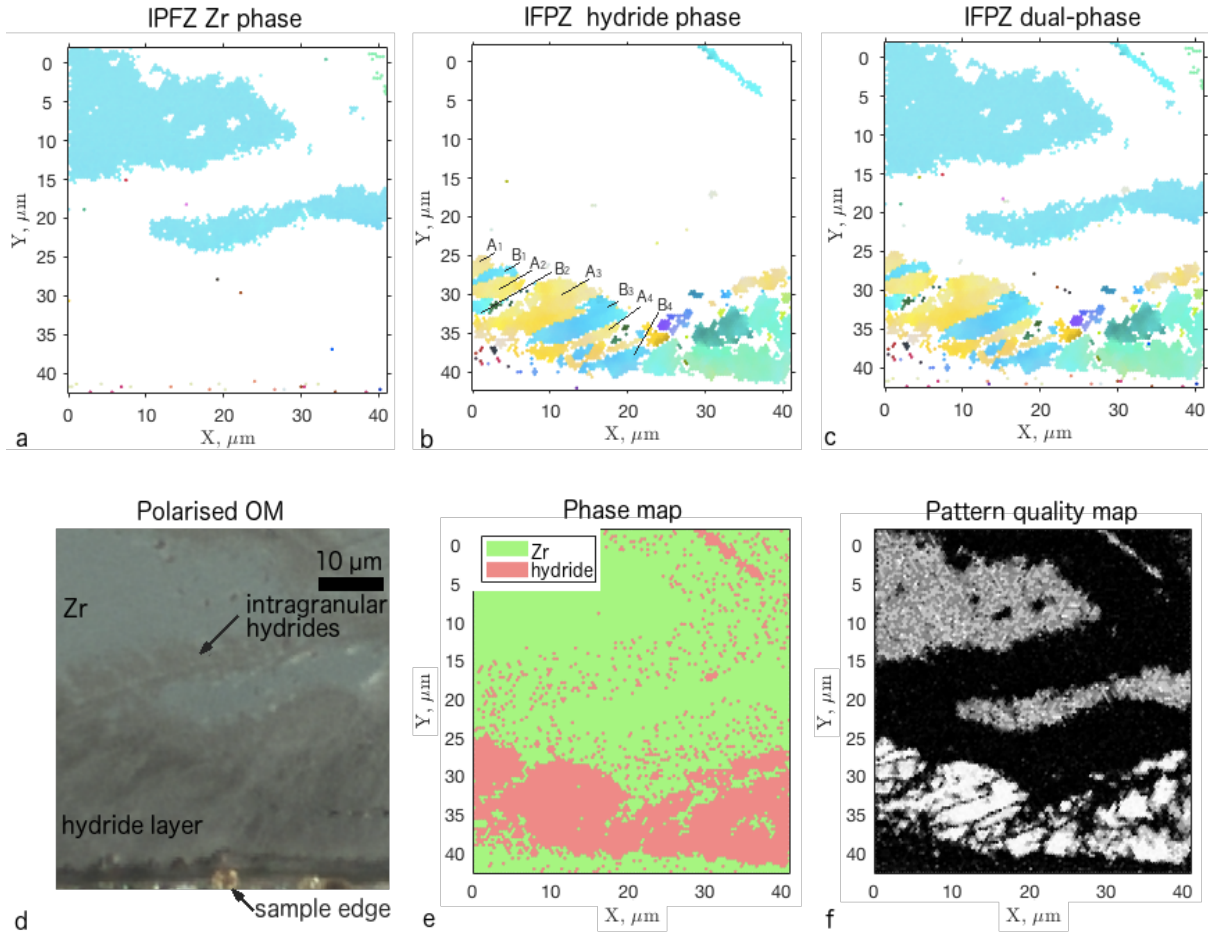


Figure 4.26 EBSD mapping near the cross-sectional edge of a hydrided sample. a) The EBSD map shows only the Zr phase. The substrate region consists of a single Zr grain. b) The EBSD map shows only the hydride phase. Microscale hydride grains A_1 , A_2 , A_3 and A_4 have similar crystallographic orientations and B_1 , B_2 , B_3 and B_4 have another set of similar orientations. The grain set A and the grain set B have a twin relationship as shown in Figure 4.27b. c) The dual-phase EBSD map indicates poor acquisition of quality data in the central white region. d) Polarised optical image suggests that the central white region consists of intragranular hydride precipitates. e) Phase map supports that the central region is a mixed-phase region in which hydride precipitates are represented by the red disperse pixels. f) The pattern quality of the hydride phase is high as indicated by the high brightness.

Figure 4.27a shows that the long axes of the hydride grains pile along $[\bar{1}\bar{1}20]_{\text{Zr}}$. This preferential precipitation direction is consistent with some reported results [37], [63] (Figure 2.9). The crystallographic relationship between the Zr grain and the hydride grains is $(000\bar{1})_{\text{Zr}} \parallel (111)_{\text{hydride}}$ and $[\bar{1}\bar{1}20]_{\text{Zr}} \parallel [0\bar{1}1]_{\text{hydride}}$ as seen in Figure 4.27b. This result is in agreement with the second EBSD experiment and the literature work listed in Section 2.2.3.

The pole figures also show that the hydride grain set A (A_1 to A_4) possesses a twin relationship with the hydride grain set B (B_1 to B_4) where $(1\bar{1}1)_A || (111)_B$.

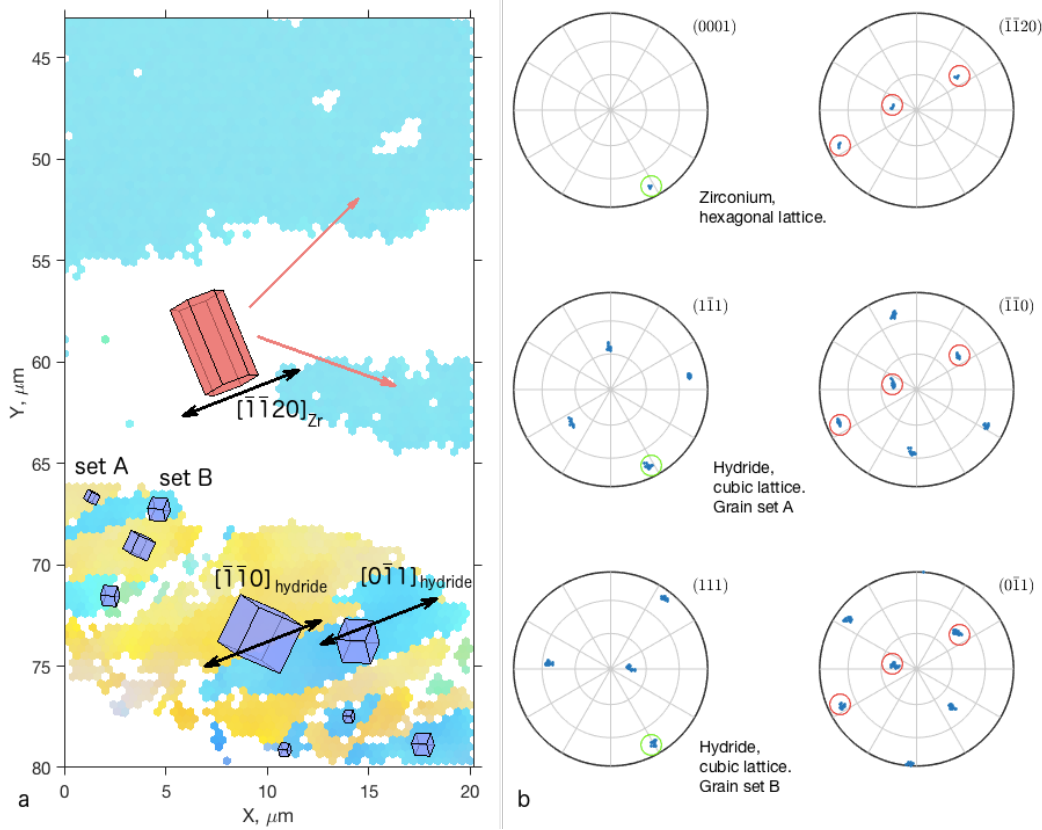


Figure 4.27 Crystallographic relationship analysis for the third EBSD experiment. a) The upper region ($Y < 65 \mu\text{m}$) is the Zr substrate of which the crystal orientation is denoted by the hexagonal cell. The lower region shows two sets of hydride grains with similar orientations. The hydride/hydride grain boundaries align along $[0\bar{1}1]_{\text{hydride}}$ or $[\bar{1}\bar{1}20]_{\text{Zr}}$. b) The pole figures show $(000\bar{1})_{\text{Zr}} || (111)_{\text{hydride}}$ and $[\bar{1}\bar{1}20]_{\text{Zr}} || [0\bar{1}1]_{\text{hydride}}$. They also show that the two sets of hydride grains have a twin relationship.

In the forth EBSD experiment, a foil was lifted out along the centreline of an isolated hydride island. The lift-out procedure and the microstructural features are described in Figure 4.18. The EBSD patterning was carried out with the help of Dr Arantxa Vilalta-Clemente of the University of Oxford. In Figure 4.28, the top dark region of the SEM image is the cross-section of the island and the bottom bright region is the Zr substrate. Dispersed hydride precipitates can be seen below the Zr/hydride phase boundary. The long axes of these

precipitates have a mutual alignment along $[\bar{1}\bar{1}20]_{\text{Zr}}$. The crystallographic orientation relationship between the two phases is $(000\bar{1})_{\text{Zr}} \parallel (111)_{\text{hydride}}$ and $[\bar{1}\bar{1}20]_{\text{Zr}} \parallel [0\bar{1}1]_{\text{hydride}}$ as determined from the pole figures in Figure 4.29.

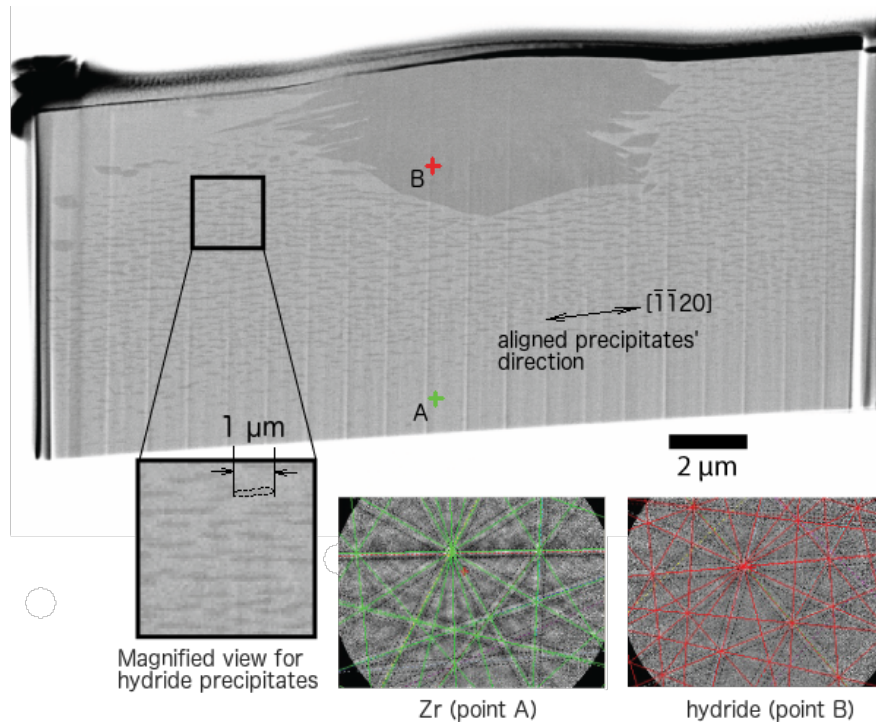


Figure 4.28 Foil sample for EBSD analysis. The bright region at the bottom of the foil represents the Zr substrate in which the diffraction pattern A was detected. The dark region at the top is the cross-section of a hydride island in which the pattern B was detected. The long axes of the dispersed hydride precipitates are parallel to $[\bar{1}\bar{1}20]_{\text{Zr}}$ or $[\bar{1}01]_{\text{hydride}}$.

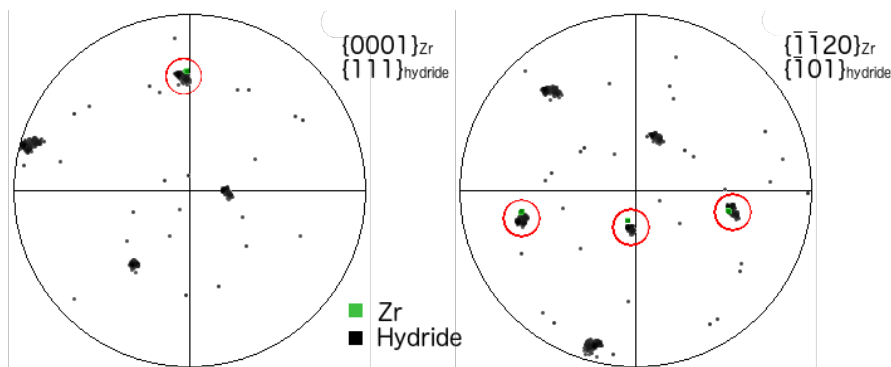


Figure 4.29 The pole figures obtained for the Zr and for the hydride in the foil sample are overlapped. The red circles mark the common positions of the poles. The crystallographic orientation relationship is $(000\bar{1})_{\text{Zr}} \parallel (111)_{\text{hydride}}$ and $[\bar{1}\bar{1}20]_{\text{Zr}} \parallel [0\bar{1}1]_{\text{hydride}}$

4.5 Discussion

Morphological features such as aligned precipitates, bulging sample edges and connected hydride islands were observed in all hydrided samples. None of these features was seen in any initial Zr samples before hydriding; they were developed during the phase transformation from the α -Zr to the δ -hydride. Figure 4.30 illustrates the formation of the microstructure observed on the cross-sectional surface of a hydrided sample. Nucleation occurs when hydrogen diffuses into the initial Zr lattice to form zirconium hydride which has a 17% increase in the unit cell volume (Section 2.2.3). The local volume expansion would then introduce protruding hydride grain nodules and their cross-sectional surface corresponds to the bulging edge. The formation of hydrides would generate dislocations [63], [64], [66]; which are favourable nucleation sites for new precipitation. Therefore hydride platelets aggregated to form islands instead of forming a thin film of uniform thickness. The elongated grain structure within an island would arise from the preferential growth of piled hydride platelets in the direction $[\bar{1}\bar{1}20]_{\text{Zr}}$. These individual islands subsequently connect to become a thin film when the sample surface is continuously supplied with hydrogen at the cathode.

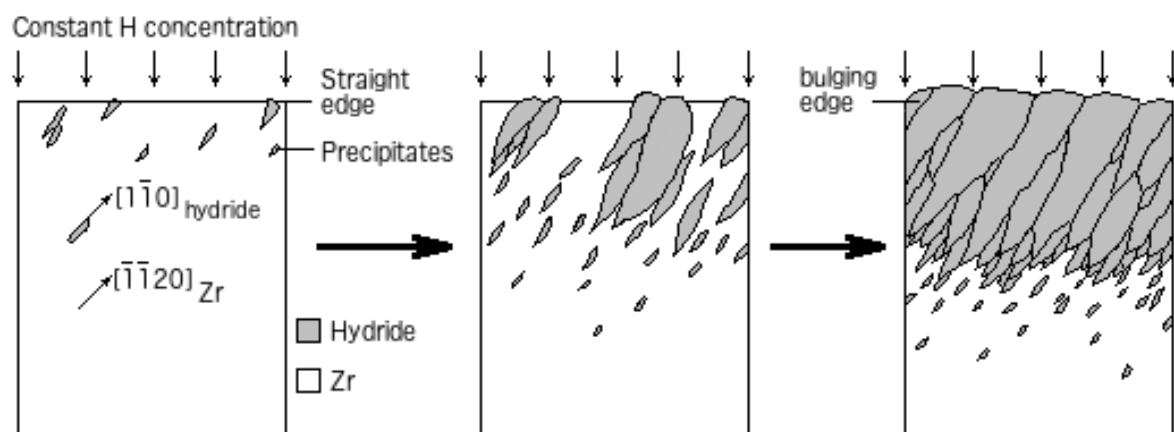


Figure 4.30 Illustration of the formation of the dual-phase microstructure from a single Zr grain. See Section 4.3.2 for SEM micrographs.

Microcracks of up to 50 μm in length were developed only within the film but not in the underlying substrate; indicating the intrinsic brittle nature of the hydride phase. Similar observations have been reported for hydrided samples that were prepared over 800°C [75], [78]. Numerous cracks were observed metallographically after the preparation. In those studies, the number of cracks was reduced by decreasing the cooling rate until no surface crack was observed. However in the SEM examination presented here, cracks were found inside the film after FIB milling (Figure 4.12d). This raised a question on whether the hydrided samples described in the literature were genuinely crack-free in the bulk. Cracks that existed inside a macroscopic scale tensile sample would reduce the fracture strength. Yielding of the bulk Zr hydrides might not be detected since external work was used for propagation of the pre-existing cracks. Therefore micromechanical tests carried out in a crack-free region are more applicable to determine the intrinsic hydride properties.

EBSD was used to characterise the dual-phase microstructure however the pattern qualities for the hydride film and the mixed-phase region were usually lower than the Zr region. First, the hydride film consists of sub-micron scale grains. It is evident in Figure 4.17 and Figure 4.19 that the hydride precipitates could be less than 0.1 μm in thickness. The local region that contained a high density of grain boundary would lead to difficulties in indexing. Secondly, the precipitation would generate dislocations that extended into the Zr matrix (Figure 2.10) and introduce residual strain that degraded the EBSD patterns [175]. Microcracks were frequently observed in the hydride film. This suggests that local stresses could attain a state that caused fracture during transformation. Plastic strain might have been introduced in the lattice resulting in poor EBSD patterning. Finally, the scan was carried out at $\sim 20\text{ }\mu\text{m}$ near

the edge. Since EBSD patterns are formed in the depth of 10-50 nm [158], the inclined and rounding edges would reduce the quality of the EBSD patterning.

4.6 Summary

The phases and composition of the materials were identified with the use of XRD and EDS. Morphological examination was carried out by combining OM, SEM and EBSD in order to investigate the formation of the Zr/hydride dual-phase microstructure. Microscale hydride islands formed when hydrogen diffused into the Zr substrate. These lens-shaped islands consist of varying sizes of elongated hydride platelets from <1 to 10 μm in length; in comparison with the average Zr grain diameter of over 90 μm . The long axes of these precipitates have a mutual alignment with $[\bar{1}\bar{1}20]_{\text{Zr}}$. The number of islands increased with hydriding time and they subsequently overlapped to form a thin hydride film. The fcc hydride possess a crystallographic relationship with the hcp Zr substrate: $(0001)_{\text{Zr}}|| (111)_{\text{hydride}}$ and $[\bar{1}\bar{1}20]_{\text{Zr}}|| [\bar{1}01]_{\text{hydride}}$ which implies their close packed planes and their close packed directions are parallel. A stack of elongated hydride grains having a twin relationship $(1\bar{1}1)_{\text{A}}|| (111)_{\text{B}}$ were observed. Naturally formed microcracks were observed in all hydride films prepared at various hydriding durations. The presence of cracks indicates the intrinsic brittle nature of the hydride; which is distinctively different from the ductile metallic Zr.

5 HYDRIDE FORMATION ANALYSIS

The morphology of the dual-phase microstructure is determined by the phase growth of hydrides. Since the TSS of H is low in Zr at the low operating temperature of 65°C, a vast amount of hydride precipitates formed at few microns underneath the surface (See Section 4.3.2). These precipitates consisted of H atoms filling the interstitial sites of the metallic Zr lattice. Therefore they slowed down the interstitial diffusion of mobile H atoms; in particular in a local region where the H concentration was high [176]. In this chapter, this concentration-dependent diffusion mechanism is discussed and a new finite difference model is presented for characterising the H concentration profile.

5.1 Surface Nucleation and Phase Growth Analysis

The nucleation and surface phase growth of hydrides can be described by a two-dimensional analysis. It is based on kinetics of phase change as proposed by Avrami [177], [178],

$$A_f = 1 - e^{-kt^n} \quad 5.1$$

where A_f is the area fraction of the transformed phase, k and n are time-independent parameters and t is the hydriding time. In order to estimate the two parameters, Eq.5.1 is rearranged as:

$$\ln \left(\ln \left(\frac{1}{1 - A_f} \right) \right) = n \ln t + \ln k \quad 5.2$$

The slope and the y-intercept of the transformed plot can then be used to determine the growth rate of surface hydrides.

5.2 Two-Phase Classical Diffusion Model

In a classical approach, the hydride layer growth along the depth can be described as a Stefan problem [178], [179]. The model consists of a sharp moving interface in a binary system. The treatment of this non-steady solid-state diffusion problem was studied by Zener [180]. The analytical solution can be produced using Fick's second law and the mass balance equation.

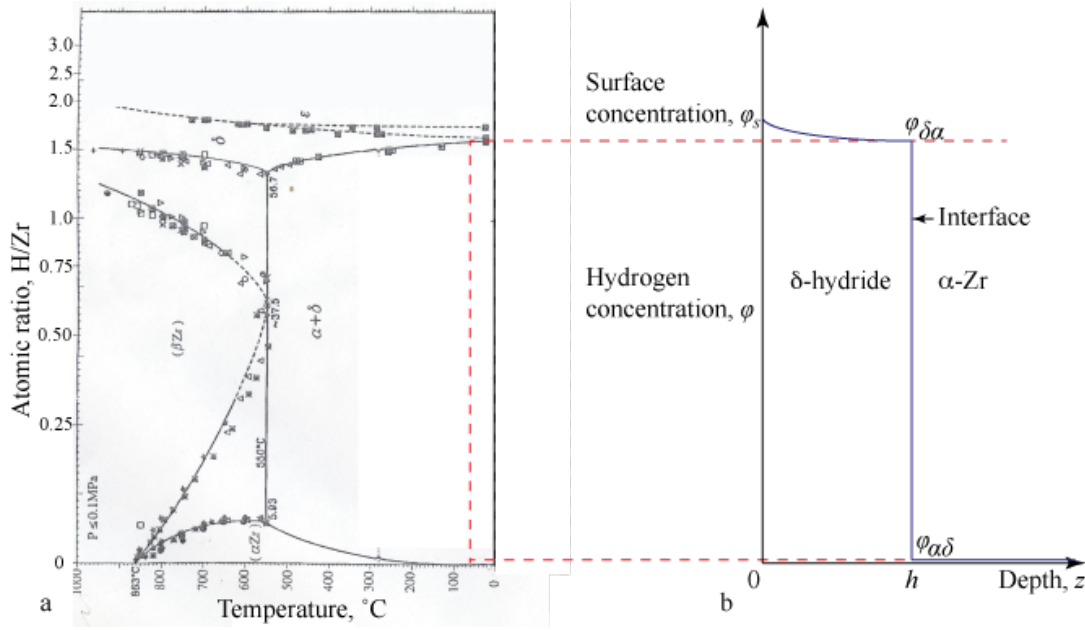


Figure 5.1 Two-phase diffusion model. a) Zr-H phase diagram [36]. b) A schematic representation of the H concentration profile near a hydrided surface at 65°C.

In a binary phase system, the local thermodynamic equilibrium is assumed at the interface. The model structure consists of a finite δ -hydride region near the surface, an α -Zr region and a sharp interface separating them (Figure 5.1b). The motion of the interface in this semi-infinite solid is controlled by atomic diffusion. Hydrogen atoms diffuse away from the interface into the α -Zr matrix through a one-dimensional plate thickening process. The concentration of hydrogen, ϕ , in each phase region will then satisfy:

$$\frac{\partial \phi}{\partial t} = D \frac{\partial^2 \phi}{\partial z^2} \quad 5.3$$

where D is the diffusion coefficient of the phase: $D = D_\alpha$ in the α -Zr and $D = D_\delta$ in the δ -hydride. Eq.5.3 can be converted into an ordinary differential equation and solved by the integrating factor method. The appropriate solution for the concentration at the depth coordinate z and time t is

$$\varphi(z, t) = A_1 \operatorname{erf}\left(\frac{z}{\sqrt{4Dt}}\right) + B_1 \quad 5.4$$

where the coefficients, A_1 and B_1 , are determined by the following boundary conditions:

$$\alpha\text{-phase: } \varphi_\alpha(\infty, t) = 0, \quad \varphi_\alpha(h, t) = \varphi_{\alpha\delta} \quad 5.5$$

$$\delta\text{-phase: } \varphi_\delta(0, t) = \varphi_s, \quad \varphi_\delta(h, t) = \varphi_{\delta\alpha} \quad 5.6$$

where h is the interface depth at time t and φ_s is the surface hydrogen concentration. $\varphi_{\alpha\delta}$ is the solubility limit for the α phase; and $\varphi_{\delta\alpha}$ is the solubility limit for the δ -phase according to the H-Zr phase diagram (Figure 5.1a and Figure 2.4).

The growth rate or the interface velocity is derived from the mass balance equation. The moving interface at an increment dh results from a net flux J acting at a time increment dt ,

$$(\varphi_{\delta\alpha} - \varphi_{\alpha\delta})dh = (J_{\delta\alpha} - J_{\alpha\delta})dt \quad 5.7$$

$$\frac{dh}{dt} = \frac{-D_\delta \frac{\partial \varphi_\delta}{\partial z} \big|_{z=h} + D_\alpha \frac{\partial \varphi_\alpha}{\partial z} \big|_{z=h}}{\varphi_{\delta\alpha} - \varphi_{\alpha\delta}} \quad 5.8$$

Combining Eq.5.4 to 5.8, finally we have

$$(\varphi_{\delta\alpha} - \varphi_{\alpha\delta})\sqrt{\pi}\lambda = \frac{(\varphi_s - \varphi_{\delta\alpha})}{\operatorname{erf}(\lambda)} \exp(-\lambda^2) + \frac{\varphi_{\alpha\delta} \exp\left(\frac{-D_\delta}{D_\alpha} \lambda^2\right)}{\sqrt{\frac{D_\delta}{D_\alpha}} [\operatorname{erf}\left(\sqrt{\frac{D_\delta}{D_\alpha}} \lambda\right) - 1]} \quad 5.9$$

where

$$\lambda = h/\sqrt{4D_\delta t} \quad 5.10$$

In order to determine the interface depth h at a given time t , Table 5.1 lists a range of parameters obtained from the literature. These values were used for model simulations and the results are presented in Section 5.5.2.

Table 5.1 Initial input parameters and diffusion properties for model simulations

Properties and parameters	Range of values	Methods	References
Solubility limit of H in the α -Zr, $\varphi_{\alpha\delta}$	0.34-1.93 ppm wt	Diffusion equilibrium and various experiments	[32], [36]
Solubility limit of H in the δ -hydride, $\varphi_{\delta\alpha}$	17300 ppm wt	Diffusion equilibrium and various experiments	[36]
Diffusion coefficient of H in the α -Zr, D_α	76×10^{-3} - $130 \times 10^{-3} \mu\text{m}^2/\text{s}$	Concentration-penetration experiments	[181]
Diffusion coefficient of H in the δ -hydride, D_δ	0.12×10^{-3} - $12.5 \times 10^{-3} \mu\text{m}^2/\text{s}$	Mechanical spectroscopy and magnetic resonance	[182], [183]
Surface H concentration to form the δ -hydride, φ_s	17100-18100 ppm wt (H/Zr = 1.6-1.7)	Diffusion equilibrium and various experiments	[36]

5.3 Hydrogen Diffusion Mechanisms in Hydrides

The hydrogen atoms produced in the reduction of an electrolytic solution are either absorbed by a metal sample, recombined to form gas bubbles or dissolved in the solution. The portion that is absorbed in the metal sample depends on the H solubility of the metal, the current density and the permeability of the surface oxides [176]. In the case of Zr, experimental studies have shown the rate of H absorption is also strongly influenced by the formation of hydrides [184]. The small size of H atoms leads to fast solid state diffusion in Zr through a direct interstitial diffusion mechanism [176], [185]. Hydrides form when the hydrogen concentration exceeds the solubility limit. Extrapolated results from mechanical spectroscopy and magnetic resonance experiments [182], [183] show that the diffusivity of hydrogen in the δ -hydride phase is approximately 0.2-16% of that in the metallic α -Zr phase [181] (Table

5.1). This relatively low diffusion rate of H in the δ -hydride can be explained by the direct jump atomistic diffusion mechanism [186], [187]. Since bonded H atoms have occupied some interstitial sites in the hydrides, jumps of mobile H atoms are blocked. This so-called blocking effect and the correlation factor due to the interaction between H atoms and vacancy sites become more important at high H concentration. This concentration-dependent diffusion mechanism provides a framework for building a new mixed-phase model.

5.4 Mixed-Phase Diffusion Model

5.4.1 Model Approach

A new finite difference model was developed to compute the H concentration profile near the hydrided surface. The diffusivity $D(\varphi)$ is dependent on the amount of hydrides formed in a local region (See Section 5.3). The governing equation for the mixed-phase model is:

$$\frac{\partial \varphi}{\partial t} = \frac{\partial}{\partial z} \left(D(\varphi) \frac{\partial \varphi}{\partial z} \right) \quad 5.11$$

The model structure is illustrated in Figure 5.2a. It consists of a hydride layer, a metallic phase region and a mixed-phase region in which hydride precipitates are modelled as oblate spheroid inclusions. In the mixed-phase region, the diffusivity is characterised by an effective diffusion coefficient, D_{eff} . This coefficient is derived from the diffusivities of hydrogen in the two constituent phases and the local phase volume ratio (See Section 5.4.2). This concept of an effective medium has also been applied in models describing transport properties such as thermal conductivity, dielectric constants and magnetic permeability in some binary composite structures [188], [189].

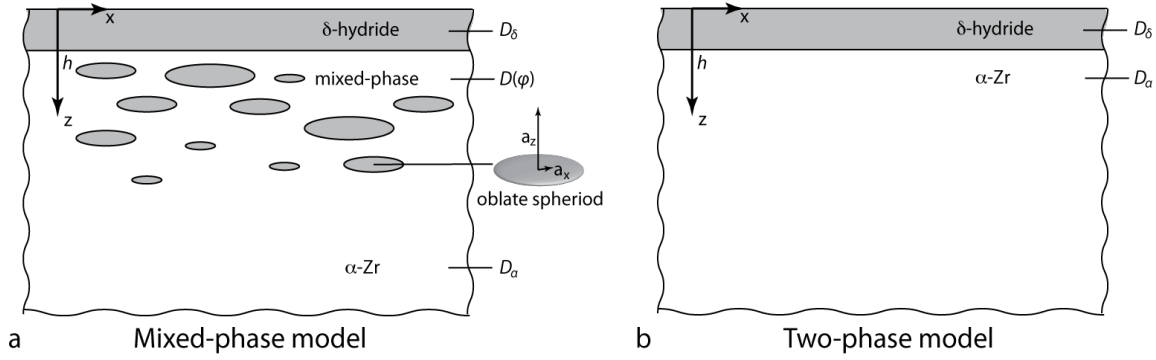


Figure 5.2 Schematic representations of the two models. a) The mixed-phase model. Hydride precipitates are modeled as plate-shaped inclusions in the Zr near the phase boundary. b) The conventional two-phase model. The binary system consists of a hydride layer and a Zr matrix.

The finite difference model first assigns D_{eff} to each point of the 1-D space at a fixed time step. The value of the coefficient is dependent on the H concentration at that spatial point. The numerical model computes the net flux between every two consecutive spatial points and solves the Fick's first law implicitly in space. The model then proceeds to the next time step and explicitly solves the Fick's second law (Eq.5.11). The new H concentration profile then defines a new set of D_{eff} in the space domain and the process repeats in the next time step.

5.4.2 Model Formulation

The first part of the formulation describes the method for determining D_{eff} . The hydride inclusions are assumed to be spherical at this stage. An additional depolarising factor will then be introduced to model the plate-shaped hydride precipitates. The bounding limits and a numerical scheme are presented in the next two sections.

The effective diffusion coefficients, D_{eff} , are determined by the Maxwell-Garnett mixing rule [189], [190], which was originally derived for investigating the optical properties of metal

glasses. The approach was extended by Kalnin, Kotomin and Maier [191] for solving solid-state diffusion problems. A schematic representation of the effective medium is shown in Figure 5.3. The figure describes a macroscopically homogeneous body; which is independent from the main model as illustrated in Figure 5.2a. This sub-section aims to derive an equation to obtain D_{eff} from a given H concentration. The solution will then be used in the main model.

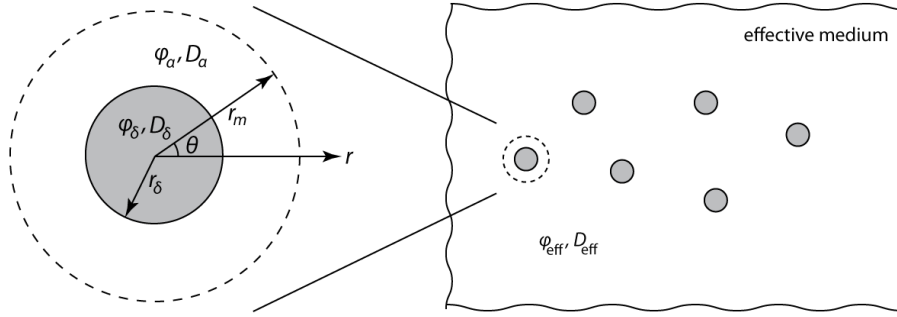


Figure 5.3 Illustration of the core-shell inclusion model for calculation of the effective diffusion coefficient.

In Figure 5.3, a sphere of radius r_m is replaced by a composite sphere consisting of an inner inclusion of radius r_δ with diffusivity D_δ and a concentric shell with diffusivity D_m . Assuming an azimuthal symmetry that the concentration does not vary with the direction pointing outside of the paper, the medium then satisfy the 2-D steady-state diffusion equation,

$$\nabla^2 \varphi(r, \theta) = 0 \quad 5.12$$

where the hydrogen concentration, φ , is expressed as a function in spherical coordinates with the origin at the centre of an inclusion. Eq.5.12 is a Laplace's equation that can be solved by separation of variables (See APPENDIX) and the solution is

$$\varphi_\delta(r, \theta) = A_2 r \cos \vartheta, \quad 0 < r \leq r_\delta \quad 5.13$$

$$\varphi_\alpha(r, \theta) = (B_2 r + \frac{C_2}{r^2}) \cos \vartheta, \quad r_\delta < r \leq r_m \quad 5.14$$

$$\varphi_{\text{eff}}(r, \theta) = -gr \cos \vartheta, \quad r_m < r \quad 5.15$$

where A_2 , B_2 , C_2 and g are non-zero constants. In equilibrium, the boundary conditions for H concentrations and fluxes at the interfaces in Figure 5.3 are:

$$\varphi_\delta(r_\delta, \theta) = \varphi_\alpha(r_\delta, \theta) \quad 5.16$$

$$D_\delta \frac{\partial \varphi_\delta(r, \theta)}{\partial r} \Big|_{r=r_\delta} = D_\alpha \frac{\partial \varphi_\alpha(r, \theta)}{\partial r} \Big|_{r=r_\delta} \quad 5.17$$

$$\varphi_\alpha(r_m, \theta) = \varphi_{\text{eff}}(r_m, \theta) \quad 5.18$$

$$D_\alpha \frac{\partial \varphi_\alpha(r, \theta)}{\partial r} \Big|_{r=r_m} = D_{\text{eff}} \frac{\partial \varphi_{\text{eff}}(r, \theta)}{\partial r} \Big|_{r=r_m} \quad 5.19$$

A continuum description of the H concentration is assumed at the phase boundary in Eq.5.16 and Eq.5.18. This treatment is different from the two-phase model as seen in Eq.5.5 and Eq.5.6. The boundary conditions, Eq.5.16 - 5.19, form a set of equations:

$$r_\delta A_2 - r_\delta B_2 - \frac{1}{r_\delta^2} C_2 + 0 = 0 \quad 5.20$$

$$D_\delta A_2 - D_\alpha B_2 + \frac{2D_\alpha}{r_\delta^3} C_2 + 0 = 0 \quad 5.21$$

$$0 + r_m B_2 + \frac{1}{r_m^2} C_2 + r_m g = 0 \quad 5.22$$

$$0 + D_\alpha B_2 - \frac{2D_\alpha}{r_m^2} C_2 + D_{\text{eff}} g = 0 \quad 5.23$$

For this homogeneous system of linear equations (Eq.5.20 - 5.23) to have a non-trivial solution where A_2 , B_2 , C_2 and g are non-zero constants, the determinant must be zero. By defining the volume fraction of inclusions as $V_f = r_\delta^3 / r_m^3$, then the determinant follows:

$$\begin{vmatrix} V_f & -V_f & -1/r_m^3 & 0 \\ V_f D_\delta & -V_f D_\alpha & 2D_\alpha/r_m^3 & 0 \\ 0 & 1 & 1/r_m^3 & 1 \\ 0 & D_\alpha & -2D_\alpha/r_m^3 & D_{\text{eff}} \end{vmatrix} = 0 \quad 5.24$$

Rearranging Eq.5.24, the effective diffusion coefficient is:

$$D_{\text{eff}} = D_\alpha \left[1 + \frac{3V_f(D_\delta - D_\alpha)}{3D_\alpha + (1 - V_f)(D_\delta - D_\alpha)} \right] \quad 5.25$$

$$= D_\alpha + \frac{V_f}{\frac{1}{D_\delta - D_\alpha} + \frac{1 - V_f}{3D_\alpha}} \quad 5.26$$

D_{eff} equals D_α when V_f reaches zero. Some bounding limits are presented in Section 5.4.3.

Inclusion Shape Transformation

The formulation is so far applicable to spherical inclusions however the δ -hydrides are likely to be plate-shaped precipitates [67]. A mathematical treatment was applied in the mixed-phase model for shape transformation. A depolarising factor, n_z , introduced in the work of Göktürk, Fiske, & Kalyon [192], [193] was used to model the hydride precipitates as oblate spheroids (See Figure 5.2a for the directions of the coordinate axes):

$$n_z = \frac{1 + \varepsilon^2}{\varepsilon^3} (\varepsilon - \tan^{-1} \varepsilon) \quad 5.27$$

$$\varepsilon = \sqrt{a_x^2/a_z^2 - 1} \quad a_x = a_y > a_z \quad 5.28$$

where ε is the ellipticity and the ratio a_x/a_z is the ratio of the major axis to the minor axis.

Eq.5.26 is then modified to give the D_{eff} in the z-direction [188]:

$$D_{\text{eff},z} = D_{\alpha} + \frac{V_f}{\frac{1}{D_{\delta}-D_{\alpha}} + n_z \frac{1-V_f}{D_{\alpha}}} \quad 5.29$$

It can be seen that the factor 1/3 in Eq.5.26 is replaced by n_z in the above expression.

5.4.3 Bounding Limits Analysis

Bounding methods were applied to verify D_{eff} obtained in Eq.5.26 and Eq.5.29. The first set of limits is derived by Hashin and Shtrikman [194] through a variational approach,

$$D_{\alpha} + \frac{1-V_f}{\frac{1}{D_{\delta}-D_{\alpha}} + \frac{V_f}{3D_{\alpha}}} \leq D_{\text{eff}} \leq D_{\alpha} + \frac{V_f}{\frac{1}{D_{\delta}-D_{\alpha}} + \frac{1-V_f}{3D_{\alpha}}} \quad , \quad 0 < D_{\delta} < D_{\alpha} \quad 5.30$$

These bounding limits can be viewed as switching the positions of the two constituent phases. Another set of bound is analogous to the rule of mixtures used in estimating the elastic properties of composites materials. The method suggests that the property of the effective medium is bounded by the parallel and the serial connection of the components' property,

$$\left(\frac{V_f}{D_{\delta}} + \frac{1-V_f}{D_{\alpha}} \right)^{-1} \leq D_{\text{eff}} \leq V_f D_{\delta} + (1-V_f) D_{\alpha} \quad 5.31$$

More details on the bounding limits are reviewed in the work of Sihvola and Lindell [188].

In Figure 5.4a, the bounding limits for D_{eff} are determined for a medium with spherical inclusions. In Figure 5.4b, plate-shaped inclusions were used. The computed values in this mixed-phase model are within all the bounds. In Figure 5.4, the ratio of the diffusivity of hydrogen in the two constituent phases is 0.03. This ratio was used for computational simulation in this study based on the range of literature data listed in Table 5.1 [181]–[183].

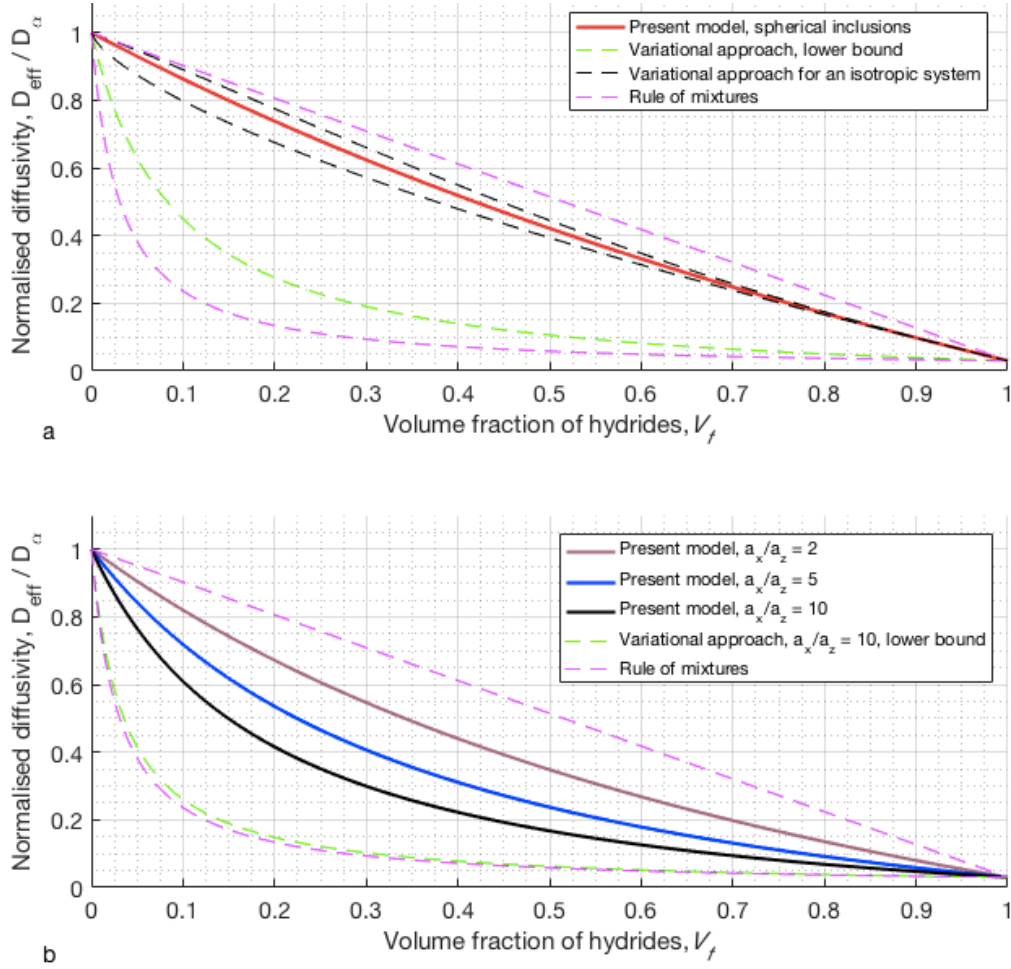


Figure 5.4 Bounding limits of the effective diffusion coefficients for a) spherical inclusions (Eq.5.26); and b) plate-shaped inclusions (Eq.5.27-5.29). The ratio a_x/a_z is ratio of the major axis to the minor axis of the model ellipsoids. [188], [194].

5.4.4 Numerical Scheme

This section describes the method for solving the time-dependent partial differential equation, Eq.5.11. The appropriate boundary conditions in the space domain $[0, z_0]$ for time $t \geq 0$ are:

$$\varphi(z, 0) = \begin{cases} \varphi_s & , \quad z = 0 \\ 0 & , \quad 0 < z \leq z_0 \end{cases} \quad 5.32$$

$$\varphi(0, t) = \varphi_s \quad 5.33$$

$$\varphi(z_0, t) = 0 \quad 5.34$$

MATLAB codes were written to assign the recursive boundary conditions (Eq.5.33 and 5.34) in each time step. Eq.5.34 is a Dirichlet condition [195] that assumes the hydrogen concentration is fixed at zero at a sufficiently large depth, z_0 . In this simulation, the typical value for z_0 was 1000 μm . A simple forward-time-and-central-space (FTCS) numerical scheme was applied for computation [195]. In any fixed time step, the concentration-dependent diffusivity is calculated from Eq.5.29 depending on the H concentration at each discrete spatial point. The flux at the i^{th} spatial step and the j^{th} time step is

$$J_{i,j} = -D_{\text{eff},z}(\varphi_{i,j}) \frac{\varphi_{i,j} - \varphi_{i-1,j}}{\Delta z} \quad 5.35$$

where Δz is the spatial step size and other symbols are defined in Section 5.4.2. The net flux between any consecutive spatial points is used to explicitly solve the discrete equation, Eq.5.35. The solution is then used to obtain the H concentration in the $(j+1)^{\text{th}}$ time step:

$$\frac{\varphi_{i,j+1} - \varphi_{i,j}}{\Delta t} = \frac{-J_{i+1,j} + J_{i,j}}{\Delta z} \quad 5.36$$

where Δt is the time step size. In order to maintain a numerical stability based on Von Neumann analysis [195], a restriction of Δt is required:

$$\Delta t \leq \frac{(\Delta z)^2}{2D_\alpha} \quad 5.37$$

5.5 Results

5.5.1 Surface Phase Growth Results

The results for the transformed area fraction are shown in Figure 5.5a. The numerical parameters of the fitting curves, n and k , are determined by the slope and the y-intercept of the transformed plots in Figure 5.5b by Eq.5.2. When the hydriding duration was 8 hours,

hydrides covered about 8% of the surface area. The coverage area monotonically increased to about 56% after 24 hours and over 99% after 96 hours. This is consistent with the cross-sectional surface examination that hydride islands overlapped to form a continuous film as the hydriding time increased (Figure 4.15). In this Avrami analysis [177], the exponent n provides some indication about the underlying kinetics of the phase growth. The discussion is presented in Section 5.6.

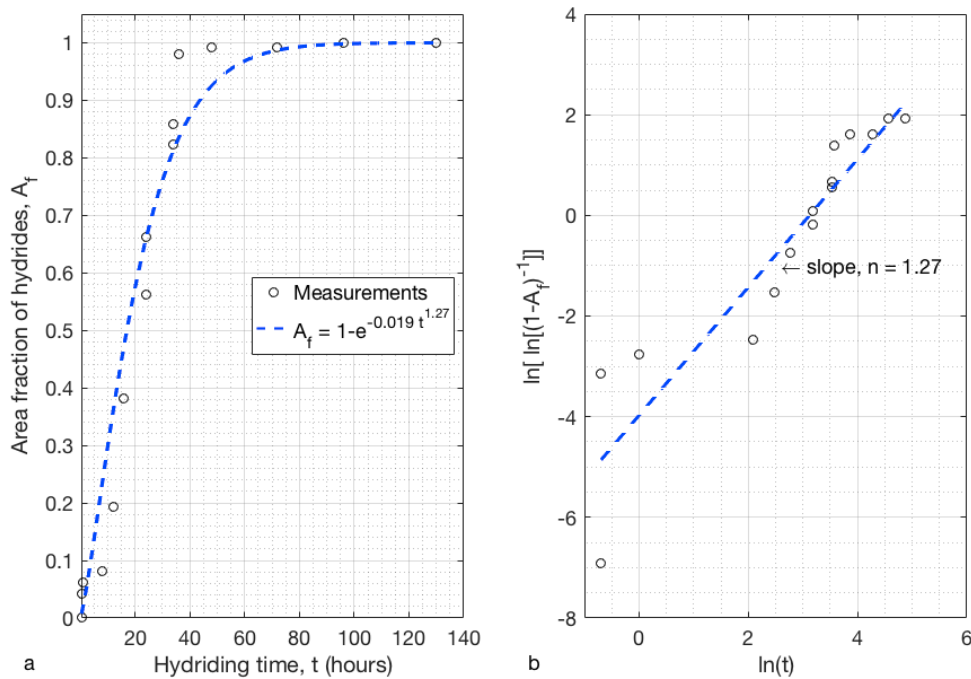


Figure 5.5 Phase growth rate of surface hydrides. a) The area fractions of hydrides were measured after various electrolytic hydriding durations. b) Transformation plot. The parameters, n and k , are determined from the slope and y-intercept according to Eq.5.2.

5.5.2 Two-Phase Model Results

The classical two-phase model assumes a concentration-independent diffusion mechanism as described in Section 5.2. MATLAB codes were written to solve the non-linear equation Eq.5.9 with the input parameters listed in Table 5.1. Figure 5.6a shows the predicted H concentration at various hydriding time. In Figure 5.6b, the experimental measurements were obtained from optical micrographs (0.28 $\mu\text{m}/\text{pixel}$). The mean values were determined by

averaging over 30 interface depths along the hydrided edge. The film thickness is approximately proportional to the square root of the hydriding time.

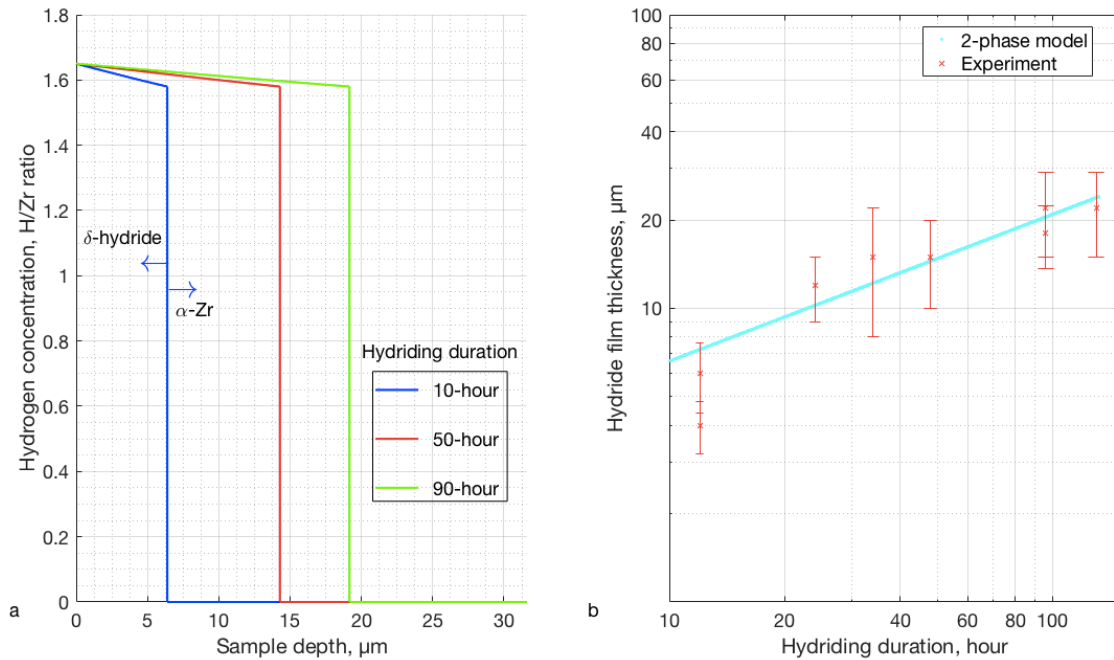


Figure 5.6 Two-phase model results. a) The hydrogen profile along the depth of a sample. b) The time dependence of the hydride film thickness compared with measurements. The error bars represent the standard deviations.

The two-phase model uses a classical approach to predict the interface velocity. The solution is however limited to a sharp drop of H concentration at the interface. This prediction is inconsistent with the SEM observation as shown in Figure 4.19; where the amount of precipitates changes gradually in the hydride-rich region.

5.5.3 Mixed-Phase Model Results

The numerical scheme described in Section 5.4.4 was written in MATLAB codes to run simulations using input parameters listed in Table 5.1. The modelling results for H concentration profiles are shown in Figure 5.7a. In all simulated durations, the H/Zr ratio decreases from 1.65 to 1.6 away from the hydrided surface. The H/Zr ratio drops to 1.1 and

gradually decreases in the mixed-phase region. In comparison, the two-phase diffusion model did not predict a gradual decrease in H concentration near the interface (Figure 5.7b).

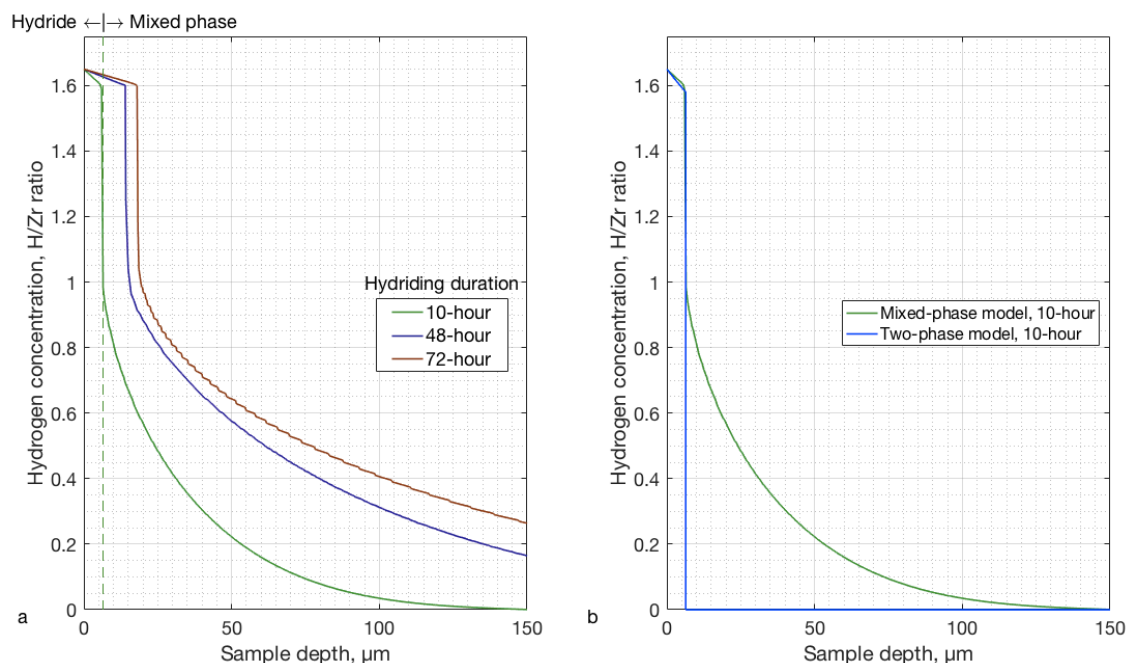


Figure 5.7 The H concentration profiles predicted by the mixed-phase model. a) The H concentration gradually decreases away from the phase boundary. The temperature for the hydriding process is 65°C. b) The result is compared with the two-phase model prediction.

In Section 4.3.2, the SEM examination shows a considerable amount of sub-micron scale hydride precipitates piled near the phase boundary in a 12-hour hydrided sample. This experimental observation is compared with the computed H concentration profile in Figure 5.8. The dark region is the hydride and the bright region is the Zr matrix. The micrograph was then converted to a binary image (Figure 5.8b) using the image processing method proposed by Otsu [196]. An optimal threshold was selected to separate the two classes, the foreground hydride and the background Zr matrix, such that the variance of grey levels within the class is minimised. A MATLAB programme was written to convert the image and count the number of black pixels along each line across the depth of the sample. The number of pixels can be viewed as a representation of the relative contents of hydrides. Figure 5.8c shows a

comparison between the number ratio of black pixels in each column and the modelling results. The modelled interface depth was fit to the average experimental measurements by the iterative process described in the following paragraph. The H concentration profile determined by the mixed-phase model (red curve) is in good agreement with the experiment. However the two-phase model noticeably underestimated the amount of hydrides.

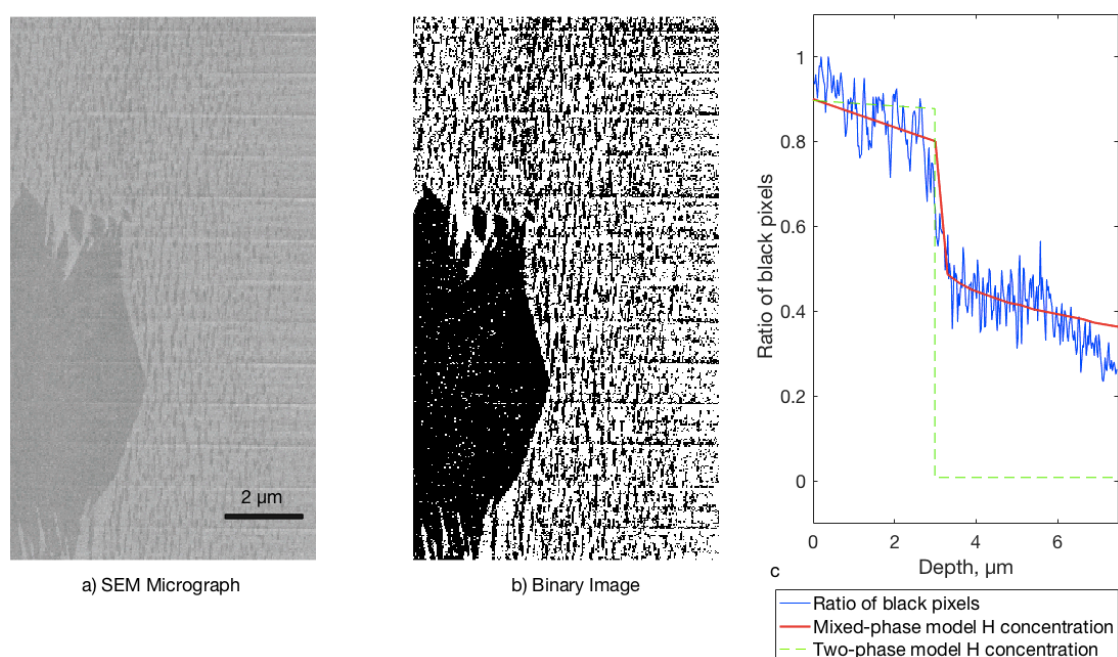


Figure 5.8 Comparison of the simulated hydride concentrations with the experimental observations. a) SEM image of the cross-sectional surface of a hydrided sample. The dark region is hydrides. b) The greyscale SEM image was converted to a binary image. c) The number ratio of black pixels in each column was counted and plotted in blue. The ratio is consistent with the normalised H concentration predicted in mixed-phase model (red curve). The two-phase model result is plotted in green for comparison.

The diffusion coefficient of H in the pure hydride, D_δ , was determined to be $2.8 \times 10^{-3} \mu\text{m}^2/\text{s}$ at 65°C by iterative model fitting of experimental measurements. The result is in agreement with the literature values, 0.12×10^{-3} to $12.5 \times 10^{-3} \mu\text{m}^2/\text{s}$, and it is about 3% of that in the Zr [182], [183], [197] (Table 5.1). The predicted interface depths at varying hydriding durations are plotted with the experimental measurements in Figure 5.9. The annotated equation is the

linear fit of the mixed-phase model results. Similar computation results were obtained from the classical two-phase model. The interface depth is proportional to the square root of the hydriding time; indicating the process is diffusion-controlled.

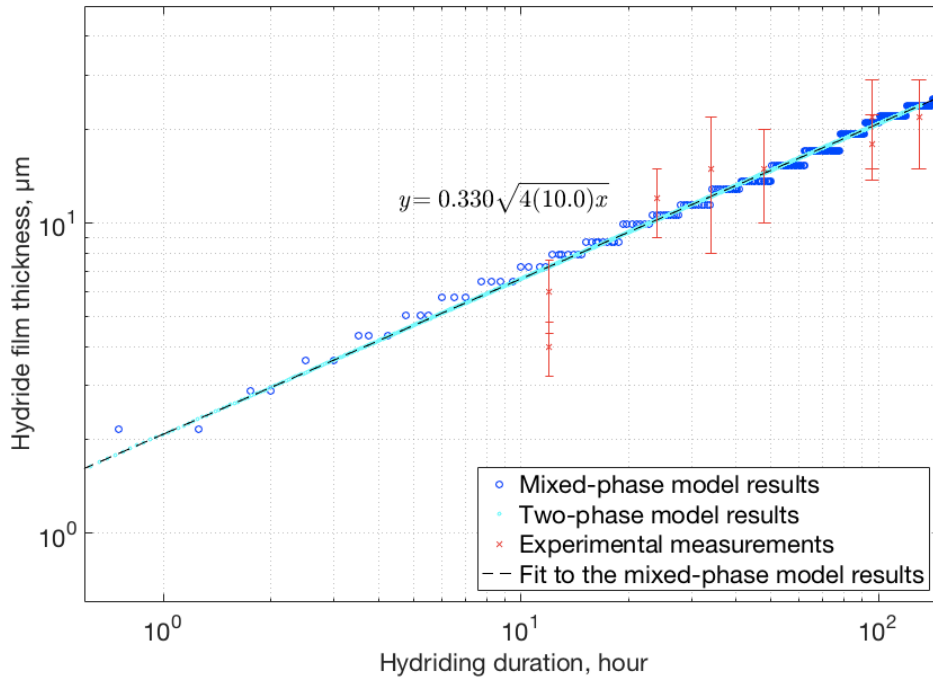


Figure 5.9 Hydride film thickness versus the electrolytic hydriding time at 65°C. The two models predict a similar result.

5.6 Discussion

The surface hydride growth was analysed in Section 5.5.1. In the case for constant nucleation rate and constant interface growth velocity, the exponent n ideally equals 3 (See Eq.5.1) [177]. However, the experimental measurements show that the fitted exponent n is less than 2 (Figure 5.5). The deviation of can be explained by experimental observations. In Section 4.3, the microstructural examination shows that the nucleation was not completely homogeneous and the hydride grains were elongated. The observed nucleation inhomogeneity and ellipsoidal growth of hydride nuclei would reduce the gradient of Figure 5.5 resulting a smaller value of n [177].

The new mixed-phase finite difference model is built on a simple framework that based on thermal activation processes and requires no empirical parameters. It could be developed to describe 2-D diffusion in a dual-phase system for investigating mechanisms such as grain boundary diffusion. The formulation describes the physical phenomena governed by Fick's second law and the mass balance equation. It can be extended to a wider application for simulating diffusion problems in an anisotropic crystalline structure other than Zr.

5.7 Summary

Hydrogen diffusion rate and hydride thickness growth were measured experimentally. The fitted exponent n in Avrami model was 1.27 for the electrolytic hydriding process. The characteristic diffusion coefficient of H in the hydride was found to be about $2.8 \times 10^{-3} \mu\text{m}^2/\text{s}$ at 65°C as determined from experimental curve fitting. The diffusion of H in Zr can be reasonably treated as a diffusion-controlled process in which the hydride film thickness, y in μm , is proportional to the square root of hydriding time, t in hour, such that $y = 2.09t^{1/2}$.

A new mixed-phase finite difference model was developed to compute the concentration-dependent diffusion process. In comparison to the classical model in which the amount of hydrogen migrated into the bulk was considerably underestimated, the newly simulated hydrogen concentration profile is in better agreement with the SEM examination. The model can be extended to simulate some diffusion processes in crystalline materials other than Zr.

6 NANOINDENTATION

6.1 Introduction

Macroscopic scale mechanical tests have shown that increasing hydrogen content could result in hardening and reduced ductility in zirconium alloys [14], [75], [78] (Section 2.3.2). These large-scale experiments measured the overall properties of bulk samples in which the hydrides usually formed as microscale precipitates. Microscale experiments are therefore more appropriate to determine the intrinsic properties of the hydride phase. In this chapter, nano- and microscale indentation results for the δ -hydride and the α -Zr are presented.

6.2 Experimental Details

Nanoindentation Test

Two sets of CSM nanoindentation tests were carried out at a strain rate of 0.01 s^{-1} in an Agilent Nano Indenter G200 that fitted with an XP head and a Berkovich tip (Section 3.4.1). The first set was performed on the cross-sectional surface of various hydrided samples. Indents were made in the α -Zr and selected crack-free regions in the δ -hydride film. The material directly underneath each indent was considered as the same as that in the deformation volume in these cross-sectional samples. The testing surfaces were prepared by mechanical polish using colloidal silica at low pressure as described in Section 3.2. The second set of tests was performed in an unhydrided Zr sample. Indents were produced in various Zr grains of which the crystallographic orientations had been identified by EBSD (Section 4.1.2). The indents were located at over $10 \text{ }\mu\text{m}$ away from grain boundaries to avoid

their influence [171]. Figure 6.1 shows a typical indent and the topographical map generated by indenter tip scanning.

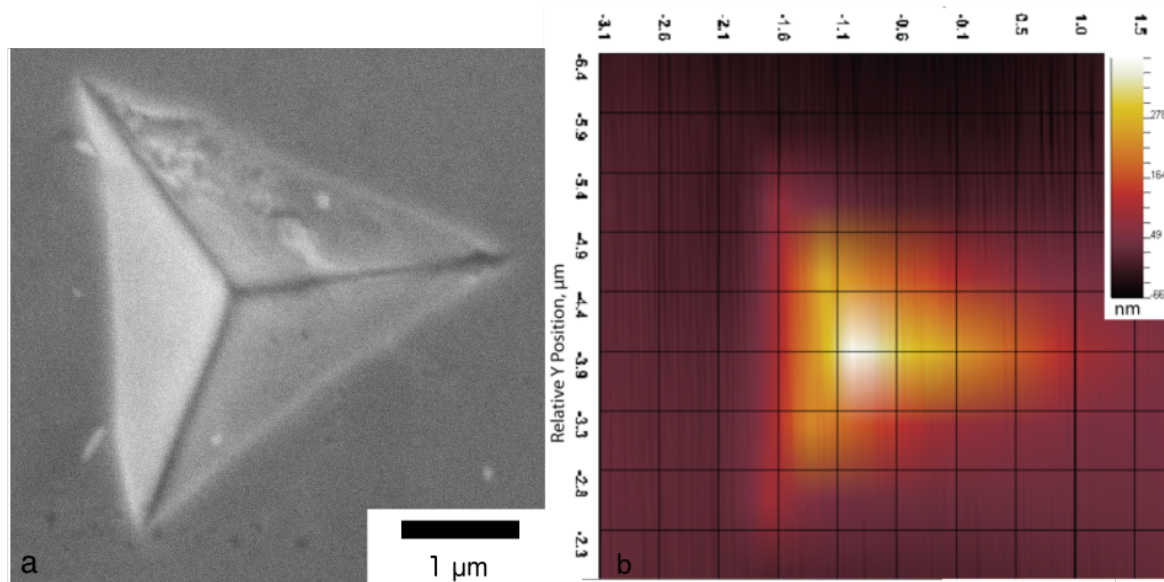


Figure 6.1 a) SEM micrograph of an indent made in the Zr. b) Topographical map.

Microhardness Test

Vickers microhardness tests were performed for a quantitative comparison with the nanoindentation test results. A Matsuzawa Seiki MHT tester was used to make indents on a ~20 μm thick hydride film at 0.25-4.9 N (25-500 gf) for 10 s. The indents made from over 2 N were used for calculating the average microhardness.

6.3 Nanoindentation Test Results

Figure 6.2 compares the load-displacement relations for the indents made in the two phases. The nanohardness of the hydride is distinctively higher than the Zr at any indent depth as a higher load was needed to generate the same depth in the hydride. Their similar initial unloading gradients indicate that the two materials have the similar elastic modulus.

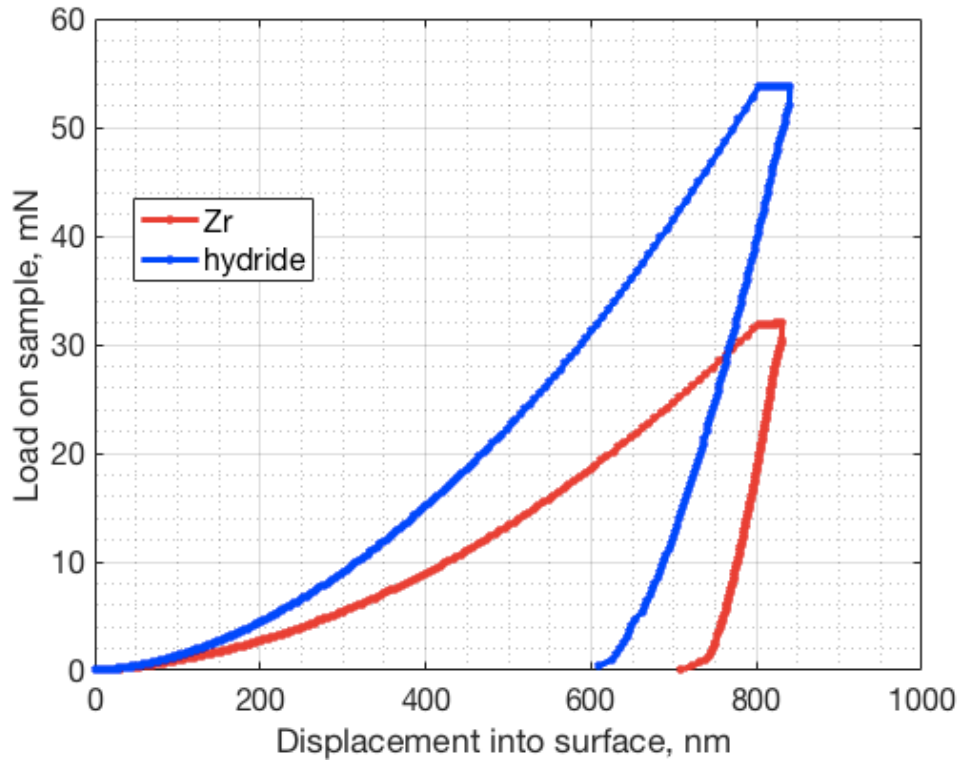


Figure 6.2 Typical load-displacement curves for the 800 nm indents made in the α -Zr and in the δ -hydride at room temperature.

Indentation arrays were made in the dual-phase region on a 24-hour hydrided sample (Figure 6.3a). The indents produced on the imperfect rounding edge, as identified by their elongated triangular residual shapes, were not used for calculation (Figure 6.3b). The nanohardness results are plotted against the distance between the indents and the phase boundary, d_i , in Figure 6.4. The nanohardness of the δ -hydride is 4.8 ± 0.25 GPa as determined from indents located at over $1 \mu\text{m}$ away from the interface. In the Zr, the nanohardness gradually decreases with increasing d_i . It attains a constant value when d_i is over $15 \mu\text{m}$. The nanohardness of the α -Zr was found to be 2.5 ± 0.17 GPa; which is about half of that of the δ -hydride. The variation of nanohardness with d_i is partly controlled by the strengthening mechanisms as discussed in Section 6.5.

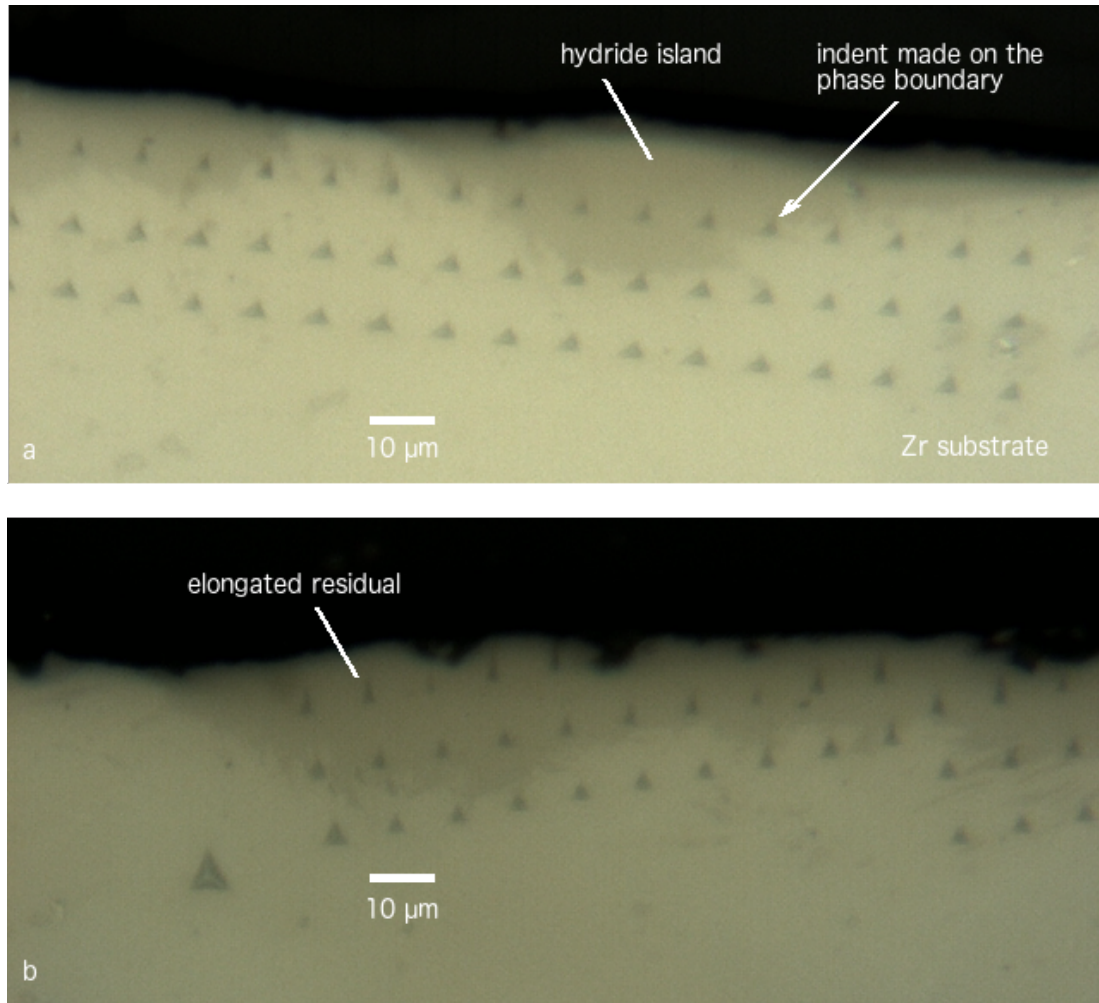


Figure 6.3 Nanoindentation arrays made at several locations along the hydrided edge of a 24-hour hydrided sample. 500 nm indents were made at a strain rate of 0.01 s^{-1} within the hydride film, within the Zr or on the phase boundary. The spacing between adjacent indents is $10 \mu\text{m}$ which is 20 times the target indent depth of 500 nm. The elongated residuals were caused by the rounding or inclined edge and those measurements were not used.

Figure 6.5 shows the nanohardness as a function of the indent depth. The average nanohardness of the δ -hydride measured at 100 nm is about 56% more than that obtained at 800 nm. In comparison, the difference is 38% for the α -Zr. The nanohardness of both phases apparently continues to decrease as the indent depth increases to over 800 nm. More results about the ISE are presented with the microhardness test results in Figure 6.11.

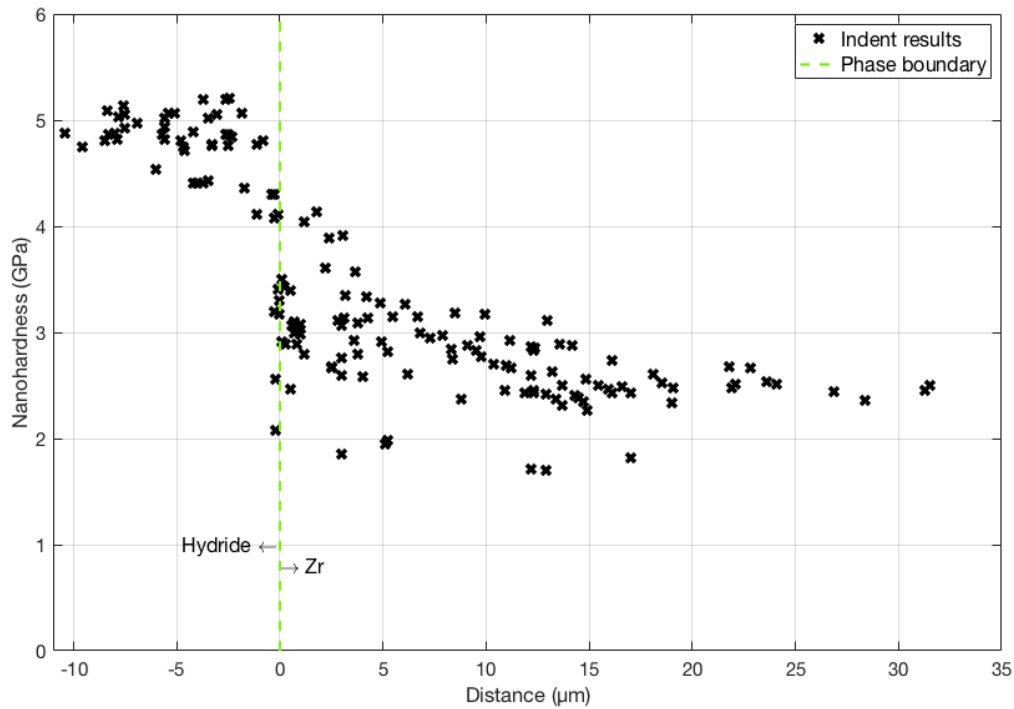


Figure 6.4 Nanohardness (500 nm depth indents) as a function of distance measured from the phase boundary. The results were collected from tests carried out on the cross-sectional surface of various samples. Nanohardness of the hydride is about double of that of the Zr.

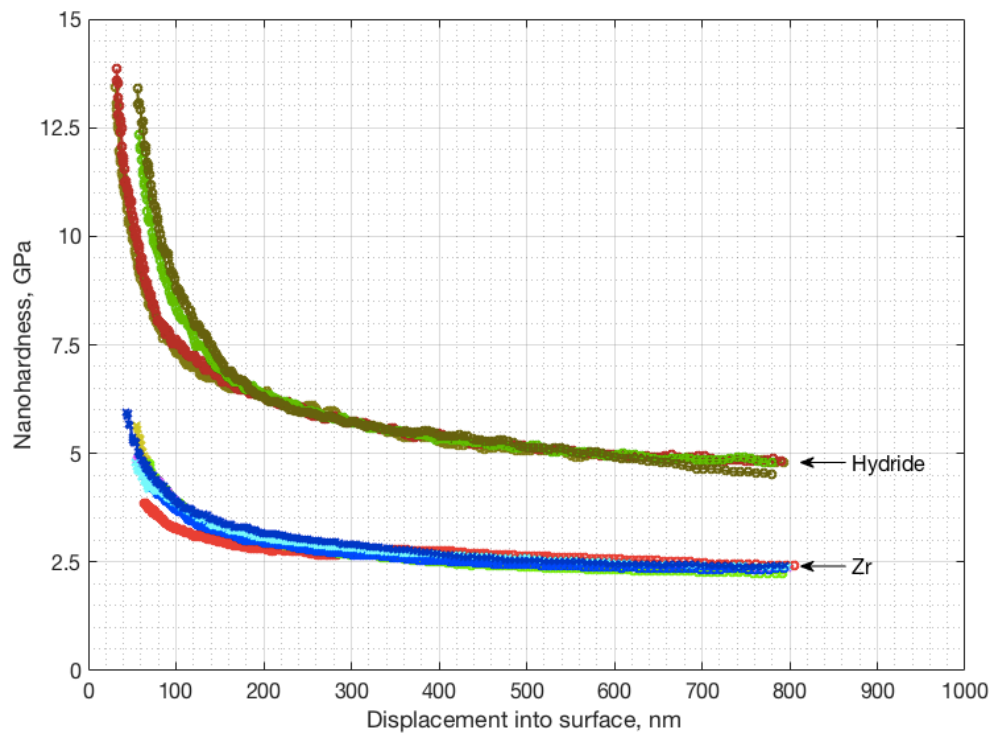


Figure 6.5 Variation of nanohardness with penetration depth. The measurements for Zr were collected from indents made at over 20 μm away from the Zr/hydride interface.

The nanohardness and Young's modulus of the α -Zr at various crystallographic inclination angles are plotted in Figure 6.6. The inclination angle is the angle between the c-axis of the hcp α -Zr lattice and the direction of maximal load. In nanoindentation the maximum loading direction is the sample normal. In Figure 6.6, the nanohardness generally decreases when the inclination angle increases. The elastic modulus is the highest along the principal c-axis and large scatters are observed at all angles. The average elastic modulus was determined by measurements recorded at the indent depth of 300-480 nm because it approaches constant when the penetration depth is over 250 nm (Figure 6.7).

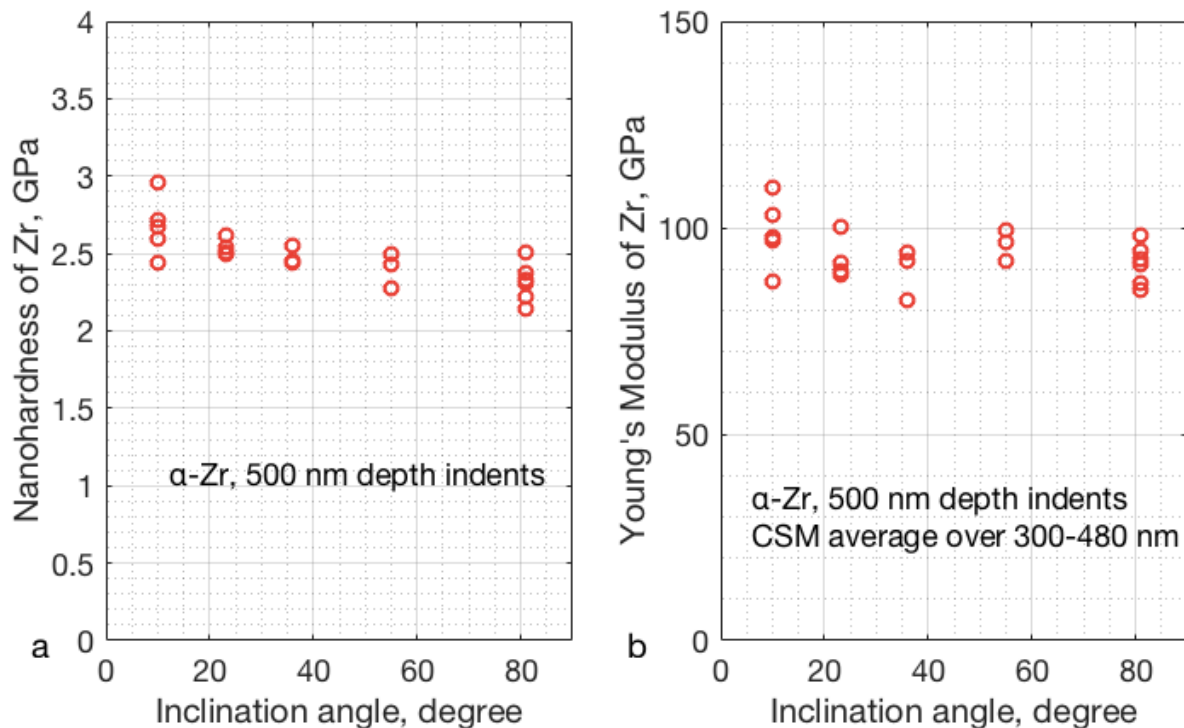


Figure 6.6 Measurements obtained from indents made in different grains in an unhydrided Zr sample. The inclination angle is the angle between the c-axis and the loading direction; here at 0° the basal plane is perpendicular to the sample normal. More discussion to the anisotropic elasticity is presented in Section 7.4.3. a) Nanohardness generally decreases with the inclination angle. b) Young's modulus varies with the inclination angle. See also Figure 6.7.

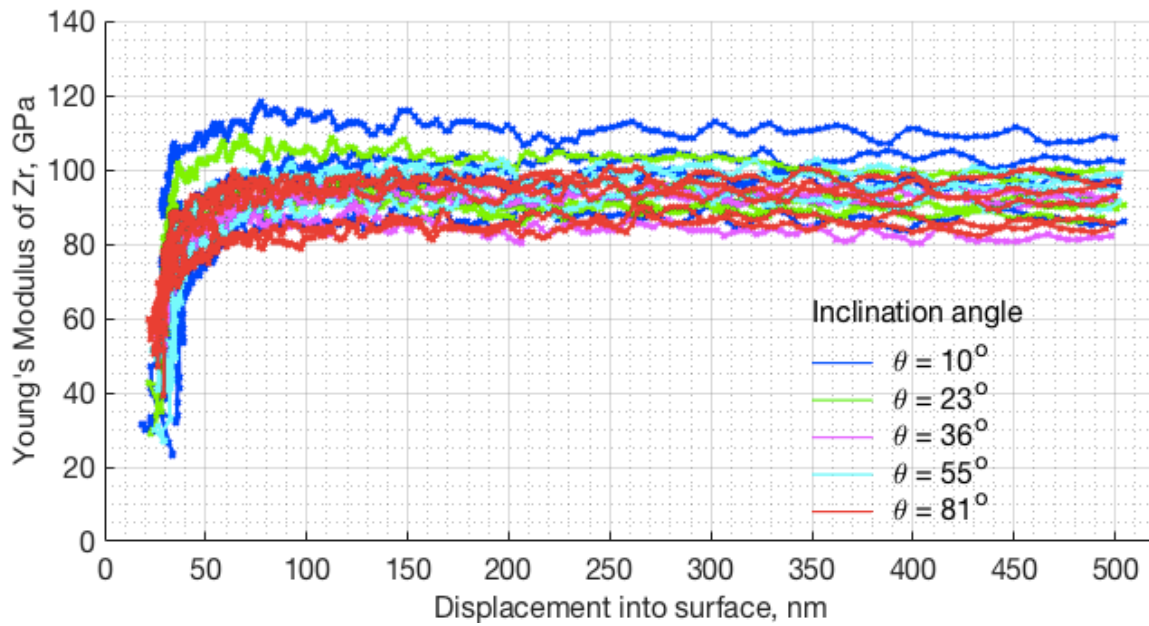


Figure 6.7 Variation of elastic modulus with penetration depth in the α -Zr. The measurements approach constant when the displacement is over 250 nm. See also Figure 6.6b.

6.4 Microhardness Test Results

Microhardness Tests on the Hydrided Surface

Vickers microhardness test was carried out on the hydrided surface as shown in Figure 6.8. The sample was hydrided for 96 hours to grow a $\sim 20 \mu\text{m}$ film. Since the film consisted of naturally formed hydride clusters (Section 4.3.1), the surface was not flat and the resulting indents were asymmetrical. This led to difficulties in determining the diagonal of an impression and hence affecting the accuracy of the results. The tested area was examined using OM and no resulting crack was observed near the indent vertices.

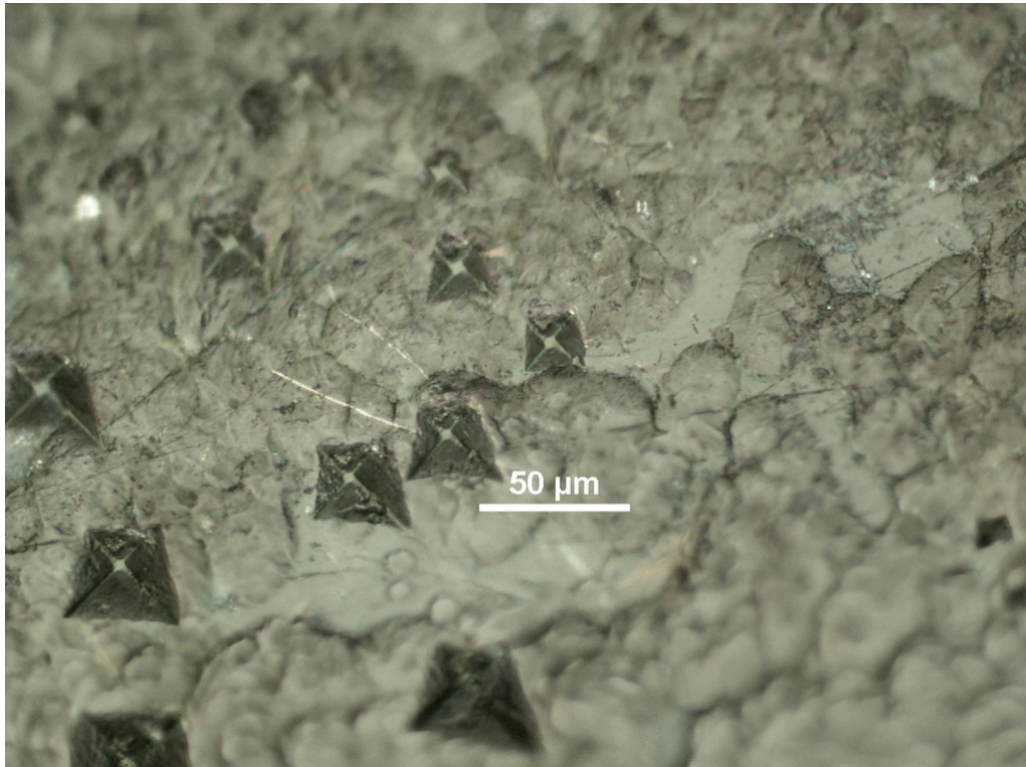


Figure 6.8 Vickers indents made on the hydrided surface. The irregular shape of indents is caused by the rough surface consisting of hydride islands.

The hydrided samples were considered as thin film solids for which the microhardness measurements were regarded as the mixed properties of the hydride film and the Zr substrate. The influence of the substrate was taken into account by applying the method as described in Section 3.4.2. Figure 6.10 shows the microhardness slightly decreases when the testing load increases from 0.25 to 4.9 N (25-500 gf). A large scatter can be seen at 0.25 N. These results were determined from small indents made on the uneven surface. The impressions were asymmetrical in shape leading to a marked scatter. The deviations observed at all loads are probably associated with the varying influence from the Zr substrate. Since the hydride film was not uniform in thickness, the resistance to deformation would vary with indent locations. This inhomogeneous response became clear when the penetration depth is relatively large ($\sim 8 \mu\text{m}$ depth in an $\sim 20 \mu\text{m}$ film) at an applied load of 4.9 N. The average microhardness determined from over 2.0 N testing loads is $3.0 \pm 0.25 \text{ GPa}$.

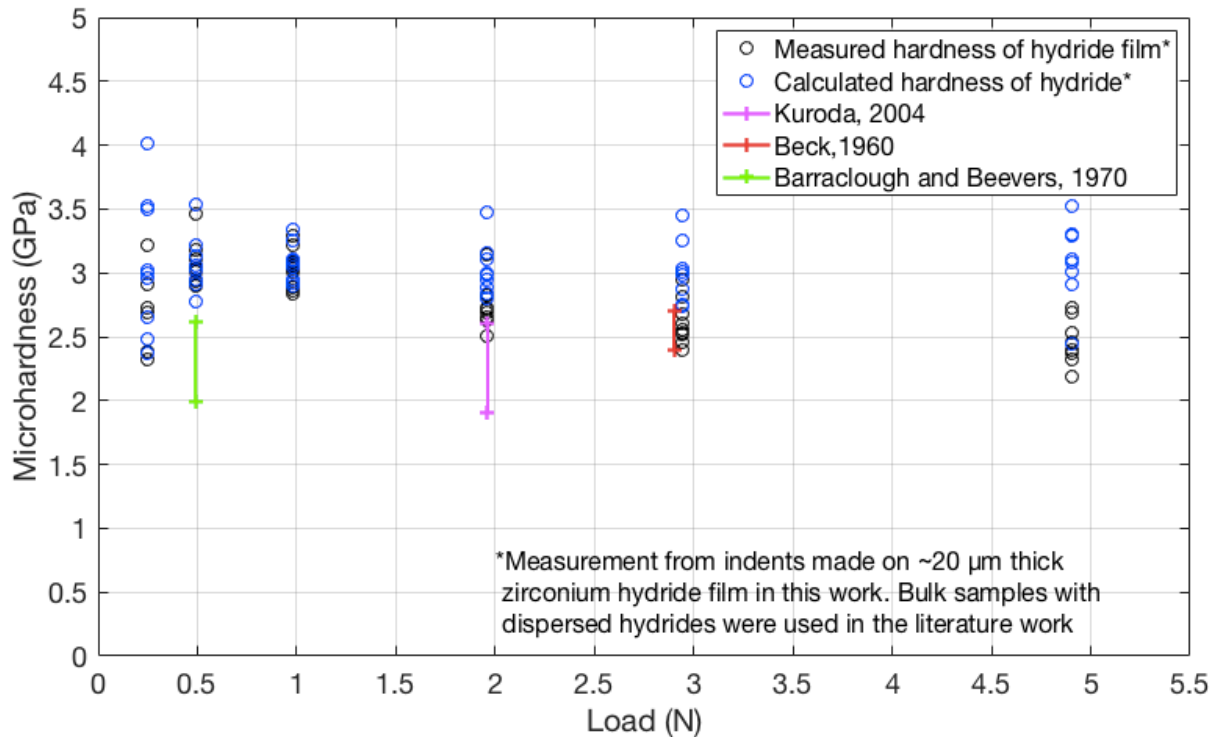


Figure 6.9 Vickers microhardness of Zr hydrides. The black circles are measured hardness of the hydride film and the blue circles are calculated values for hydrides using the method as described in Section 3.4.2. The scatter is mainly caused by non-uniform film thickness and the irregular film surface. Literature results are plotted for comparison [17], [19], [74].

Microhardness Tests on the Cross-sectional Surface

Vickers hardness test was carried out on the cross-sectional surface for a qualitative comparison between the mechanical properties of the Zr and the hydride. Microhardness indents made in the two compositional phases with the same load are shown in Figure 6.9. The smaller residual areas in the film show that the hardness of the hydride is higher than the Zr. Since all the indents made within the cross-sectional hydride film were merely few microns away from the phase boundary and the sample edge, the Zr substrate would be within the yield zone. Therefore this microhardness test was considered as a composite phase measurement and it could not generate intrinsic result for the δ -hydride.

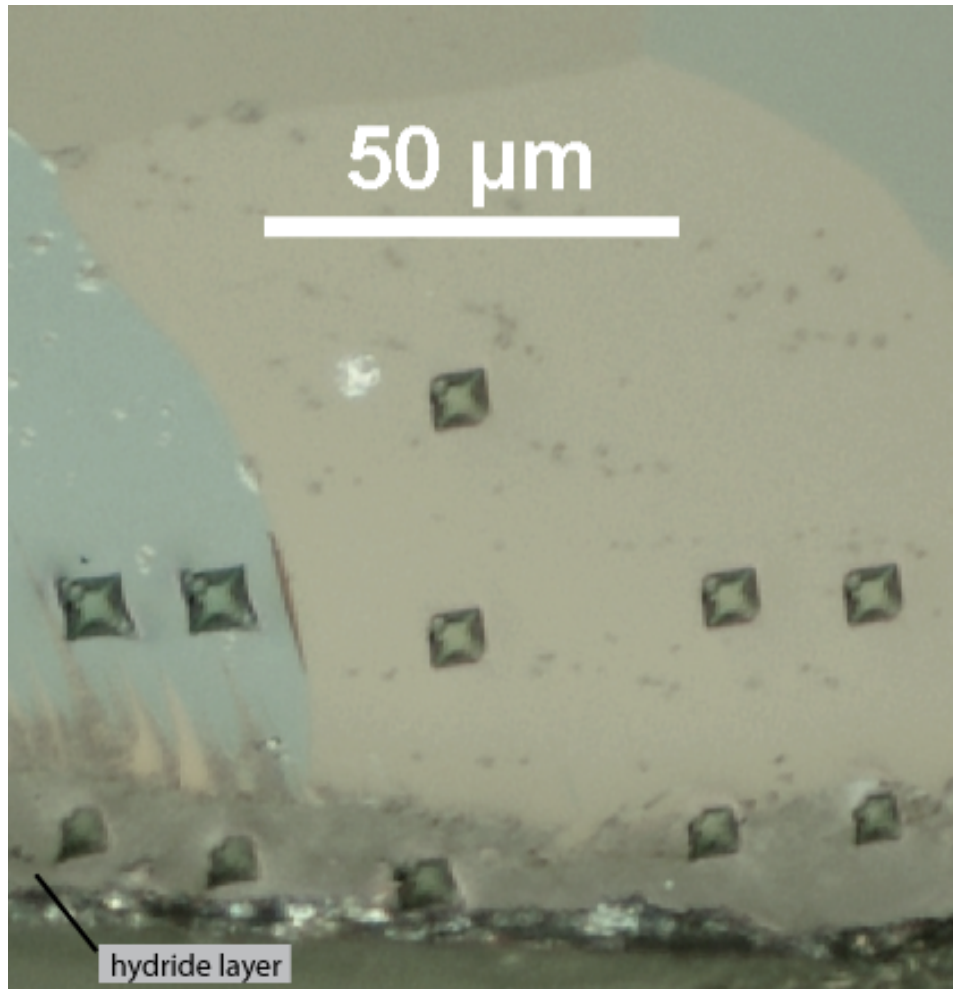


Figure 6.10 Vickers hardness indents made on the cross-sectional surface. The smaller residual areas in the hydride film indicate its higher hardness value compared to the Zr.

Comparison Between Microhardness and Nanohardness

The measurements of microhardness and nanohardness are plotted in Figure 6.11 to show the ISE. The hardness of both phases attains a constant value over a penetration depth of roughly 5 μm. The hardness of the hydride phase is noticeably higher than the metallic Zr matrix at any given depth. The hardness of the hydride increases by 65% when the penetration depth is reduced an order of magnitude from 5 μm to 0.5 μm. In comparison, a smaller increase of 34% can be seen for the Zr with the same reduction in depth. Table 6.1 summarises the hardness test results and the reported values in the literature [16]–[19], [74].

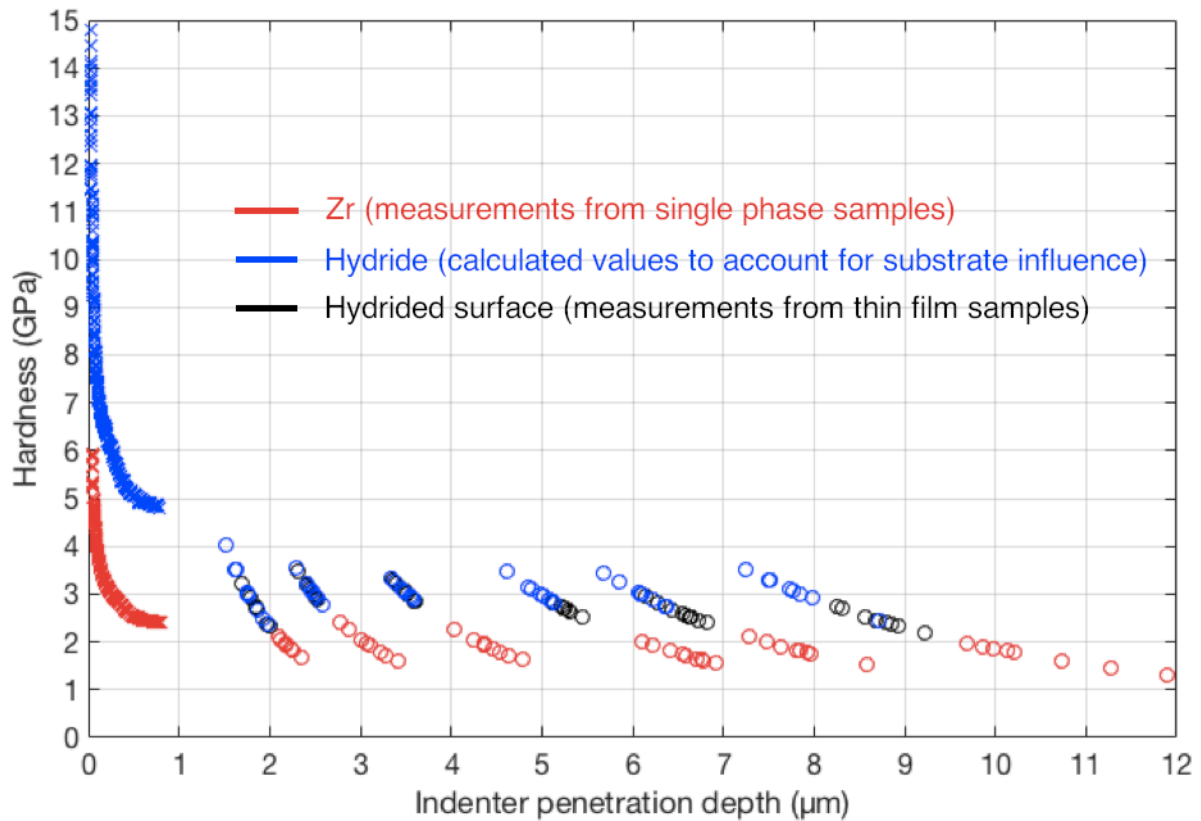


Figure 6.11 The hardness measurements for the two phases at various penetration depths clearly show the indentation size effect (ISE). The data in black are measurements obtained on the hydrided surface and they are considered as composite properties (Section 3.4.2).

Table 6.1 Summary of the hardness test results. The variability given to each average value represents the standard deviation. Literature references: [16]–[19], [74]

	δ -hydride		α -Zr	
	Average	Range	Average	Range
Microhardness, > 2.0 N load (GPa)	3.0 ± 0.2	2.5 - 3.5	1.8 ± 0.2	1.3 - 2.1
Microhardness, 4-6 μm depth (GPa)	3.1 ± 0.2	2.8 - 3.5	1.9 ± 0.2	1.6 - 2.3
Microhardness, literature (GPa)		1.9 - 2.8		0.9 - 1.7
Nanohardness, 400-600 nm depth (GPa)	5.1 ± 0.1	4.9 - 5.2	2.6 ± 0.1	2.5 - 2.7
Nanohardness, literature (GPa)		3.3 - 4.9		2.9 - 4.9

6.5 Discussion

The extent of strengthening of the α -Zr is different from that of the δ -hydride in the region close to the phase boundary (Figure 6.4). In the Zr substrate, the nanohardness decreases gradually away from the phase boundary until it reaches a constant value when the distance is over 15 μm . The microstructure of the region consists of large Zr grains ($>50\ \mu\text{m}$) with embedded sub-micron scale hydride precipitates as described in Section 4.4 (Figure 4.23). The deformation volume in this mixed phase region therefore inevitably contained a portion of hard precipitates resulting enhanced hardness. These precipitates may lead to precipitation hardening by obstructing the dislocations when local plastic deformation was generated by indentation. Additional phase boundary strengthening may also occur as the Zr/hydride interface may act as a barrier to dislocations. In contrast, strengthening was not clearly observed in the hydride film when indents were made in proximity to the phase boundary (Figure 6.4). It is probably related to the limited dislocation motion in the relatively small grains of brittle hydrides. The influence of hydride precipitates on the localised mechanical properties was further investigated through testing microcantilevers (Section 7.3.3).

The range of Young's modulus obtained for the Zr, 82-110 GPa, is in good agreement with the literature values, 80-126 GPa (Figure 6.6b and Table 2.1). However the variation of the elastic moduli with the inclination angles is smaller than that reported for the highly anisotropic Zr [20]–[22]. The maximum difference from the average is merely 6% over the range of measured angles. The result may be ascribed to the non-uniaxial applied load on the sample (See Section 2.4.1). Further investigation on the anisotropic elasticity of the Zr is presented in Section 7.4.3.

6.6 Summary

Nano- and micro-indentation experiments were carried out in the dual-phase region to measure the micromechanical properties and the size effect. The results show the localised plasticity is dependent on the inhomogeneous microstructural phase composition. The average nanohardness of the hydride (5.1 GPa) is about double that of the Zr (2.6 GPa) when the penetration depth is 500 nm. The average nanohardness of the hydride measured at 500 nm is about 65% more than that obtained at 5 μm due to the ISE. In comparison, the difference is 34% for the α -Zr with the same reduction in penetration depth. The large difference in their nanohardness suggests that in order to characterise other intrinsic micromechanical properties of the hydride and avoid the influence of the Zr, small deformation volume should be contained within the microscale hydride film.

7 MICROCANTILEVER TESTING

7.1 Introduction

The presence of hydrides in Zr alloys can significantly reduce the fracture toughness and lead to brittle failure [3], [4], [85] (See Section 2.3.2). Fracture tests carried out for compact tension specimens have shown that the fracture toughness of bulk Zr hydride is about $1 \text{ MPam}^{1/2}$ and transgranular cleavage has been observed on the δ -hydride fracture surfaces [91]. However, these tests were carried out on large-scale bulk hydrided samples, rather than 1-100 micron-scale precipitates involved in DHC. Direct loading tests on micron-scale crack-free hydrides should provide data more applicable to investigate DHC. Nanoindentation can allow fracture toughness determination by measuring crack lengths generated in controlled indentation (See Section 2.4.1). However experiments show that the deviation between true crack geometries and model assumptions may result in poor accuracy [109]. Other applicable methods involve specimens prepared on a selected local area by micro-machining techniques such as FIB, photolithography or plasma etching. A variety of geometries including pillars, clamped beams, cantilevers and double cantilevers have been used in microfracture tests (See Section 2.4.2). In the case of testing fracture properties of Zr hydrides by pillars or double cantilevers, the friction coefficient between the indenter tip and the sample can influence the results and its value is largely unknown. Clamped beams are capable of supporting stable crack growth however the residual stress may influence the fracture process [140]. Since tension is more deleterious than compression to produce cracks in hydrides, microcantilevers seem more appropriate than micro-pillars for fracture property characterisation [198]. In this chapter, pre-notched microcantilever tests are presented for investigating the micromechanical properties of the α -Zr/ δ -hydride dual-phase microstructure.

7.2 Experimental Details

The micro-fracture tests were carried out near the cross-sectional hydride film. Microcantilevers were made: (a) wholly within the δ -hydride; (b) wholly within the α -Zr; and (c) having the pre-notch along the α -Zr/ δ -hydride interface. The use of the pentagonal cross-section allows milling of cantilevers at selected locations anywhere on the sample surface, rather than being restricted working along the sample edges (Section 3.4.3). All cantilevers were fabricated with the use of 30 keV Ga as described in Section 3.4.3. A scanning current of 100 pA was used in the final polishing step to produce sharp corners. The notch tip was produced by using single passes of 10 pA followed by 1 pA. In order to ensure positional accuracy, location reference indents and T-shaped marks were made at known distances from the specimens (Figure 7.1).

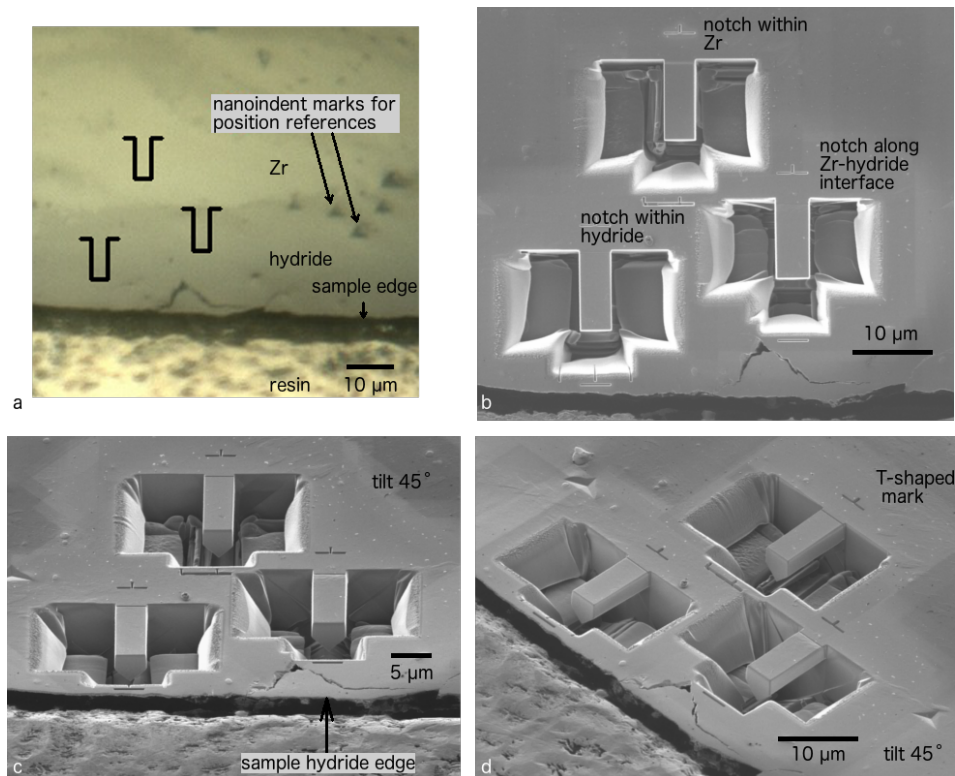


Figure 7.1 Typical microfracture specimens. a) Optical micrograph obtained prior to machining. The cross-sectional hydride film is the dark region as annotated. Nanoindents were made as position references preparatory to FIB fabrication. b) SEM image shows the same region. c) and d) The sample was tilted at 45° for an inspection of fabrication quality.

The microcantilevers were tested in an Agilent Nano Indenter G200-XP using a Berkovich tip. In each test, a topographical map of the T-shaped mark (Figure 7.1d) was first produced in the scanning mode in order to set up a reference position and surface height. The specimen was then moved along its longitudinal centre-line below the nanoindenter tip to reach the loading position. The deflection test was carried out at a constant displacement rate of 5 nm/s to meet the quasi-mechanical loading condition until a sharp load drop occurred, indicating that fracture had occurred, or to a maximum preset displacement of 2 μm .

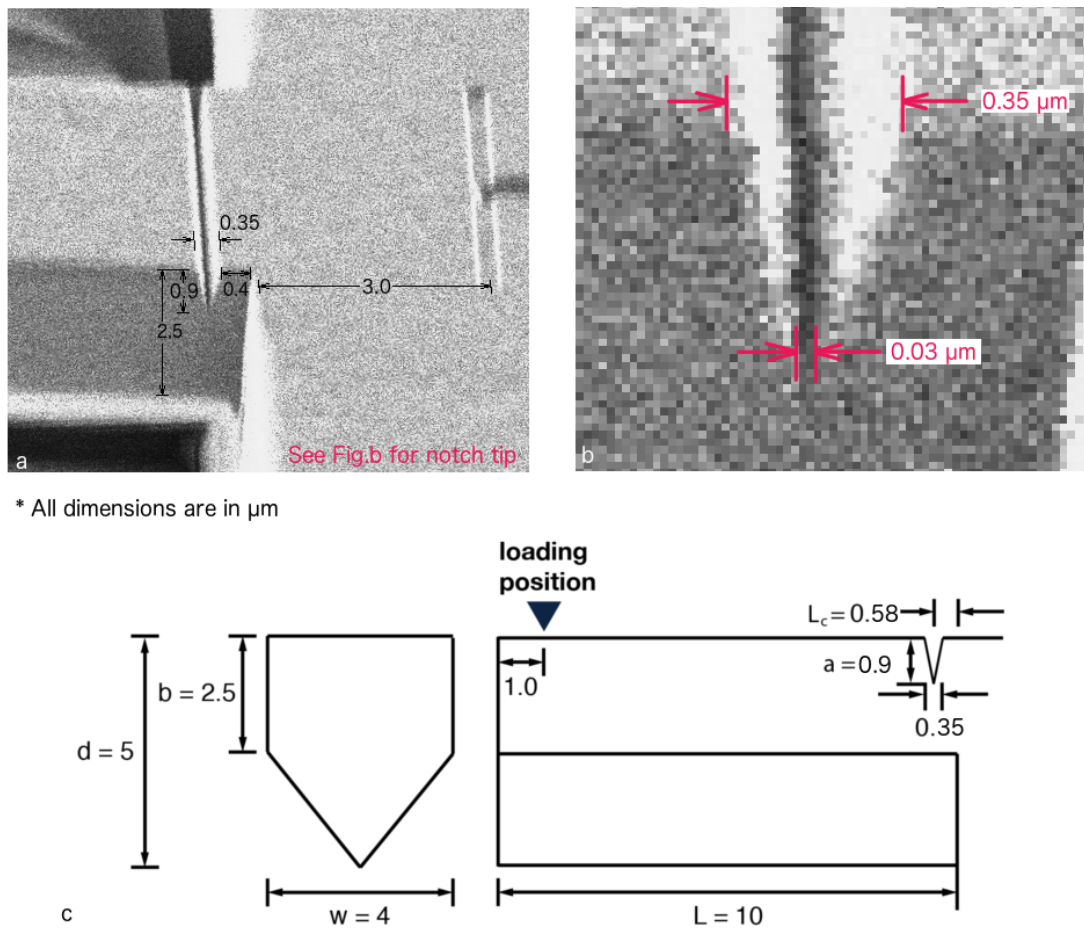


Figure 7.2 a) Hydride specimen H1 was tilted at 45° for dimensional measurement. b) Digital zoom of the SEM image was used to measure the notch tip radius. Each pixel corresponds to 15 nm. The notch tip was produced by 1 pA in an FIB 200. High resolution electron image was not produced to avoid radiation damage near the sharp notch tip. c) Illustration of the specimen's dimensions in μm .

Each microcantilever was imaged at the tilt angles of 0° , 30° and 45° before and after the tests (Figure 7.2 and Figure 7.6). The dimensions of each cantilever were measured by counting the number of pixels in these SEM micrographs. Figure 7.2 shows that the radius of the notch tip occupies 1-2 pixels; which is equivalent to 15-30 nm. This demonstrates the low FIB current of 1 pA is capable of producing a sharp notch tip relative to the scale of a hydride precipitate ($\sim 1\mu\text{m}$).

7.3 Surface Examination Results

7.3.1 δ -Hydride Microcantilevers

Microcantilevers were prepared within the cross-sectional δ -hydride film. The dimensions of the specimens are summarised in Table 7.1. The specimens were aligned to a variety of crystallographic orientations as shown in Table 7.4.

Table 7.1 Dimensions of the hydride cantilevers in μm . See Figure 7.2c for symbol notation.

Specimen number	Width, w	Length, L	Depth of uniform section, b	Total depth, d	Notch depth, a	Horizontal distance between notch front and fixed-end, L_C	Calculated second moment of area, $I (\mu\text{m}^4)$
H1	4.0	10.0	2.5	5.0	0.9	0.6	21.4
H2	3.7	10.0	2.7	5.0	0.9	0.5	20.7
H3	3.5	10.0	2.5	5.0	1.5	0.5	18.7
H4	3.0	9.9	2.4	4.2	0.8	0.4	10.3
H5	2.0	10.1	2.0	3.9	0.3	0.6	5.15
H6	4.0	10.0	2.5	5.0	0.3	0.3	21.4

Figure 7.3a shows the EBSD map obtained prior to fabrication of two polycrystalline hydride microcantilevers, H1 and H2. Their notch region, denoted as point A and B, was individually made within a single grain. The crystallographic planes that are normal to the principal axes

of the spatial frame, X_S - Y_S - Z_S , are plotted in Figure 7.3b. The specimens' longitudinal direction connecting from the fixed end to the free end is parallel to $-Y_S$, therefore the plane of symmetry of the notch is $(\bar{4}3\ \bar{1}9\ \bar{6})$ for H1 and $(\bar{1}4\ \bar{7}\ \bar{2})$ for H2. This information was used for analysing the anisotropy of fracture toughness as presented in Section 7.4.2.

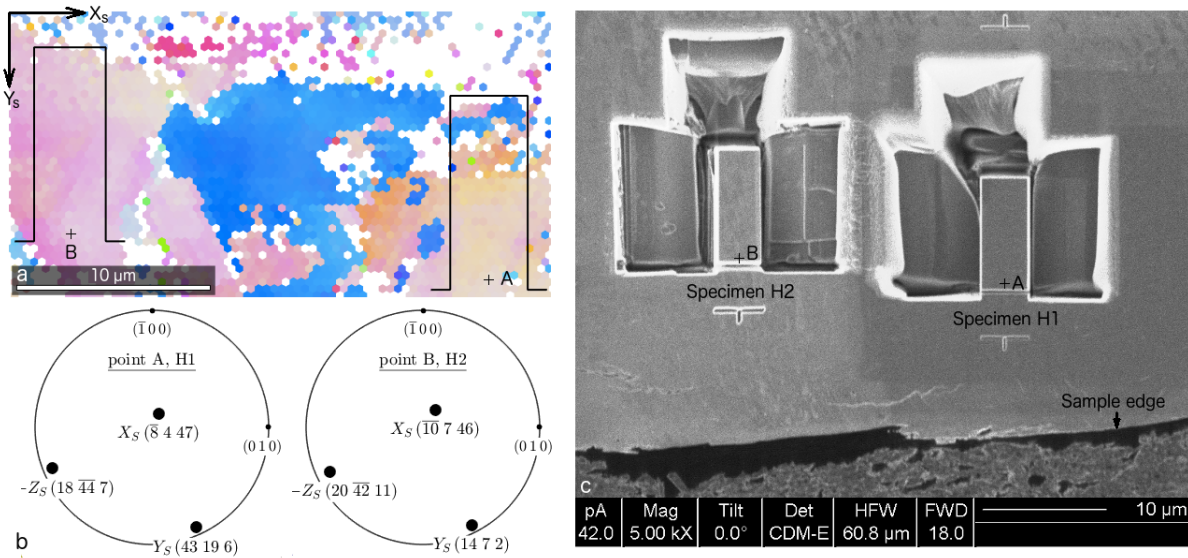


Figure 7.3 a) Single-phase hydride EBSD map used for fabrication of specimens H1 and H2. X_S and Y_S represent the spatial frame directions. b) The inverse pole figures show the crystallographic planes that are perpendicular to the principal spatial frame axes at point A and B. c) SEM micrograph of the hydride film region obtained subsequent to FIB milling.

In Figure 7.4, the similar mechanical response for H1 and H2 arises from their similar dimensions and comparable crystallographic microstructures. The linear portion at the displacement $<600\text{ nm}$ represents the extrinsic stiffness of the specimens. When the displacement is $\sim 600\text{ nm}$, the sharp load drop indicates that the brittle fracture had occurred. Since the nanoindenter tip was no longer in contact with the cantilever, the acquired slope during the release of load relates only to the internal dynamics of the nanoindenter rather than the specimens' material properties. This is different from a nanohardness test in which the unloading curve is usually used for extracting elastic properties. An FE model was used to

simulate the linear load-displacement response (See Section 7.4.3). The resulting fitting curves are shown as dotted lines in Figure 7.4.

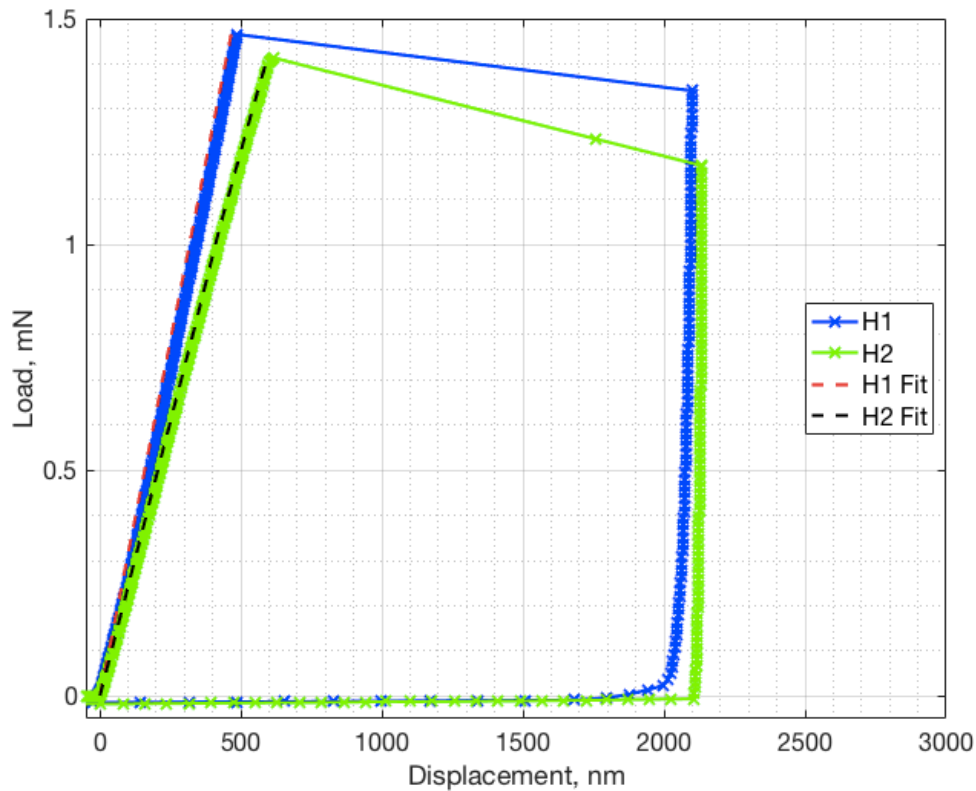
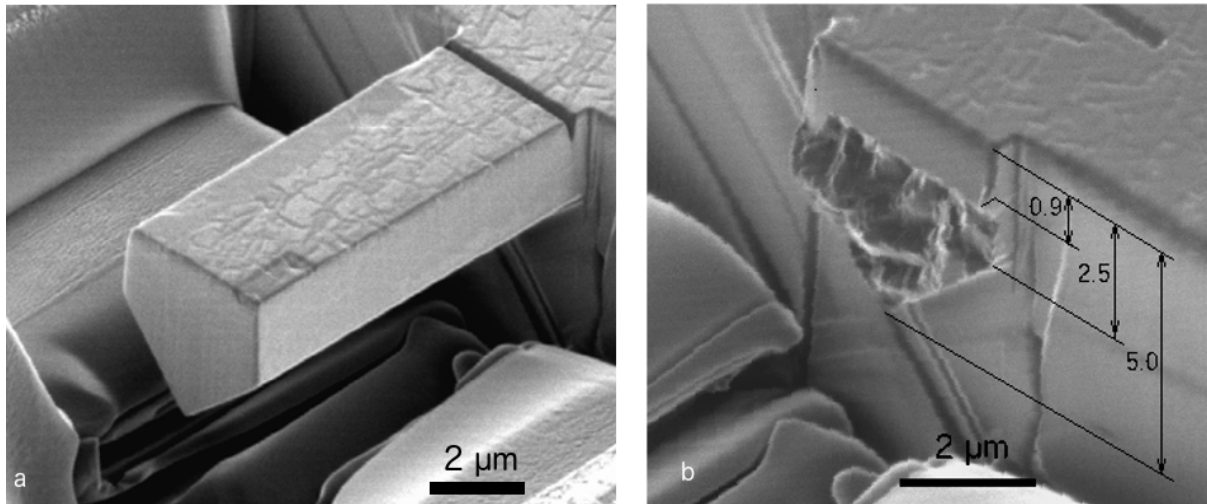


Figure 7.4 Load-displacement relations of the pre-notched hydride cantilevers H1 and H2.

Specimens H1 and H2 were imaged at the same angle prior and subsequent to the loading test for comparison. In Figure 7.5b, the undamaged surface on the top section ($0.9\ \mu\text{m}$ in depth) corresponds to the uniform notch face being milled. In the lower section, cleavage ridges can be observed on the fracture surfaces. This characteristic surface feature of brittle fracture is consistent with the abrupt load drop as seen in the corresponding load-displacement curve (Figure 7.4). Cleavage was also observed in specimen H2 as shown in Figure 7.6. It can be seen that the main crack path propagated vertically downwards into the sample's normal direction.



* All dimensions are calculated values in μm .

Figure 7.5 Pre- and post-examination of the hydride microcantilever H1. The micrographs were captured at the same angle. All dimensions are corrected measurements in μm . The surface cleavage indicates that the specimen underwent brittle fracture.

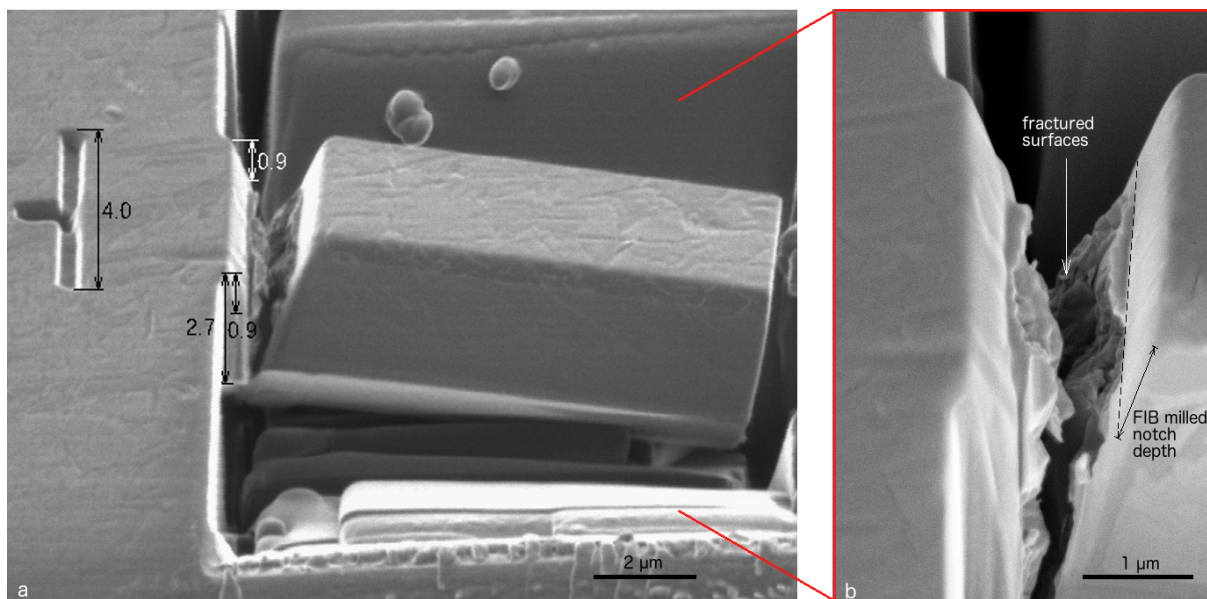


Figure 7.6 Fractured hydride specimen H2. a) The dimensions in μm were measured with reference to the T-shaped calibration mark. The main crack advanced downwards along the sample normal. b) The specimen was imaged at the same angle with high resolution SEM. Cleavage is seen on the fractured surfaces below the notch face.

Figure 7.7 shows the fractured hydride specimen H3. Its geometry was aligned with crystallographic planes different from H1 or H2. Since the whole notch was designed to be

contained within an individual hydride grain, the specimen was restricted to be milled in proximity to hydride-hydride grain boundaries due to the small grain size. Figure 7.7b to d show the presence of cleavage on both the fixed and detached sections. The failure mode is considered as transgranular brittle fracture with the assumption that the region underneath the notch front is contained in the same grain. The irregular fracture surfaces do not show any clear preferential crystallographic fracture plane.

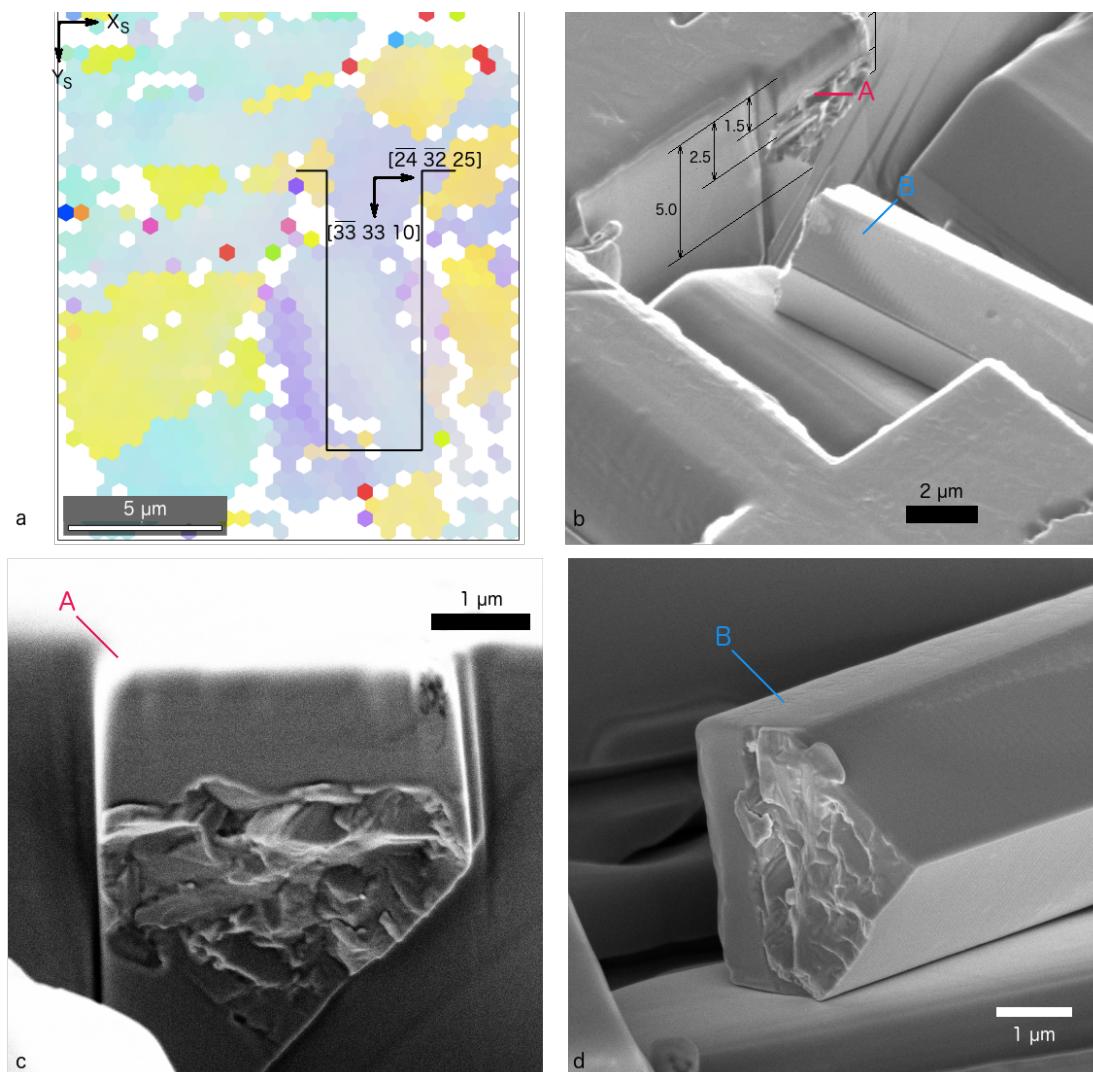


Figure 7.7 Hydride specimen H3. a) Single-phase EBSD map of the hydride region for fabrication. The Miller indices indicate the crystallographic directions. b) The SEM image was used for dimensional measurement. Annotation markers A and B denote the two sections. c) The cantilever's fixed end imaged in an Auriga using an SE2 detector. The fracture surfaces below the notch shows irregular pattern. d) The detached beam, section B, shows cleavage as a characteristic feature of brittle fracture.

The experimental procedure was repeated for the hydride specimen H4. In Figure 7.8, the main crack propagated downwards along the sample's normal; which is similar to other specimens shown previously. Figure 7.8b shows the load dropped sharply after linear elastic deformation and this response is consistent for all hydride specimens.

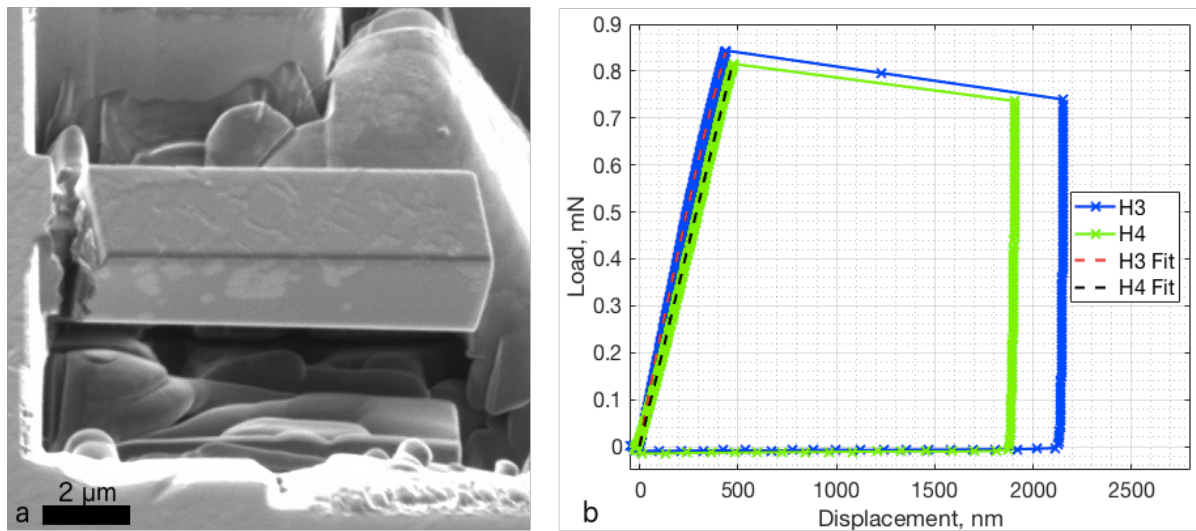


Figure 7.8 a) Post SEM examination of H4. b) The load-displacement response and fitting curves for the hydride specimens H3 and H4. See Figure 7.7 for SEM micrographs of H3.

All the single δ -phase hydride microcantilevers underwent brittle fracture as supported by the presence of surface cleavage and sudden load drop. In addition to the SEM observations and the linear elastic load-displacement response described in this section, fracture toughness calculation is presented in Section 7.4.1.

7.3.2 α -Zr Microcantilevers

Microcantilevers were prepared within the α -Zr for testing. Table 7.2 lists the dimensions.

Table 7.2 Dimensions of α -Zr cantilevers in μm . The notations are illustrated in Figure 7.2c.

Specimen number	Width, w	Length, L	Depth of uniform section, b	Total depth, d	Notch depth, a	Horizontal distance between notch front and fixed-end, L_C	Calculated second moment of area, $I (\mu\text{m}^4)$
Z1	4.0	10.0	2.4	4.9	0.2	0.5	19.9
Z2	3.9	10.0	2.5	5.0	0.2	0.5	20.9
Z3	4.0	10.0	2.5	5.0	0.3	0.6	21.4
Z4	4.0	10.0	2.4	4.8	0.3	0.5	18.9
Z5	4.0	10.0	2.4	4.8	0.0	0.5	18.9
Z6	4.0	10.0	2.3	5.0	1.3	0.5	20.5
Z7	3.9	9.9	2.5	5.0	1.0	0.5	20.9
Z8	2.2	10.0	2.2	3.8	0.2	0.5	5.65

Figure 7.9 shows the Zr specimens Z1 to Z3 before and after the micromechanical tests. All three microcantilevers were tested with the same instrumental parameters as for testing the hydride specimens. In Figure 7.9c, the curves show that the Zr specimens yielded similarly without a noticeable load drop after being loaded to $2 \mu\text{m}$ tip deflection. The absence of crack initiation at the notch tip is attributed to the high fracture toughness of the metallic Zr at room temperature ($\sim 15 \text{ MPam}^{1/2}$) [100]. Since the notches are below the critical flaw size for the ductile Zr specimens' testing configuration, fracture process did not occur under the preset loading condition.

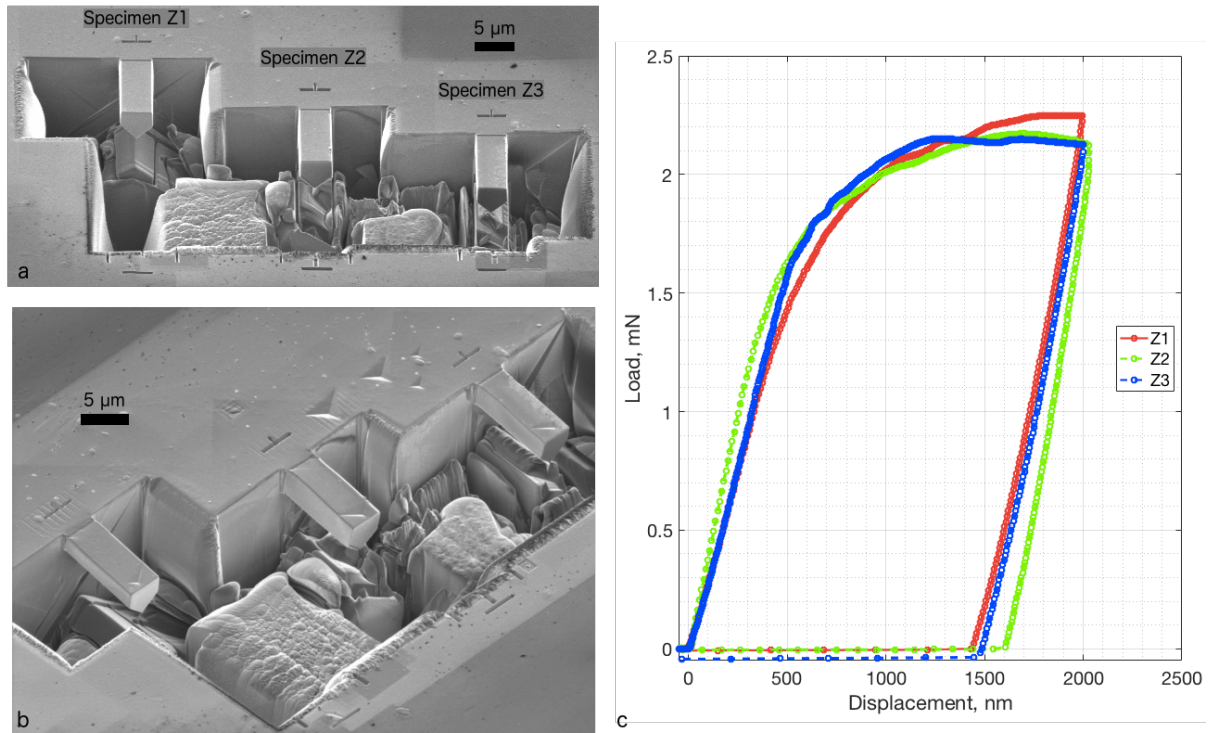


Figure 7.9 Zr microcantilevers Z1 to Z3. a) Pre-test micrograph shows the dimensions of the specimens are similar. b) Post-examination of the yielded specimens. c) The load-displacement curves show permanent deformation without any sharp load drop.

A pre-notched specimen, Z4, and an un-notched specimen, Z5, were prepared within a single grain in the centre of a Zr sample. Figure 7.10a shows that the specimens' longitudinal axes align with the same crystallographic direction at the inclination angle of 34° (See Section 7.4.3 for analysis). The grain was sufficiently large such that the specimens were over $5\ \mu\text{m}$ away from any grain boundary. In Figure 7.10b and c, the SEM micrographs show that the specimens underwent permanent deformation without material failure. Figure 7.10d shows that the specimens yielded similarly until the maximum deflection.

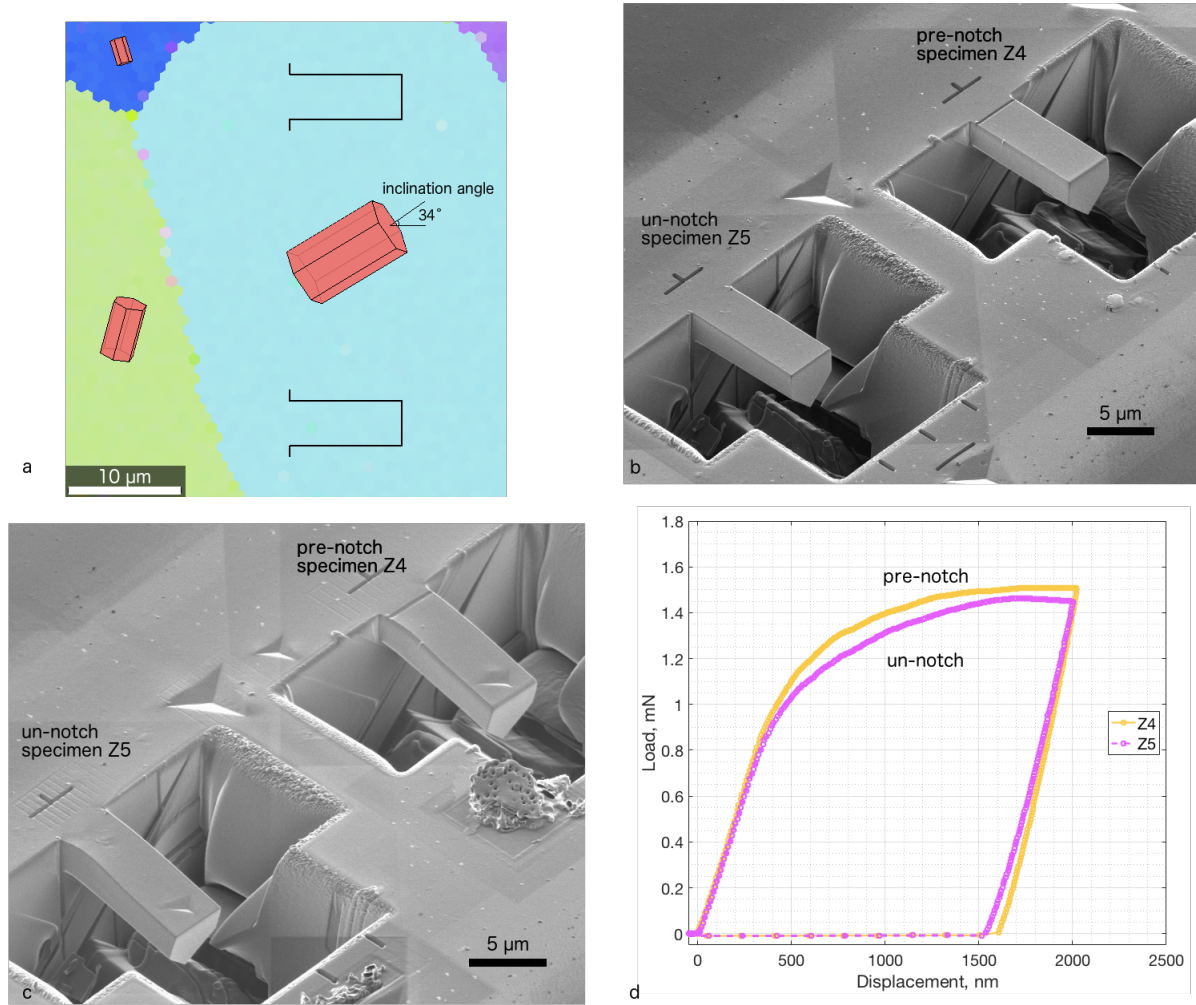


Figure 7.10 Zr microcantilevers Z4 and Z5. a) The two 4 x 10 μm specimens were prepared on a single Zr grain at the same direction. b) and c) The pre- and post-test examinations shows the two specimens deformed similarly. d) The load-displacement curves.

A deep notch of over 1 μm in depth was made in the microcantilevers Z6 and Z7. Figure 7.11a and b show the pre- and post-examination of Z6. The specimen substantially deformed without disrupting into two parts in contrast to the behaviour of any hydride specimen (Figure 7.5). High resolution SEM was used to image the highly stressed notch front region of Z7 as shown in Figure 7.11d. The notch became blunt with the absence of crack initiation after the micromechanical test. The notch front opened with the presence of some evenly distributed shallow dimples. These elliptical depression features likely correspond to the early stage of microvoid formation under extensive plastic deformation.

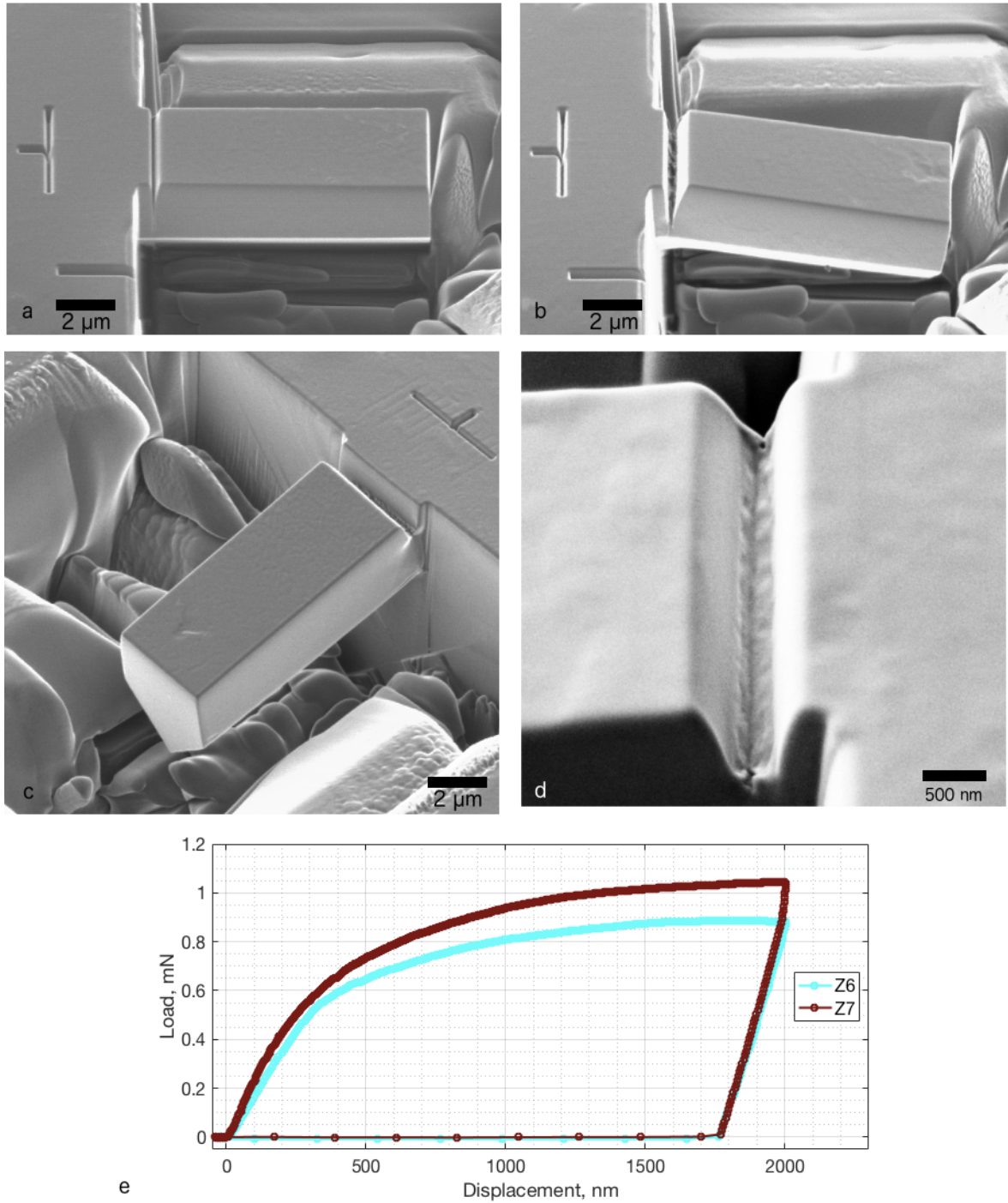


Figure 7.11 Zr specimens Z6 and Z7. a) and b) Z6 deformed plastically without separating into two sections. c to f) The notch front of Z7 did not propagate downwards as contrast to the hydride specimens' behaviour as shown in the previous section. The early stage of localised plastic failure can be observed along the notch front. e) Load-displacement curves show that the specimens underwent permanent deformation.

Comparison between the δ -hydride and the α -Zr Specimens

Figure 7.12 shows a 96-hour hydrided sample in which a dense hydride film formed along the edge. The two indexed phases are presented individually in Figure 7.12b and c. More details about the microstructure and the crystallographic relationship are presented in Figure 4.27.

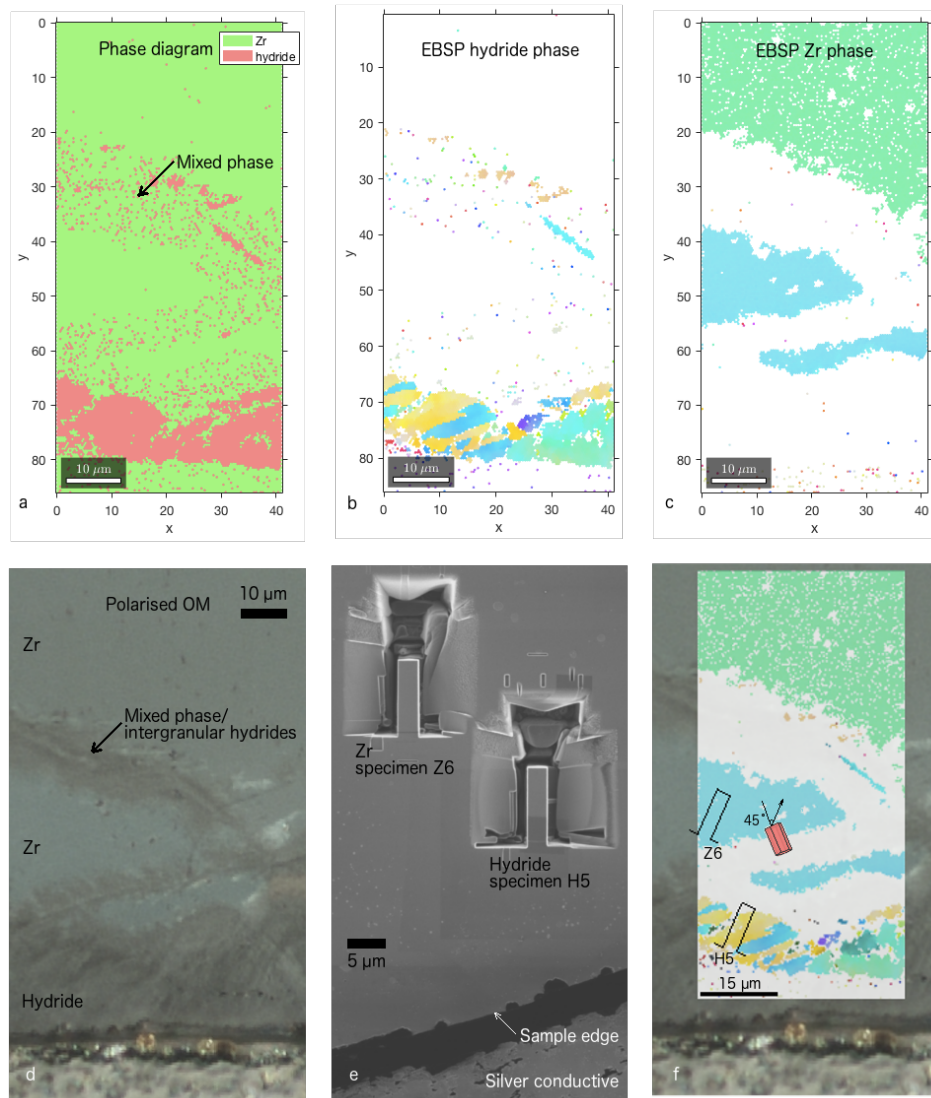


Figure 7.12 Microcantilevers fabricated in a dual-phase region. a) Phase map. b and c) Each EBSD map shows an individual phase. The hydride grains have a twin relationship as described in Figure 4.27. d) Polarised optical micrograph. The grey area is the hydride rich region. e) SEM micrograph imaged before the micromechanical test. f) The dual-phase EBSD map overlaps with the optical image. The mixed-phase region indexed with low confidence level is shown as white. The inclination angle between the longitudinal direction of Z6 and the c-axis of the hexagonal crystal is 45° as indicated. The crystallographic relationship between the two phases is analysed in Figure 4.27.

Figure 7.12a shows the hydride specimen H5 and the Zr specimen Z8. They were both 2 μm wide and loaded under the same condition. Their distinct mechanical properties can be seen clearly in the post-examination (Figure 7.13b). The occurrence of abrupt brittle fracture in H5 is consistent with other hydride specimens. In contrast, Z8 yielded without failure and slip lines can be observed below the notch region (Figure 7.13e). In Figure 7.13c, the load-displacement curve for H5 shows small plastic deformation followed by a sharp load drop where the brittle fracture occurred; while that for the α -Zr shows large-scale yielding.

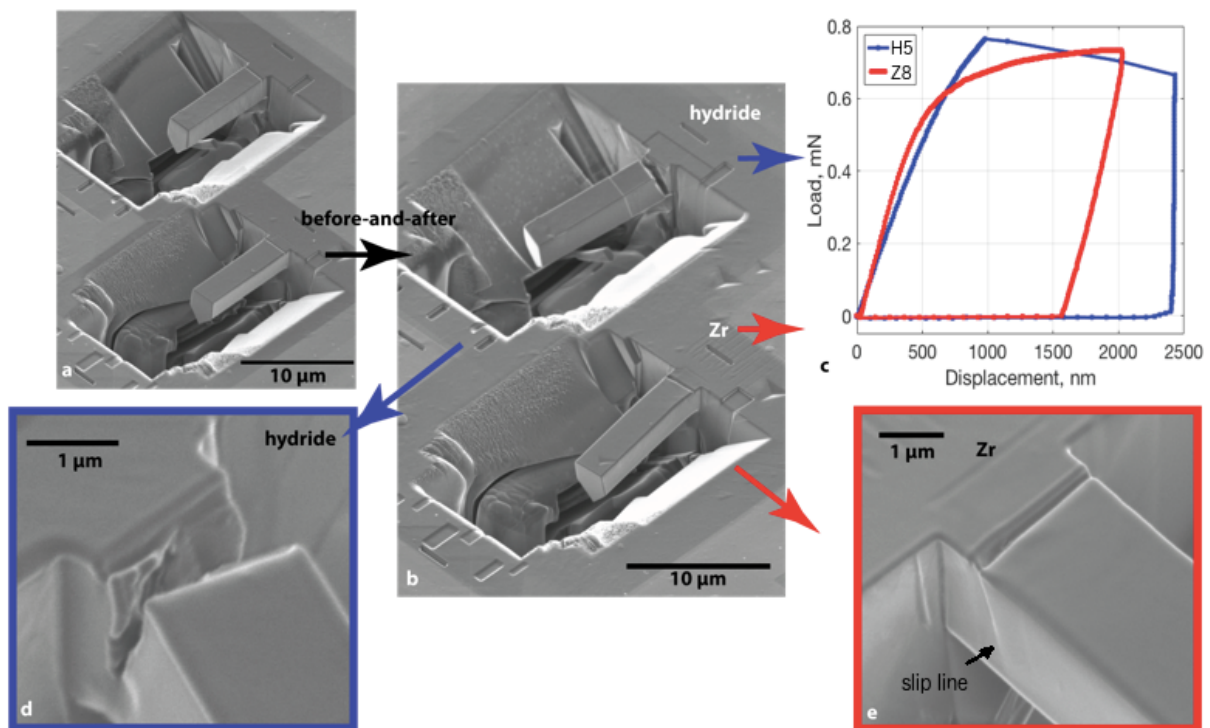


Figure 7.13 Comparison between the α -Zr specimen, Z8, and the δ -hydride specimen, H5. a) and b) Pre- and post-test examinations. c) Their corresponding load response curves show distinct deformation properties. d) Fracture surface of H5 shows that the crack initiated at the notch front. e) Slip lines were observed near the highly stressed region in Z8.

7.3.3 Dual-Phase Microcantilevers

The micromechanical properties of materials near a Zr/hydride interface were investigated by testing the dual-phase (DP) microcantilevers. Table 7.3 lists the dimensions of the specimens.

Table 7.3 Dimensions of dual-phase (DP) cantilevers in μm . The geometry notations are illustrated in Figure 7.2.

Specimen number	Width, w	Length, L	Depth of uniform section, b	Total depth, d	Notch depth, a	Horizontal distance between notch front and fixed-end, L_C	Calculated second moment of area, $I (\mu\text{m}^4)$
DP1	3.8	10.2	2.5	5.0	0.5	0.5	20.3
DP2	3.2	10.0	2.6	5.0	0.3	0.6	17.5
DP3	4.0	10.0	2.8	5.0	0.2	0.5	22.9
DP4	4.0	10.0	2.6	5.0	0.8	0.5	21.9
DP5	3.9	10.1	2.6	4.9	0.2	0.5	20.3

Pre-test Examination and Crystallographic Properties of the Specimen DP1

Surface examination was carried out for the milling location of DP1 before fabrication (Figure 7.14). The region consisted of a continuous hydride film on the sample's edge and a mixed phase region where precipitates were embedded in a single Zr grain. In the EBSD map as shown in Figure 7.14b, the region with low index quality is presented as white. The low quality is likely caused by the presence of dispersed hydride precipitates; as indicated by the scattered index points in the phase diagram in Figure 7.14c. The microcantilever was made mainly inside a Zr grain and the notch was made fully inside a hydride precipitate. The notch front was parallel to the long axis of the precipitate (Figure 7.14d to g).

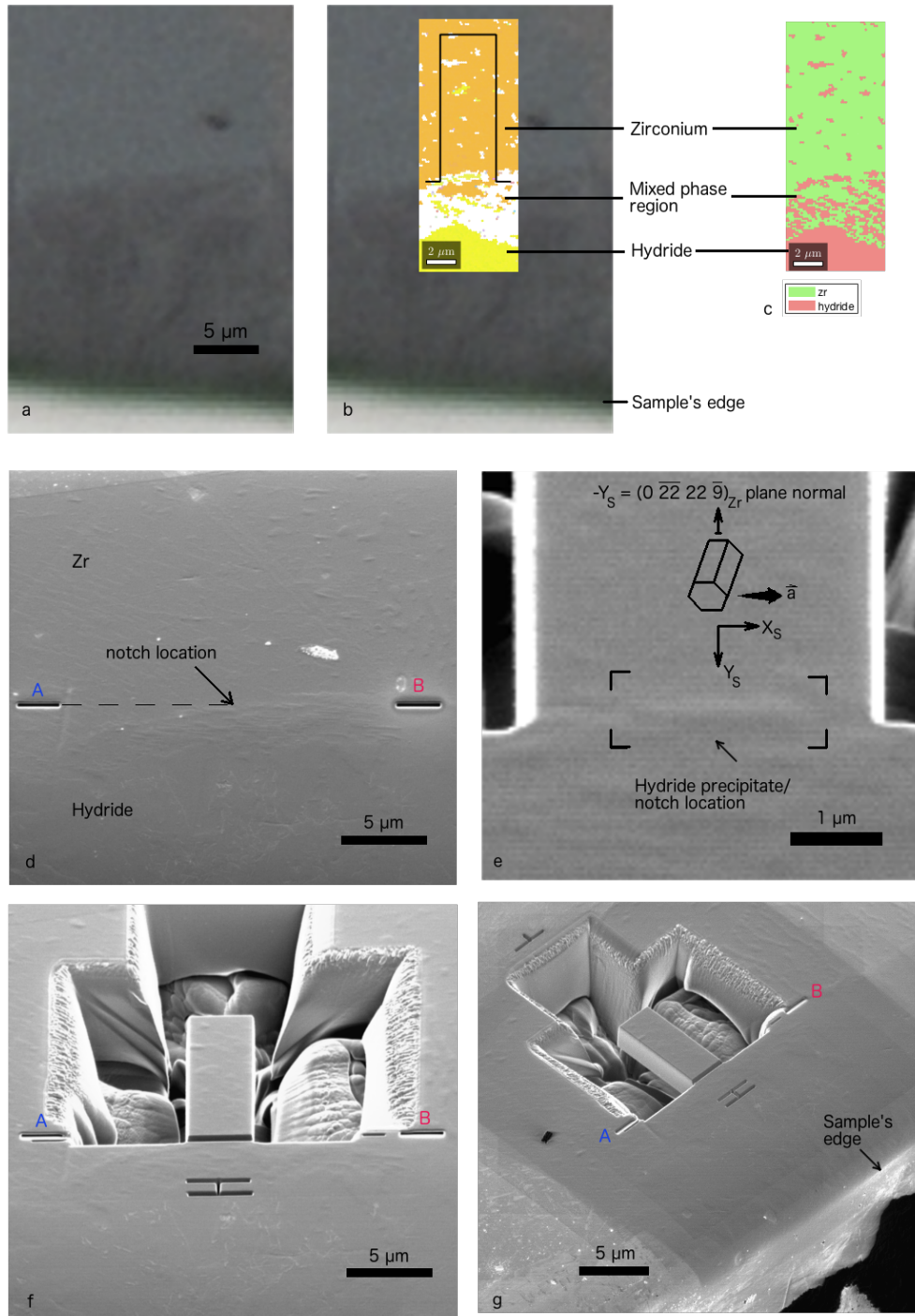


Figure 7.14 Pre-test examination of the dual-phase specimen DP1. a) Polarised optical image taken before fabrication. b) EBSD map overlaps with the polarised optical image. Details of the crystallographic information are described in Figure 7.15. c) Phase diagram. The scattered index points indicate the presence of hydride precipitates in the mixed-phase region. d) SEM image captured before fabrication. The sample was tilted at 45° . Two marks, A and B, were made to provide reference positions. e) SEM image captured immediately before making the notch. The selected notch direction is parallel to a hydride precipitate. The labelled plane normal is used for determining the precipitation direction. The hexagonal crystal a -direction points out of paper. f and g) DP1 prior to testing. The sample was tilted at 45° in both images.

The crystallographic microstructure of DP1 is analysed in Figure 7.15. The poles used in the pole figures were collected from the EBSD indexing points with a pattern quality over a threshold confidence index: 791 data sets were used for the Zr and 813 data sets were used for the hydride. In Figure 7.15b, the coloured circles represent the stereographic projection of identical points. Since the poles are situated inside the circles, the close packed plane of the Zr is parallel to that of the hydride: $(0001)_{\text{Zr}} \parallel (111)_{\text{hydride}}$ and their close packed directions are parallel: $[11\bar{2}0]_{\text{Zr}} \parallel [1\bar{1}0]_{\text{hydride}}$. This type of Zr/hydride relationship has been reported in the literature (Section 2.2.3).

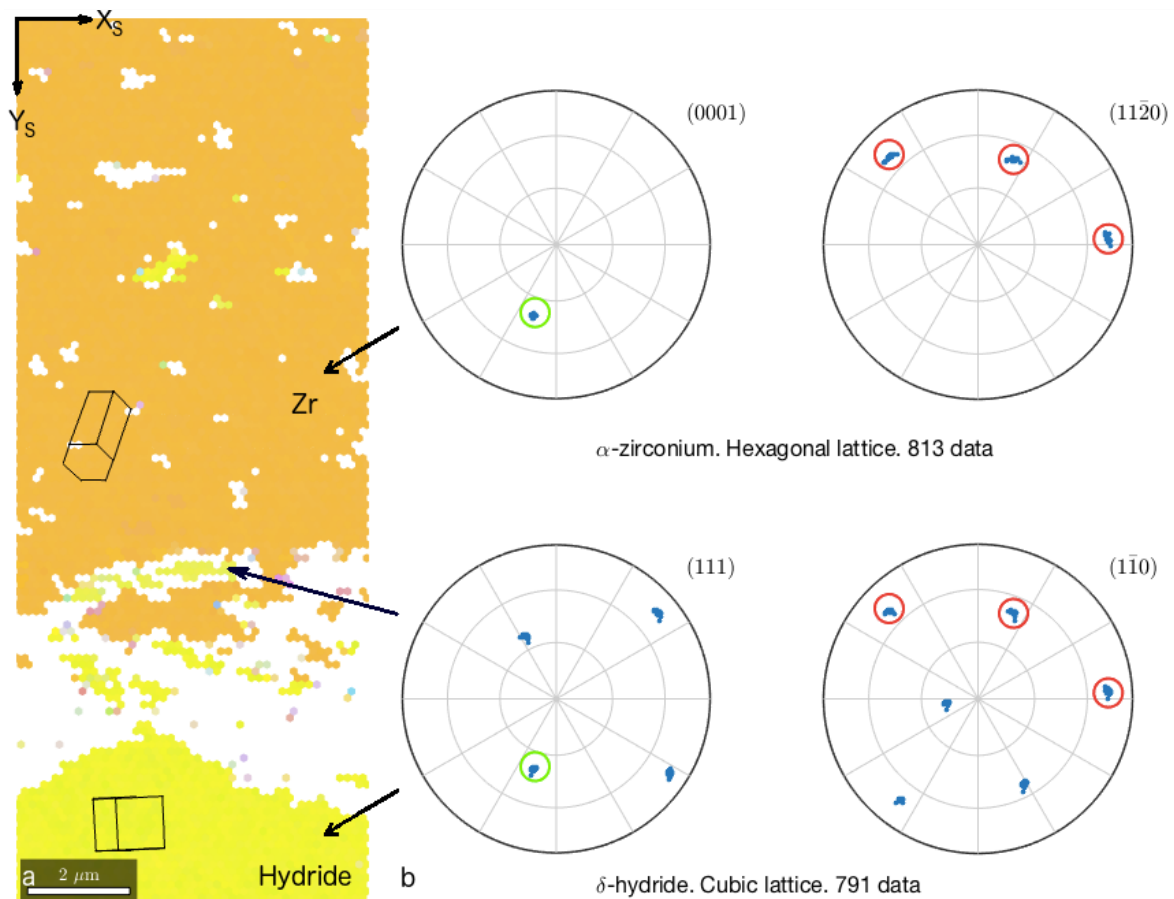


Figure 7.15 The crystallographic relationship of the mixed phase region for preparing the specimen DP1. a) EBSD IPF map of the hexagonal Zr phase and the cubic hydride phase. b) The pole figures show parallel crystal planes and crystal directions: $(0001)_{\text{Zr}} \parallel (111)_{\text{hydride}}$ and $[11\bar{2}0]_{\text{Zr}} \parallel [1\bar{1}0]_{\text{hydride}}$. This figure is generated by MTEX.

The Precipitation Direction of Hydrides in DP1

The precipitation direction of hydrides in DP1 was analysed from SEM images obtained on the sample's surface (Figure 7.14e) and that on the cross-sectional surface (Figure 7.18d). As denoted in the figures, the long axis of the precipitates simultaneously lies in the Zr crystal planes $(0\ \bar{2}\bar{2}\ 22\ \bar{9})$ and $(0\ \bar{3}\ 3\ 7)$. Since both planes are in the form of $(0\ k\ \bar{k}\ l)$, their reciprocal indices can be factorised to $(0\ 1\ \bar{1}\ l_1)$ and $(0\ 1\ \bar{1}\ l_2)$, where $l_1 \neq l_2$. These two <a>-pyramidal planes have a common direction or a unique zone axis $\langle 2\ \bar{1}\ \bar{1}\ 0 \rangle$ as stated by Weiss zone law. Therefore the long axis of the precipitates aligns with $\langle 2\ \bar{1}\ \bar{1}\ 0 \rangle$, denoted as a-direction of the hexagonal crystal in the figure. This direction has been reported as a preferential precipitation of Zr hydrides in the literature (Section 2.2.4).

Post-test Surface Examination of the Specimen DP1

Figure 7.16 compares the SEM examinations carried out before and after the mechanical test for DP1. The load being applied on the free end resulted in notch front opening and partial failure. The nucleation of elliptical cavities along the notch front direction, X_S , is indicative of the initial stage of dimple fracture. The diameter of the microvoids along the specimen's longitudinal direction, Y_S , ranges from 75 nm to 250 nm. The ratio of diameter in Y_S to that of X_S is ~ 0.75 . Figure 7.17 shows the process of FIB cross-sectioning that was used to reveal the sub-surface features of the specimen. The preparation started with the deposition of a 0.1 μm thick carbon coating on the microcantilever. A medium low current of 300 pA was then used for initial cuts in an FEI FIB 200. In order to reduce the ion damage, the final foil surface was polished with 30 pA low scanning current. The thickness of the foil is 0.1 μm .

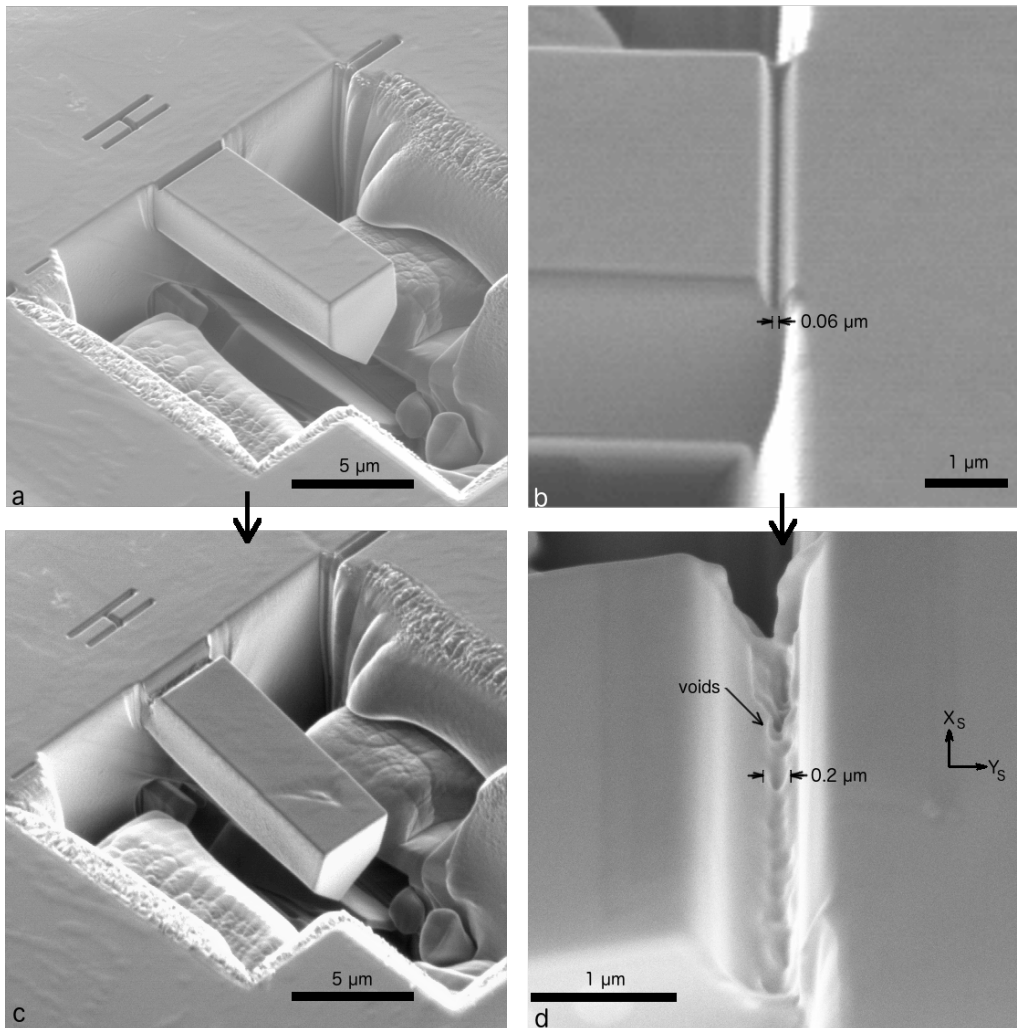


Figure 7.16 SEM examination of the dual-phase specimen DP1 before and after the loading test at the same imaging angle. Voids were developed along the notch tip.

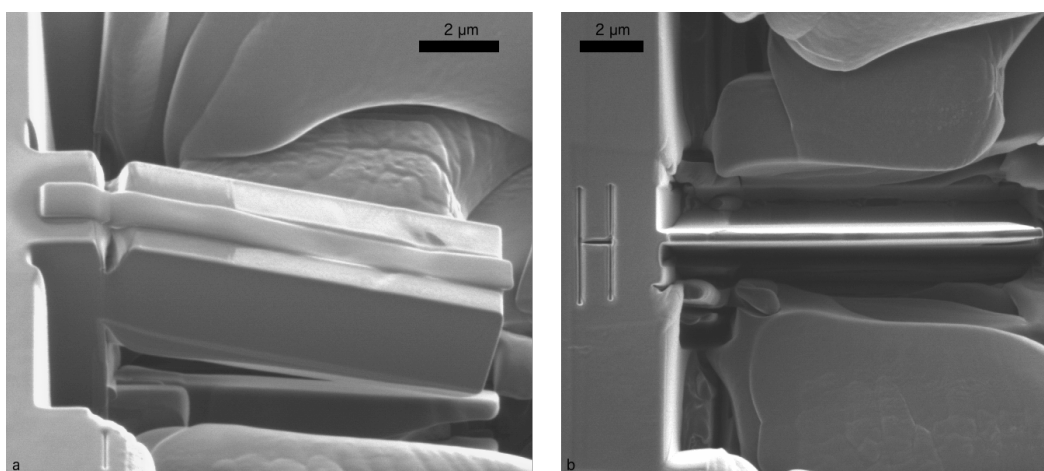


Figure 7.17 FIB cross-sectioning of the specimen DP1. Carbon coating was deposited on the centreline region before milling. The final 0.1 μm thick foil was finished with 30 pA.

Post-test Cross-sectional Surface Examination of DP1

Figure 7.18 shows the SEM examination of the cross-sectional surface of DP1. Since the greyscale contrast between the two phases is low, an illustration is provided in Figure 7.18d. The free end of DP1 mainly consisted of the Zr in which hydrides precipitated on the top edge. The highly stressed region underneath the notch tip is located inside a hydride island. Figure 7.18e shows the notch on the side of DP1. Cleavage hydride fracture occurred in the stress concentration region below the notch tip. However cracking did not only initiate at the notch tip; instead new secondary microcracks of less than $0.5\text{ }\mu\text{m}$ were generated. The crack paths of these resulting microcracks are generally perpendicular to the tensile stress in the specimen's longitudinal direction, Y_s , and therefore they produced elongated cracked openings in the Z_s direction. In Figure 7.18f, the SEM micrograph shows the strained tip on the centreline of the specimen. The notch opened but did not extend through the hydride island. In comparison to any pure hydride specimen where the main crack always spontaneously propagated downwards, crack extension was hindered in this dual-phase specimen. The FIB-machined notch tip, denoted as point A, is located in the hydride and the notch face on the fixed end is partially situated in the Zr. The notch permanently deformed to geometries with three distinctive vertices: the FIB-machined tip (A), the vertex on the Zr/hydride interface (B) and the vertex in the hydride (C). The opening of the notch, in particular the deformation at the vertices A and C, shows that the hydride exhibits yielding ability to allow plastic deformation. In this plastic zone, the applied work results in yielding and partial failure of both the Zr and the hydride. However the Zr/hydride interface, extending from B to B', remains intact in the specimen. Despite a small region adjacent to B was stress free, the phase boundary processes some adhesion strength to withstand stresses.

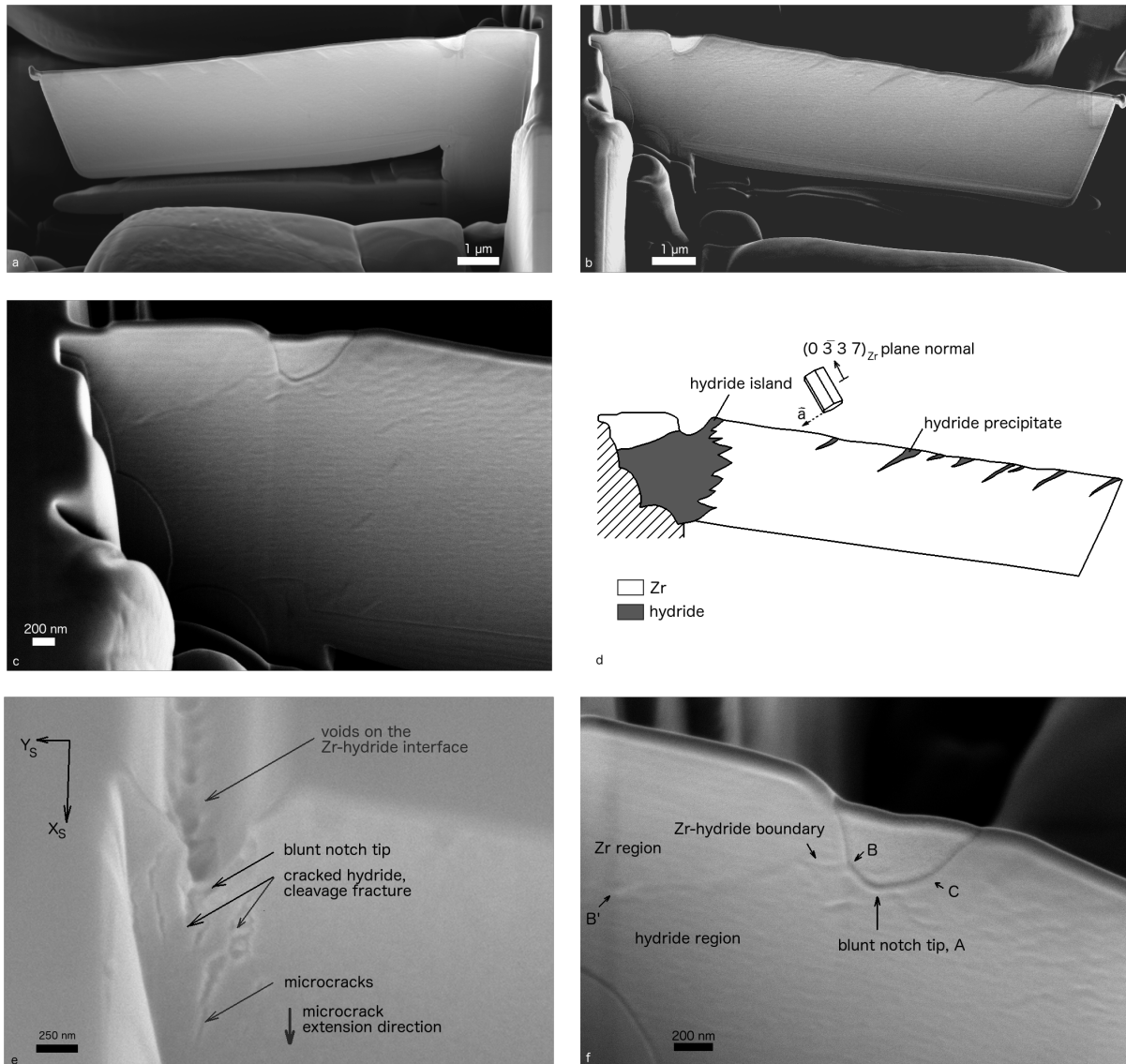


Figure 7.18 SEM examination of the cross-sectional surface of DP1. a to c) High resolution SEM images show both sides of the foil. The notch tip is located in a hydride island as identified by EBSD prior to specimen fabrication (Figure 7.14b and e). d) The diagram illustrates the phase region and the crystallographic directions of the Zr as determined from the EBSD results as shown in Figure 7.15. The $\vec{a}$ -direction of the hexagonal crystal points into paper. e) Microcracks extended from fractured hydrides are perpendicular to the tensile stress direction. Microvoid coalescence can be seen along the notch front. f) The local region of the deformed notch and the phase boundary (BB').

Void Formation Near the Zr/hydride Interface of DP1

In Figure 7.16d and Figure 7.18e, microvoids are observed on the Zr/hydride phase boundary along the notch front. These elliptical cavities are morphologically different from cleavage in fractured hydrides. Figure 7.18f shows that the cross-sectional profile consists of deformed Zr/hydride interface (vertex B) and deformed hydrides (vertices A and C). The asymmetric deformation of the notch would be attributed to the marked difference between the yielding responses of the two phases. The yield strengths of the hydride and the Zr are ~1100 MPa and ~600 MPa respectively in the micron scale (Section 2.3.2 and Table 7.5). The Zr near the interface would be plastically strained prior to the hydride under the applied load, resulting in localised inhomogeneous deformation. Since the hard hydride deformed at a different rate from the ductile Zr, microvoids were developed to accommodate the incompatibility. Although the probable crack path was located in the hydride, the released strain energy was predominantly dissipated through plastic flow in the surrounding Zr and therefore the crack growth was impeded. More discussion is presented in Section 7.5.2.

Load-displacement Response of the Specimen DP1

The load-displacement curve for DP1 is shown in Figure 7.19. Subsequent to the initial linear portion, a slight curvature is observed at ~300 - 730 nm (Region I). This portion indicates the specimen underwent elastic deformation followed by yielding. The material near the notch was highly strained and contributed to part of the notch front opening as seen in Figure 7.16d.

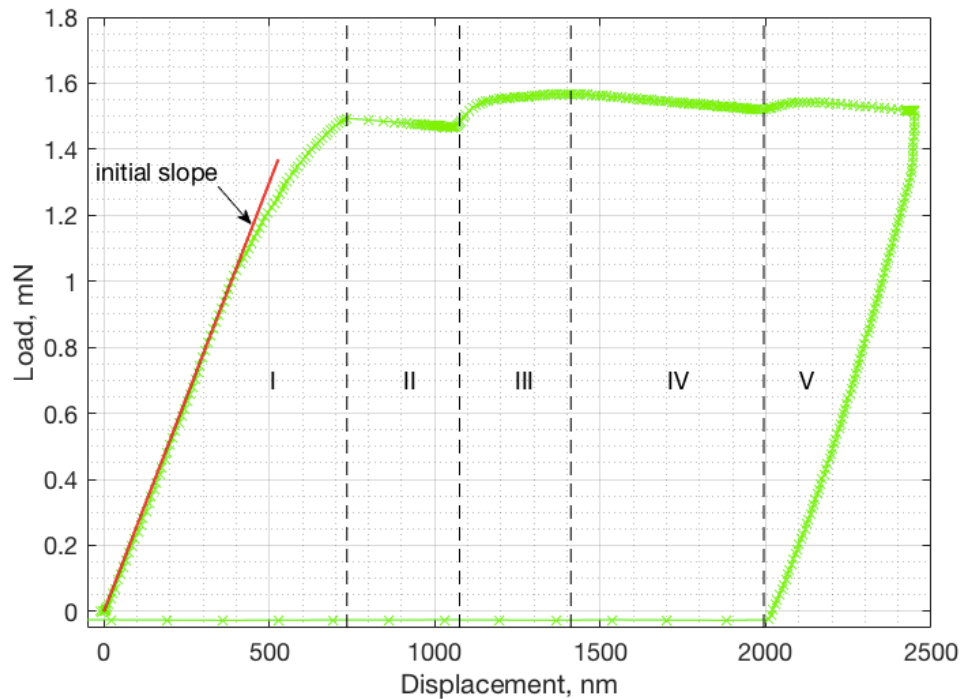


Figure 7.19 Load-displacement curve of the dual-phase microcantilever DP1.

When the displacement reached ~ 730 nm, a sharp load drop was recorded. The decrease in load is associated with hydride fracture, leading to cracked openings as seen in Figure 7.18e. In Region II, where the displacement was ~ 730 -1100 nm, the nanoindenter tip was in contact with the microcantilever. The gradual decrease in load is attributed to stable microcracks extension from the existing cracked openings and nucleation of new fracture sites near the notch front (Figure 7.18e). When the specimen's tip was deflected to ~ 1100 nm, the load started to rise in Region III. This pop-in feature suggests that hydride fracture was impeded and plastic deformation of the Zr became dominant. Following the maximum load plateau at ~ 1400 nm, the small load drop recorded in Region IV would be caused by simultaneous occurrence of microcrack growth, void development and plastic yield. The competition continued in Region V until the nanoindenter tip was retracted manually. The unloading gradient is similar to that of the initial loading portion due to elastic recovery of the partially failed specimen. More are discussed in Section 7.5.2.

SEM examination of the specimens DP2 and DP3

The same experimental testing procedure was repeated for DP2. Figure 7.20a shows the EBSD map and the phase map of the region. The fixed end of DP2 is located in the hydride and the free end is in the Zr. The crystallographic relationship between the two phases is presented in Figure 7.20b. It satisfies $(0001)_{\text{Zr}} \parallel (111)_{\text{hydride}}$ and $[11\bar{2}0]_{\text{Zr}} \parallel [1\bar{1}0]_{\text{hydride}}$ as indicated by the poles being inscribed in the coloured circles.

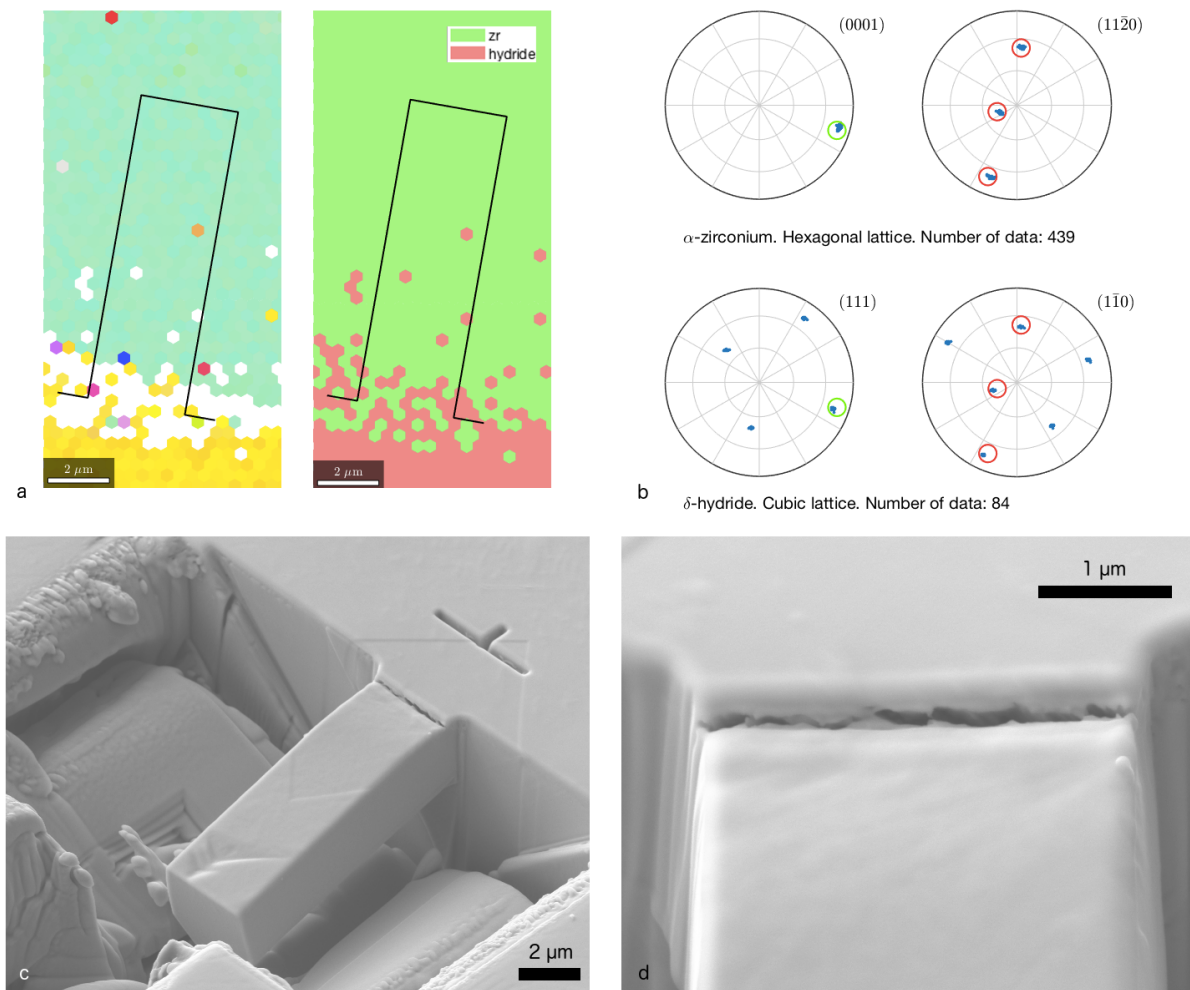


Figure 7.20 Surface examination of the dual-phase specimen DP2. a) EBSD IPF map and phase map of the region. The fixed end is located in the hydride and the notch was made parallel to the Zr/hydride interface. b) The pole figures show parallel crystal planes: $(0001)_{\text{Zr}} \parallel (111)_{\text{hydride}}$ and $(11\bar{2}0)_{\text{Zr}} \parallel (1\bar{1}0)_{\text{hydride}}$. The circles of same colour denote the same pole direction. c and d) Hydride fracture occurred along the notch front and the specimen underwent incomplete failure.

In the SEM examination carried out for DP2, cleavage cracking was observed on the opened surfaces along the notch front but it ceased to extend to the bottom of the specimen (Figure 7.20d). This suggests the brittle hydride had fractured in the stress concentration region but then further external work was absorbed for deformation of the surrounding ductile Zr. Therefore the specimen remained attached without complete failure. This observation is different from any single-phase hydride specimen (Figure 7.5).

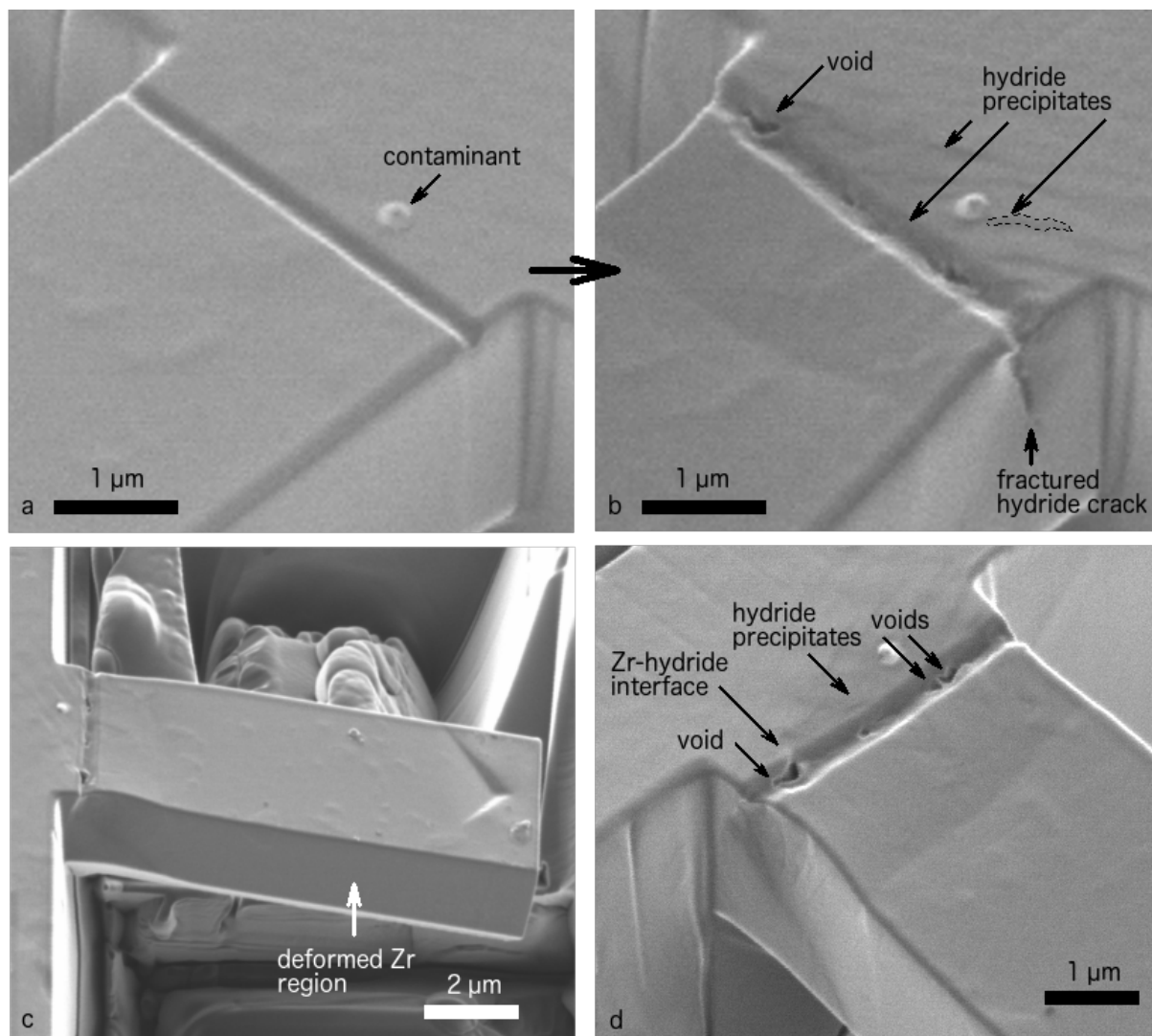


Figure 7.21 SEM examination of the microcantilever DP3. a and b) Cracked hydride was observed on the side of the specimen after loading. Microscale voids were seen along the notch within the hydride precipitates rich region. c) The free end mainly consists of the Zr and it underwent large-scale yielding. d) DP3 was imaged at a different angle to reveal the features developed after loading.

In the specimen DP3, the notch was made across the Zr/hydride interface (Figure 7.21). Cracked hydride was observed on the side of the specimen after loading. Separate microvoids were developed on the Zr/hydride interface along the notch. The diameter of the cavity openings ranges from 90 to 250 nm; which is consistent with DP1 as seen in Figure 7.16d. All observed failure features were contained along the notch front and the specimen underwent plastic deformation with the absence of main crack advance.

Load-displacement response of the specimens DP2 and DP3

DP2 and DP3 underwent elastic deformation, followed by yielding until the first load drop (Figure 7.22). By inspecting the SEM images in Figure 7.20d and Figure 7.21b, the sudden decrease in reaction force corresponds to hydride fracture. In the displacement region of ~650-1750 nm, the continuous drop in load would be attributed to microcracks extension and growth of the multiple cavities along the highly stressed notch. When the displacement reached ~1600-1750 nm, microcrack growth was impeded and plastic deformation became dominant. The load continued to rise owing to strain hardening until the maximum deflection.

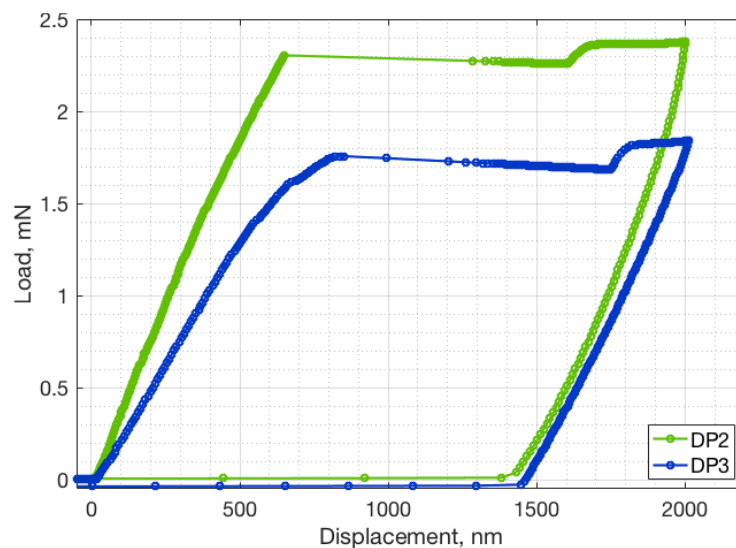


Figure 7.22 Micromechanical load response of the dual-phase specimens DP2 and DP3.

Experimental results of the specimen DP4

The notch of DP4 was made in the α -Zr and it was roughly parallel to the long axes of the hydride precipitates (Figure 7.24). The post-examination showed that microvoids formed along the notch front; suggesting that ductile fracture had occurred. However the growth and coalescence of voids was insufficient to facilitate crack extension at maximum tip deflection.

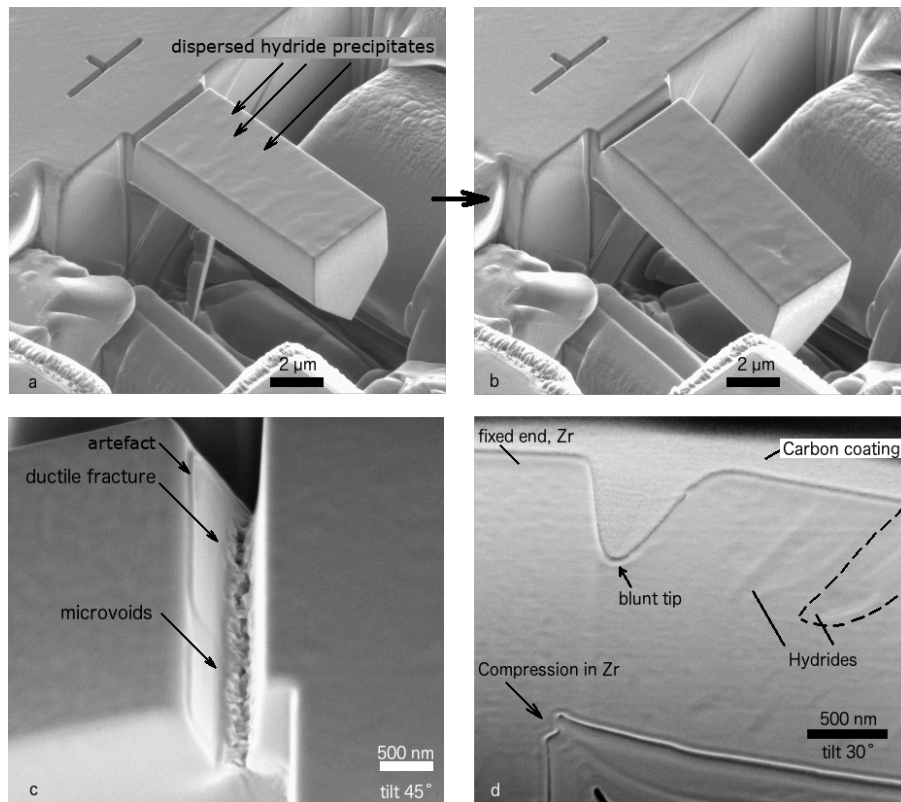


Figure 7.23 SEM examination of DP4. a) The lateral axis of the specimen was parallel to the hydride precipitates. b) DP4 permanently deformed without crack extension. c) Microvoids coalescence shows early stage of ductile failure. The artefact as indicated was unintentionally made during fabrication of the notch tip. d) FIB cross-sectioning shows the blunt notch tip and deformation underneath the specimen.

FIB cross-sectioning was then carried out with the procedure similar to that for DP1. Figure 7.24d shows that the whole notch is situated in the Zr and hydride precipitates are embedded in the free end. The blunt tip opening indicates that the ductile Zr substantially yielded under the applied bending moment. The bottom of the microcantilever experienced compression

resulting in permanent deformation as annotated in the figure. Figure 7.24 shows the load-displacement curve for DP4. In comparison to the results of other dual-phase specimens, neither load drop nor pop-in is observed. The whole notch front of DP4 was located in the ductile α -Zr in which brittle fracture did not occur. Therefore yielding continued and led to strain hardening when the displacement increased.

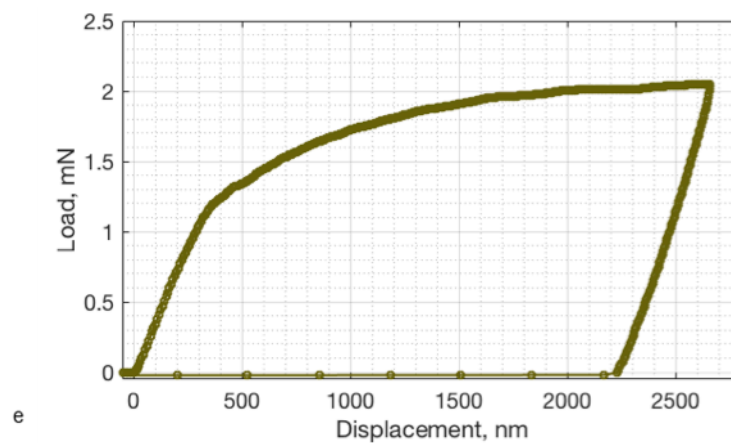


Figure 7.24 The load-displacement response of the dual-phase specimen DP4.

Serial loading and imaging test for the specimen DP5

The fixed end of the specimen DP5 was fabricated in the hydride and its free end was situated in the Zr. The specimen was first loaded slightly above the limit of proportionality for an SEM examination. It was then placed in the nanoindenter again to generate more plastic deformation. The procedure repeated until a sharp load drop was observed. In Figure 7.25b, the specimen shows only plasticity up to a sudden fracture at the maximum load. Therefore crack initiation occurred only in the third cycle of loading (Figure 7.25d, e and f). This indicates that loads below the maximum value relates to the plastic deformation alone, rather than to any crack opening or extension. The yield and flow behaviour can therefore be modelled independently from fracture behaviour using the first two loading cycles.

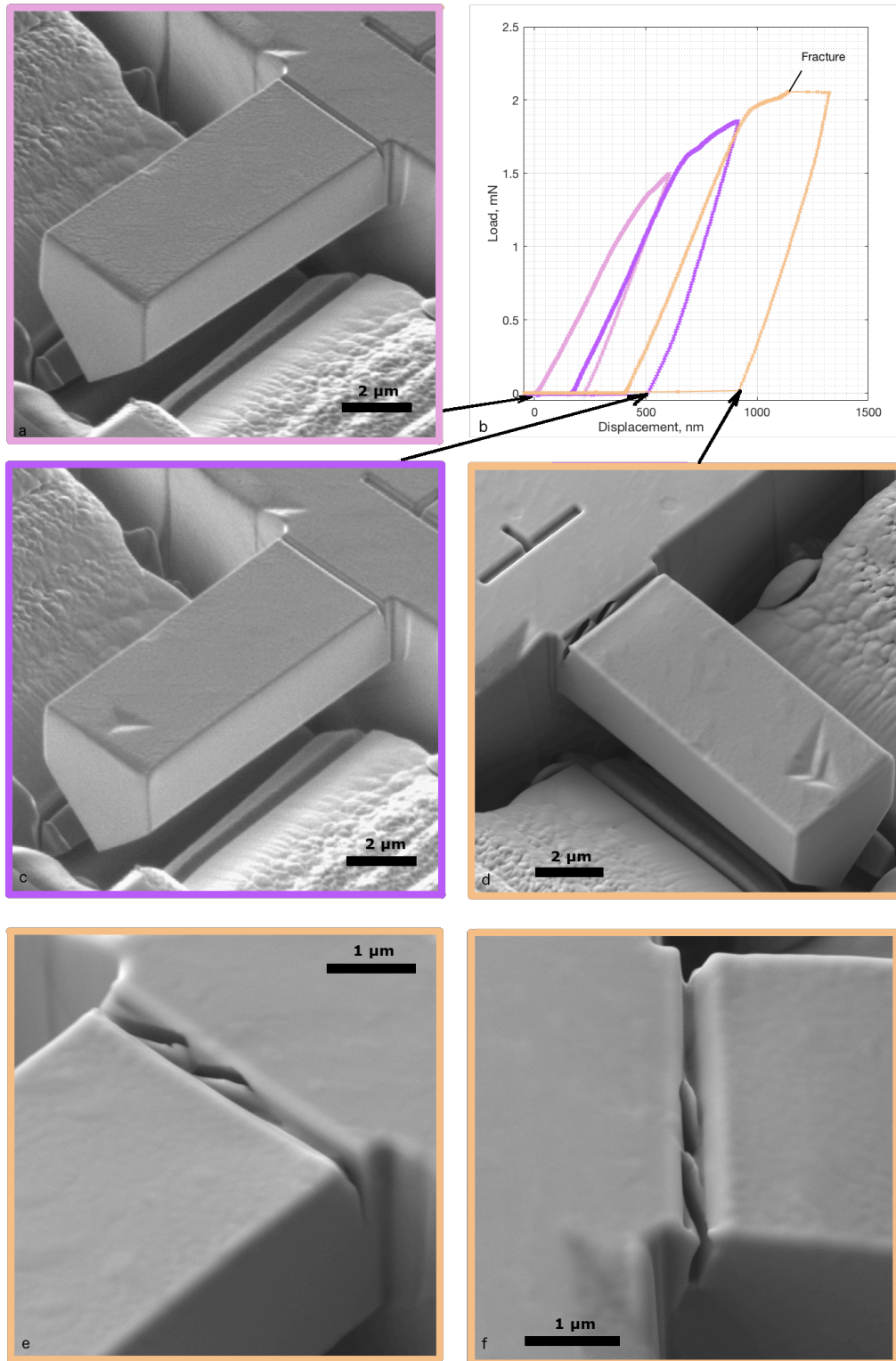


Figure 7.25 Serial loading and imaging test for DP5. a) SEM examination before the first loading cycle. b) DP5 was bent three times and the load dropped only in the last cycle. c) SEM examination was carried out after each loading cycle. No crack initiation occurred when the displacement was below 1000 nm. d, e, and f) Fractured hydrides were seen on the notch after the last loading cycle.

Load responses of different types of specimens

The typical load-displacement curves of the Zr, the hydride and the dual-phase microcantilevers are compared in Figure 7.26. The specimens had similar second moment of area ($20.9 - 22.9 \mu\text{m}^4$), notch depth ($0.2 - 0.3 \mu\text{m}$) and length ($10.0 - 10.1 \mu\text{m}$). The hydride specimen H6 yielded slightly until a sudden failure. Conversely, the Zr specimen Z2 continued to undergo plastic deformation without a sharp load drop. The single-loading dual-phase specimen DP3 and the serial-loading specimen DP5 both yielded similarly with Z2; but both fractured subsequent to a moderate degree of plastic deformation. The load needed to form voids near a Zr/hydride boundary in DP3 ($\sim 1.8 \text{ mN}$) is lower than that which initiates brittle fracture in the pure hydride specimen H6 ($\sim 2.5 \text{ mN}$).

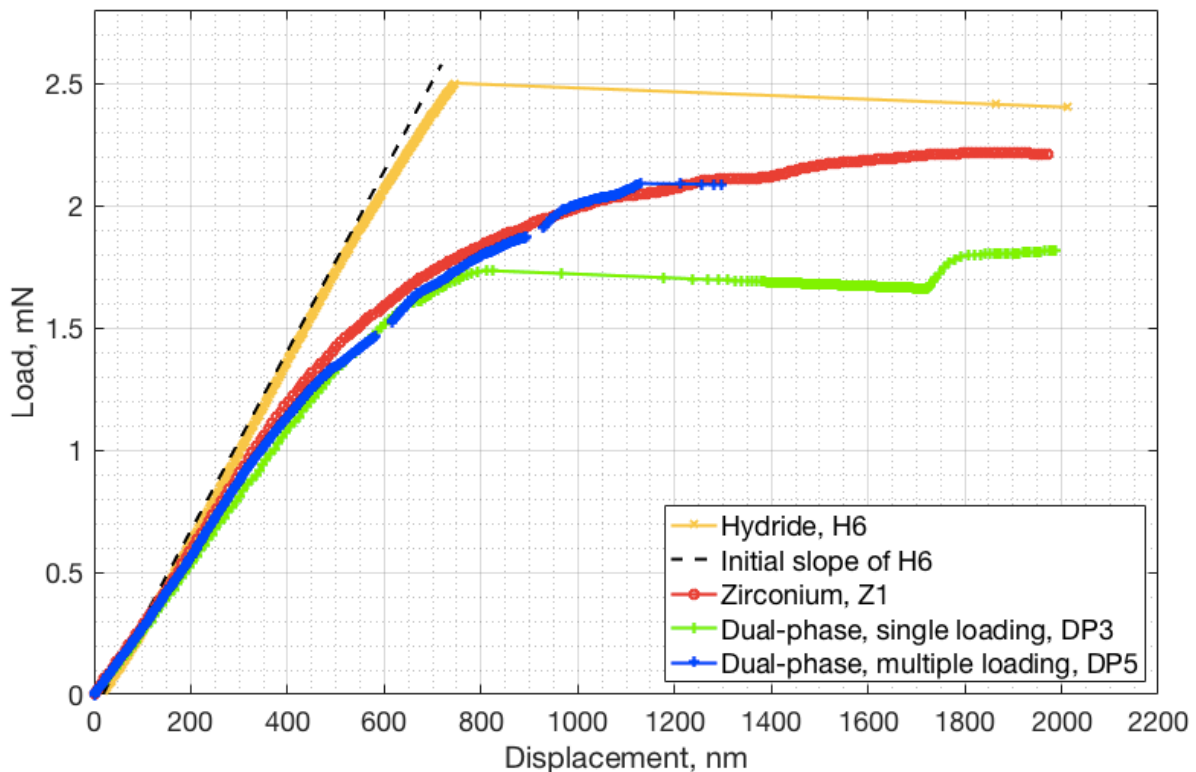


Figure 7.26 Typical load-displacement curves of different types of microcantilevers. The second moment of area, length and notch depth of all the specimens are similar.

7.4 Micromechanical Properties

7.4.1 Fracture Toughness Calculation

The method for determining the fracture toughness of the δ -hydride, K_C , is adopted from the relevant ASTM macroscopic test methods [199]. The hydride is assumed to be linear elastic as an approximation to the curves in Figure 7.4 and Figure 7.8b. The methodology of linear elastic fracture mechanics (LEFM) is applied as in the work of Di Maio and Roberts [130] and Matoy et al. [135]:

$$K_C = \sigma_0 \sqrt{\pi a} F\left(\frac{a}{2\bar{y}}\right) \quad 7.1$$

$$\sigma_0 = \frac{P_0 L_0 \bar{y}}{I} \quad 7.2$$

where a is the notch depth and $\bar{y}$ is the vertical distance between the upper surface and the centroid of the cross-section. P_0 is the fracture load, L_0 is the longitudinal distance between the notch and the indenter tip loading point, and I is the second moment of area. For the pentagonal cross-section shape as illustrated in Figure 7.2 where b is half of the total depth d ,

$$\bar{y} = \frac{\left[\frac{b}{2}(bw) + \frac{4b}{3}\left(\frac{bw}{2}\right)\right]}{\frac{3bw}{2}} = \frac{7b}{9}, \quad b = \frac{d}{2} \quad 7.3$$

$$I = \frac{b^3 w}{12} + bw\left(\frac{7b}{9} - \frac{b}{2}\right)^2 + \frac{b^3 w}{36} + \frac{bw}{2}\left(\frac{4b}{3} - \frac{7b}{9}\right)^2 = \frac{999w\bar{y}^3}{1372} \quad 7.4$$

The dimensionless shape factor $F(a/2\bar{y})$ was determined by FEM in ABAQUS. Three-dimensional reduced integration quadratic elements C3D20R and isotropic material properties were used to create the cantilever model. The *encasté* boundary condition was assigned to the bottom, back and side surfaces of the attached block as shown in Figure 7.27.

The notch was modelled as a seam crack; which consists of overlapping duplicate nodes on a two-dimensional face that can be opened during simulation.

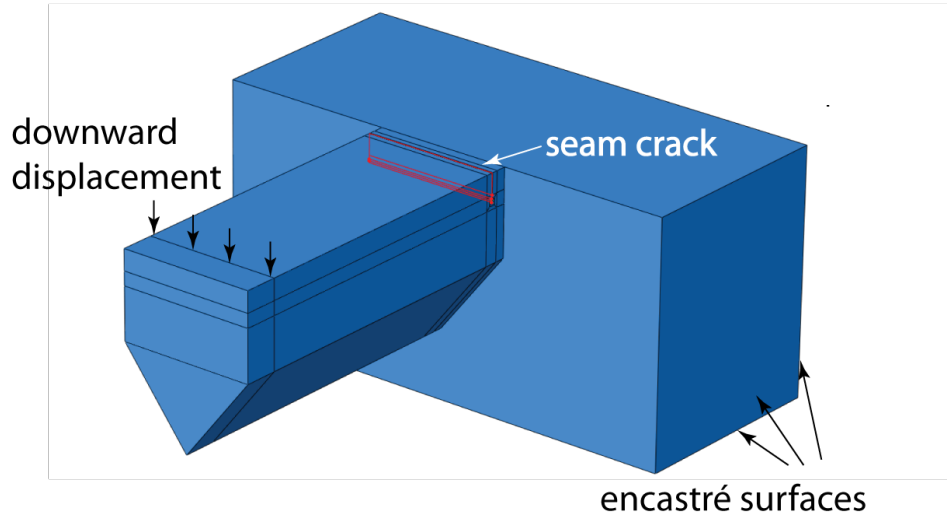


Figure 7.27 Seam crack and other main features of the three-dimensional FE model.

The simulation was performed by applying a downward displacement on the whole width of the free end. The contour integrals surrounding the crack front and the free end reaction forces were computed for various notch depths. The J-integral was used to characterise the strain energy release rate. The stress intensity factor K is equal to $(JE)^{1/2}$ in LEFM mode I fracture for plane stress condition. Convergence studies were carried out to optimise the mesh sizes and the output number of contours (Figure 7.28). A typical result of von Mises stresses is shown in Figure 7.29.

The dimensionless shape factors provided in various research studies are plotted against $a/2\bar{y}$ in Figure 7.30. All the factors were deduced from finite element models for isotropic elastic materials based on LEFM. A main difference between the models is the designed cross-sectional shape of the cantilevers. Rectangular cantilevers were used in the work of

Iqbal et al. [131], Matoy et al. [135], and Wurster, Motz and Pippan [7] and pentagonal cantilevers were used in the others. The factor obtained in the work of Di Maio and Roberts [130] is noticeably higher than the others, and is probably erroneous. The maximum percentage difference from the mean of those factors is 5.1% in the range $0.2 \leq a/2\bar{y} \leq 0.5$.

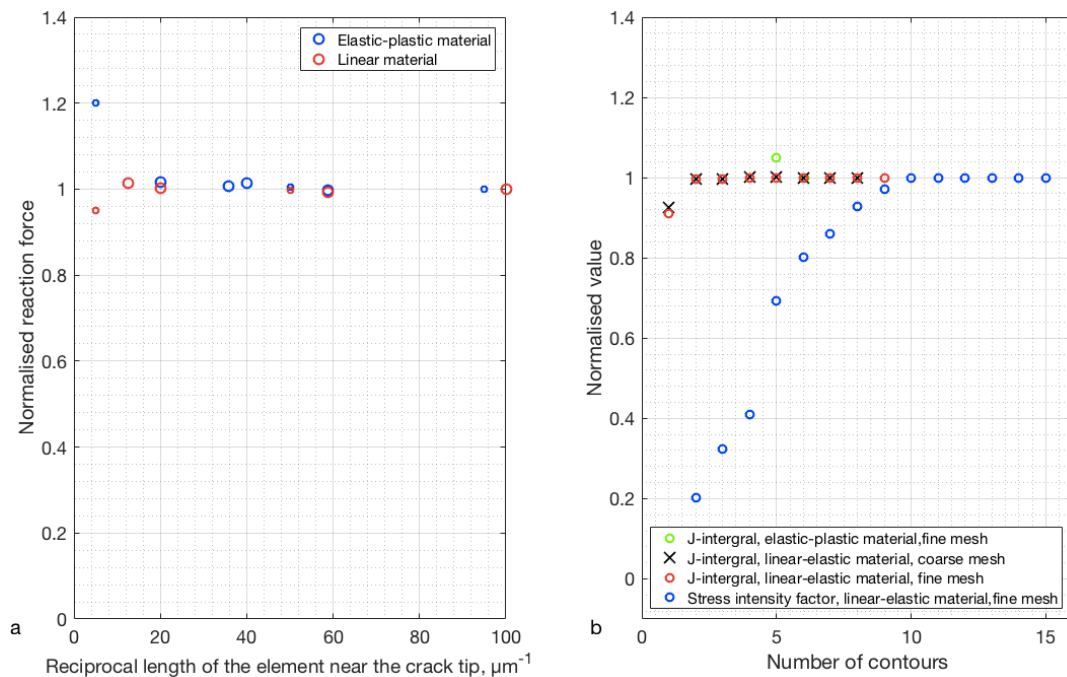


Figure 7.28 Convergence study for optimising a) the mesh sizes; and b) the output number of contours for the calculation of J-integral.

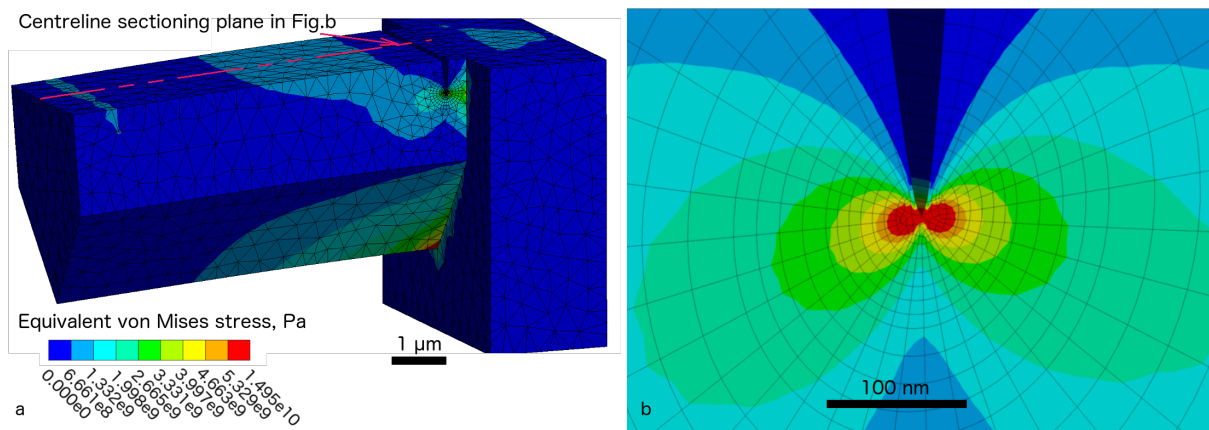


Figure 7.29 Typical von Mises stress field of the FE model. a) Stress concentration occurs at the notch tip and at the bottom of the specimen. b) The stress field at the notch tip on the centreline cross-sectional surface.

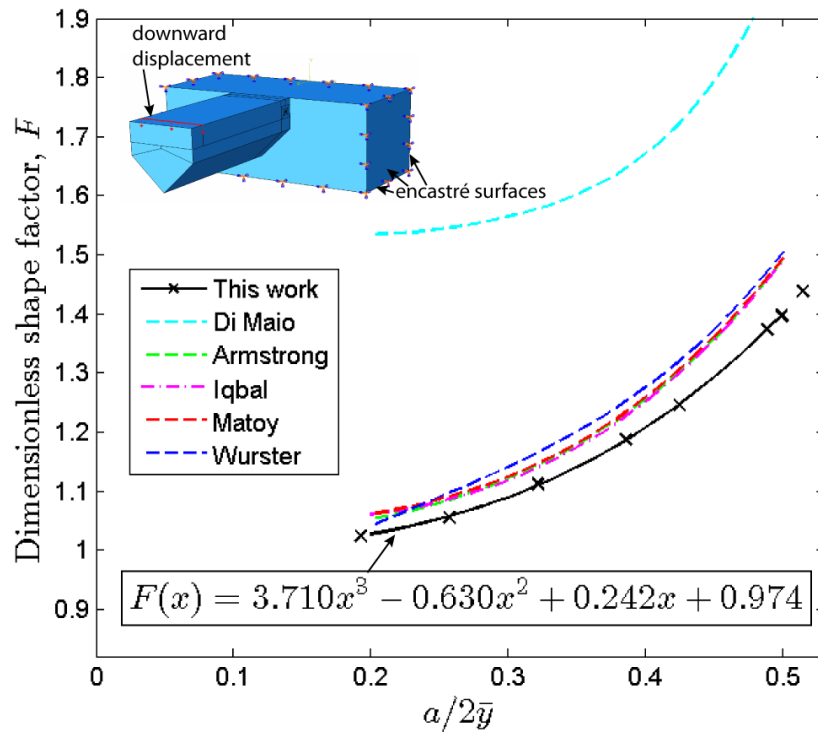


Figure 7.30 Three-dimensional FEM for calculating the dimensionless shape factor F . The J-integral was computed for various crack lengths, a , to determine the value of fracture toughness. $\bar{y}$ is the distance between the upper surface and the centroid of the cross-section. The cubic polynomial fitting curve of F is plotted in black. Dashed curves are generated from equations provided in the literature [7], [130], [131], [134], [135]. The microcantilevers used in these studies vary in dimensions and shapes.

7.4.2 Fracture Toughness Results of Hydrides

The fracture toughness of the single-phase δ -hydride was calculated from the testing of H1 to H6 as described in Sections 7.3.1 and 7.4.1. The results are summarised in Table 7.4.

Table 7.4 Crystallographic information and fracture toughness of the hydride specimens

Hydride specimen number	Width, μm	Crack propagation direction, Z_S^*	Longitudinal direction of the specimen*	Fracture toughness, K_{IC} , $\text{MPa}\sqrt{\text{m}}$	Measurement uncertainty, $\text{MPa}\sqrt{\text{m}}$	Percentage of measurement uncertainty, %
H1	4.0	$[\bar{1}8\ 44\ \bar{7}]$	$[\bar{4}3\ \bar{1}9\ \bar{6}]$	1.97	0.10	5.1
H2	3.7	$[\bar{2}0\ 42\ \bar{1}1]$	$[\bar{1}4\ \bar{7}\ \bar{2}]$	2.01	0.10	5.0
H3	3.5	$[\bar{8}\ \bar{4}\ \bar{1}3]$	$[\bar{3}3\ 33\ 10]$	1.91	0.12	6.5
H4	3.0	$[\bar{2}0\ 34\ \bar{2}7]$	$[\bar{4}1\ \bar{3}3\ \bar{3}2]$	1.90	0.13	6.8
H5	2.0	$[\bar{4}3\ \bar{2}0\ \bar{3}]$	$[\bar{4}\ 1\ 48]$	1.85	0.16	8.6
H6	4.0	$[\bar{1}\ \bar{8}\ \bar{9}]$	$[\bar{2}9\ 30\ \bar{2}3]$	1.89	0.10	5.2

* The calculated angle between the two ideally orthogonal directions in each row is $90^\circ \pm 0.6^\circ$ due to rounding.

The average fracture toughness was determined to be $1.92 \pm 0.16 \text{ MPam}^{1/2}$. The error range given is the uncertainty resulting from scatter in the dimensional measurements and load measurements; rather than from any variability in the calculated dimensionless shape factor F . The fracture toughness values are similar for all specimen sizes (Figure 7.31).

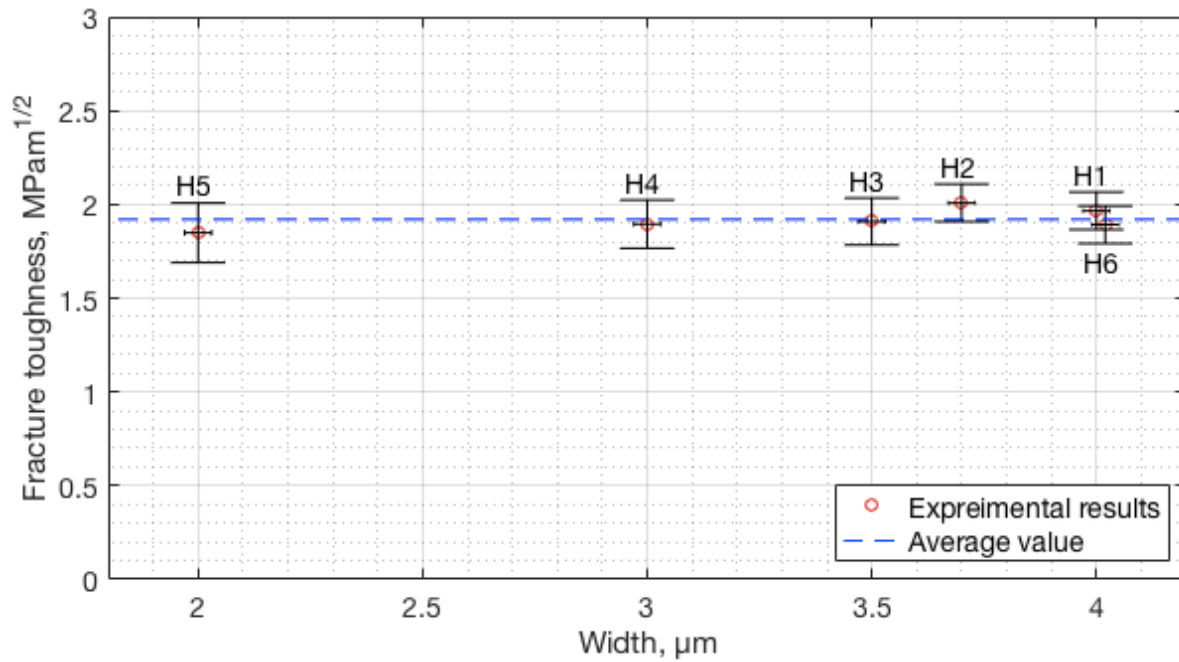


Figure 7.31 Fracture toughness of the δ -hydride as determined from the microcantilever tests. No strong size-dependence of K_C is observed. The average K_C is $1.92 \text{ MPam}^{1/2}$.

The alignments of the cubic crystal planes relative to the hydride specimen's geometry were used for examining the dependence of fracture toughness on crystallographic anisotropy (Figure 7.32). The crack propagation direction is considered as the normal direction into the sample. This is based on the SEM observations that the crack generally advanced downward (Figure 7.5 to Figure 7.8). The plane of symmetry of the notch is perpendicular to the specimens' longitudinal direction. Figure 7.32 shows no noticeable correlation between the fracture toughness and the hydride orientation.

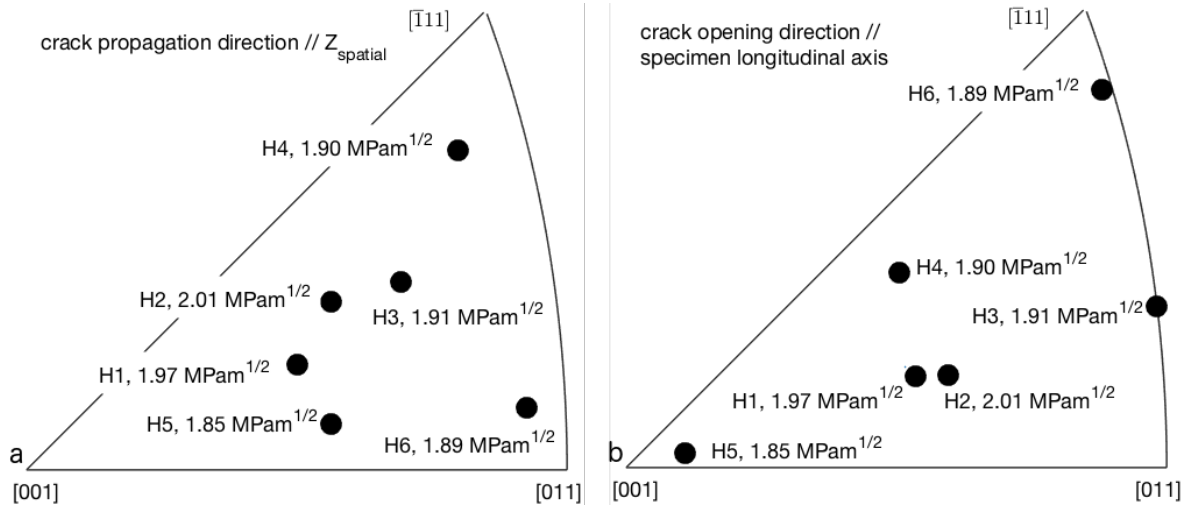


Figure 7.32 The result shows no correlation between the fracture toughness and the crystallographic orientation of the δ -hydride. The specimens were made specifically to represent a large variety of crystallographic orientations. The Miller indices of the markers are presented in Table 7.4. This figure is generated by MTEX.

7.4.3 Elastic and Plastic Properties Results

Stress-strain relation calculation

The serial loading and imaging test showed that the plasticity occurred independently from the crack initiation (Figure 7.25). An FE model was therefore developed to determine the yielding properties from the load-displacement curves. The model codes were adapted from the automated fitting process introduced in the work of Hardie [200]. The original un-notched triangular cantilever model was replaced by the pre-notched pentagonal cantilever model. Input files created in MATLAB were used to control the simulations in ABAQUS. A non-linear experimental curve was first divided into at least five segments; of which the first one being the linear elastic portion. The simulations of load-displacement were then fitted to the segmental experimental curves through progressive convergent approximation by modifying the model material's stress-strain response. The iterative process continued until all the simulation loads reach the predefined accuracy in comparison to the experiments.

Stress-strain relation results

The simulated load-displacement and stress-strain relations of the elastic-plastic model materials are shown in Figure 7.33 and Figure 7.34. The computed results are in good accord with the literature as shown in Table 7.5. All the micromechanical properties obtained for the δ -hydride show weak dependence on crystallographic directions (See also Table 7.4). In contrast, an appreciable range of Young's moduli and yield strengths were obtained for the Zr specimens, indicating strong anisotropy of the metallic phase.

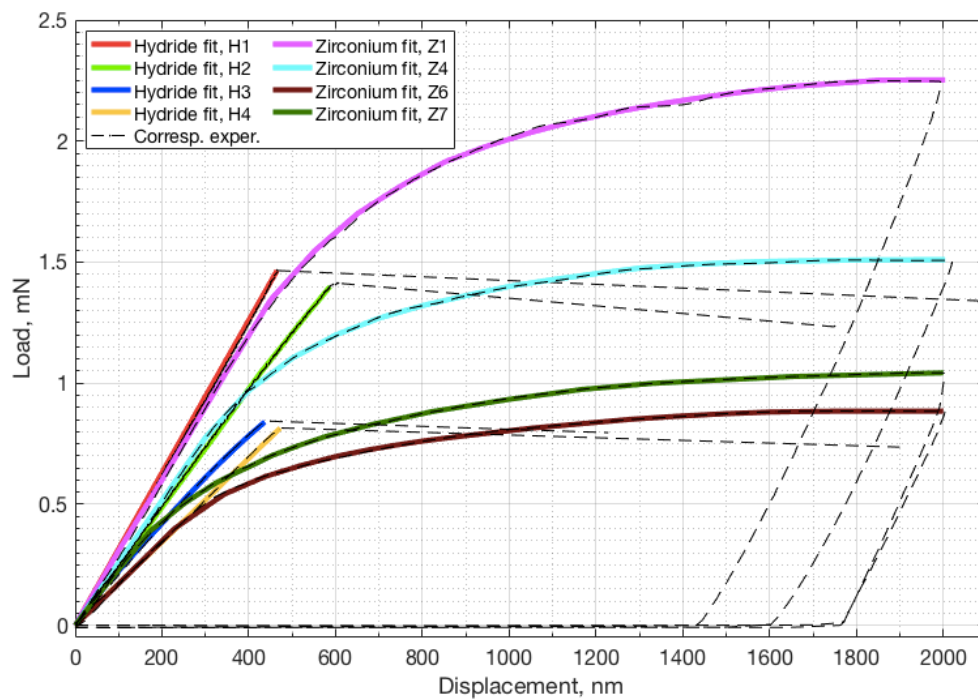


Figure 7.33 Computational simulated fitting curves and the corresponding experimental data. The experimental load-displacement relations are also shown in Section 7.3.

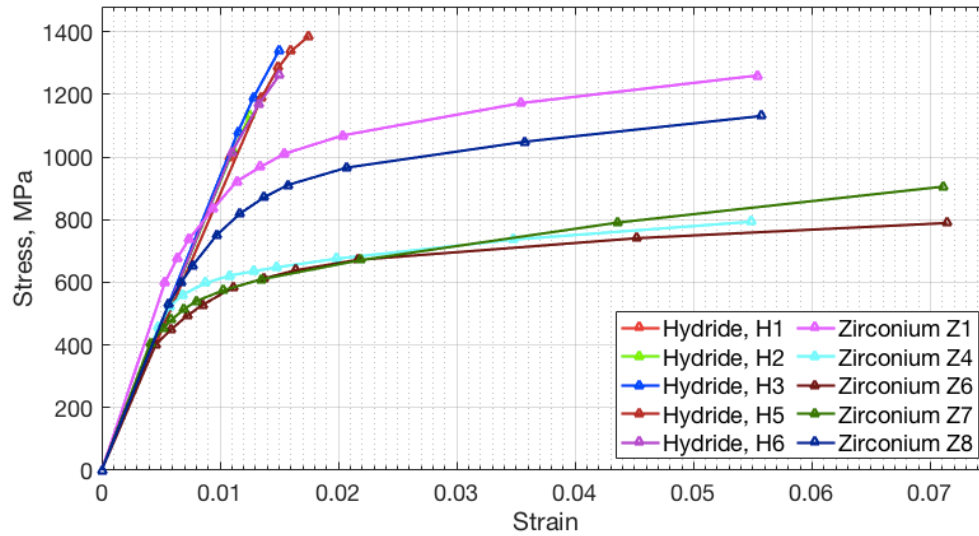


Figure 7.34 Calculated stress-strain relations. FE model material properties were adjusted to obtain good fits for experimental load-displacement curves. See Table 7.5 for summary.

Table 7.5 Micromechanical properties determined from FE modelling. The presented uncertainties arise from the dimensional measurement and fitting deviation.

Hydride microcantilever specimens

	Width (μm)	Young's modulus (GPa)	Proportional limit (MPa)	Fracture toughness ($\text{MPa m}^{1/2}$)
H1	4.0	92.6 ± 2.9	-	1.97 ± 0.10
H2	3.7	91.9 ± 3.0	1020 ± 67	2.01 ± 0.10
H3	3.5	93.8 ± 3.8	1079 ± 77	1.91 ± 0.12
H4	3.0	89.4 ± 3.8	-	1.90 ± 0.13
H5	2.0	88.1 ± 4.5	1189 ± 68	1.85 ± 0.16
H6	4.0	92.4 ± 3.4	1016 ± 64	1.89 ± 0.10
Literature*	-	80 - 99	Microscale: 900 - 1600 (Macroscale: 600 - 800)	(Macroscale: 0.6 - 1.3)

H1 and H4 fractured during the linear elastic loading therefore the proportional limits are undetermined.

Zirconium microcantilever specimens

	Width (μm)	Young's modulus (GPa)	Proportional limit (MPa)	Yield strength, 0.2% offset strain (MPa)
Z1	4.0	112 ± 3.9	600 ± 43	837 ± 58
Z2	3.9	115 ± 4.4	586 ± 43	845 ± 60
Z3	4.0	111 ± 4.5	576 ± 35	872 ± 55
Z4	4.0	95.2 ± 4.5	458 ± 36	586 ± 47
Z5	4.0	94.3 ± 4.3	453 ± 38	605 ± 47
Z6	4.0	87.9 ± 4.6	401 ± 31	508 ± 38
Z7	3.9	98.8 ± 4.6	405 ± 23	522 ± 41
Z8	2.2	93.8 ± 5.2	530 ± 44	767 ± 68
Literature*	-	80 - 126	Microscale: 300 - 800 (Macroscale: 100 - 300)	Microscale: 410 - 960 (Macroscale: 205 - 310)

* Literature: Zr: [8], [10], [11], [15], [16], [18], [20]–[22]. Hydride: [15], [75], [77], [78], [80], [83], [88], [91]

The strong dependence of micromechanical properties of the α -Zr on the inclination angle is shown in Figure 7.35 and 7.36. The inclination angle is defined as the angle between the hexagonal lattice c-axis and the maximal load direction, which is the longitudinal axis of a microcantilever or the bulk sample normal in a nanoindentation test. In Figure 7.35, the elastic modulus obtained from both tests decreases when the inclination angle increases until it reaches the minimum at ~ 50 - 60° . The scatter obtained from the microcantilever tests is smaller than that of the indentation modulus at all individually measured angles.

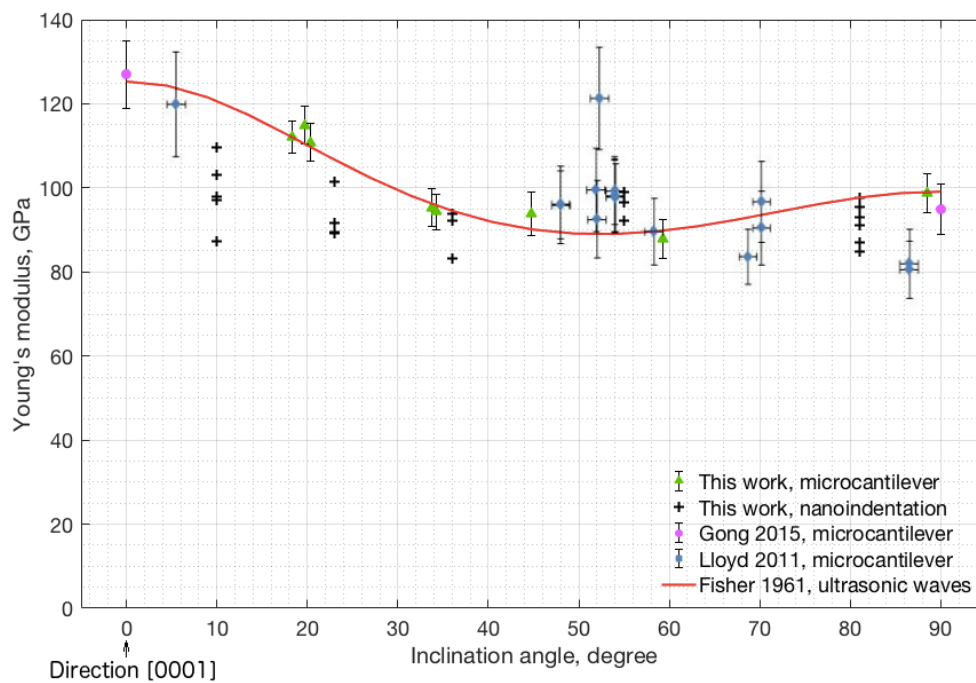


Figure 7.35 Dependence of Young's modulus on crystallographic orientation of the α -Zr. The microcantilever test results and the nanoindentation test results are in agreement with the work of Fisher and Renken [20], Lloyd [21] and Gong et al. [22].

Figure 7.36 shows that the α -Zr possesses strong anisotropic plasticity. The 0.2% offset yield strengths acquired from the $4 \times 10 \mu\text{m}$ microcantilevers remarkably decrease with an increase in crystal inclination. This observation is comparable with the calculated yield strengths from the work of Gong et al. [22]. The anisotropic behaviour of the α -Zr is attributed to the significant difference in CRSS of various slip systems. In addition, the yield strengths

obtained for the α -Zr from these small-scale specimens are higher than the literature macroscopic test values as a result of the ISE (See Section 2.4.3).

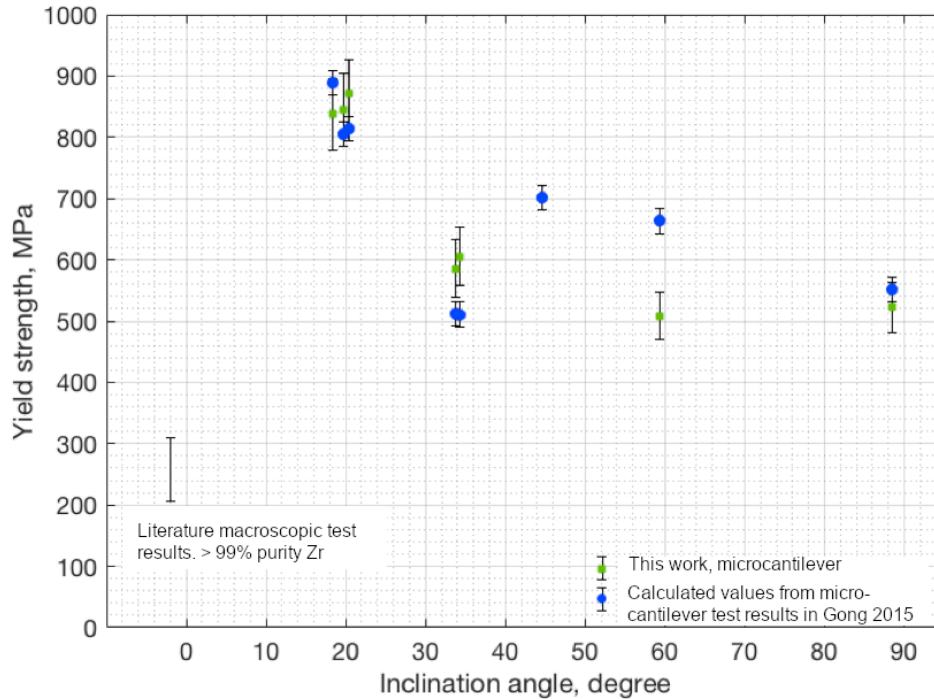


Figure 7.36 Dependence of yield strength on crystallographic orientation of α -Zr. The 0.2% offset yield strengths were obtained from 4 μm wide microcantilevers fabricated within individual Zr grains in this work. The calculated values as indicated by the blue markers are computed from CRSS reported in the work of Gong [22] using Schmid's law. The large range of yield strengths indicates strong anisotropic plasticity of the material [8], [10], [22].

7.5 Discussion

7.5.1 Fracture Toughness and Micromechanical Properties

The microfracture tests show that the pure δ -hydride phase is relatively brittle with $K_C = 1.9 \pm 0.2 \text{ MPam}^{1/2}$. This result was determined from the pre-notched microcantilevers which did not contain any naturally formed crack and the K_C values were similar for all the 2-4 μm wide specimens. The average K_C is higher than the macroscopic measurement of about $1 \text{ MPam}^{1/2}$ that obtained from testing bulk Zr hydride samples (Figure 2.30) [91]. It may be related to the

observation that the δ -hydride is not completely brittle on this small scale, as indicated by the non-linear load-displacement response before fracture in Figure 7.13. This is possibly due to deformation produced by the high local shear stresses at the notch tip. The higher K_C also arises from the size and geometry since the plane-strain condition was not reached [7]. The minimum width limit for macroscopic testing is $2.5K_{IC}^2/\sigma_y^2$ as recommended in ASTM E399 [199], [201]. In this study, the size of the plastic zone is comparable to the hydride grain size ($\sim 1 \mu\text{m}$); and the width of the cantilevers ($4.0 \mu\text{m}$) is lower than the ASTM limit ($8.0 \mu\text{m}$). Furthermore, macroscopic polycrystalline samples described in the literature might contain pre-existing hydride cracks that nucleated inside the bulk during precipitation (Sections 2.3.4 and 4.5). Those sub-surface cracks could lead to underestimation of crack resistance. The microfracture tests also show that K_C is independent of the crystallographic orientation of the δ -hydride. This result was established from microscale transgranular cleavage fracture where the plastic zone was confined inside a single hydride grain. The isotropy of crack resistance would be associated with disordered arrangement of interstitial hydrogen and attributed to insufficient active slip systems in the hydride lattice.

7.5.2 Crack Growth near Zr/Hydride Interface

The deformation behaviour and crack growth near the Zr/hydride interface differ from that in the individual phases. In the experimental arrangement described for each dual-phase microcantilever, a notch front was specifically made within $0.5 \mu\text{m}$ from a Zr/hydride boundary. The region ahead of the notch tip consisted of: i) the hydride which might yield slightly before brittle fracture occurred; and ii) the Zr which underwent strain hardening without material failure after moderate deflection. This composite arrangement would lead to a complicated asymmetric stress field adjacent to the faces of the notch. In order to account

for the deformation mechanism with the SEM features, some simplified conditions are applied in the following discussion with the aid of illustration presented in Figure 7.37.

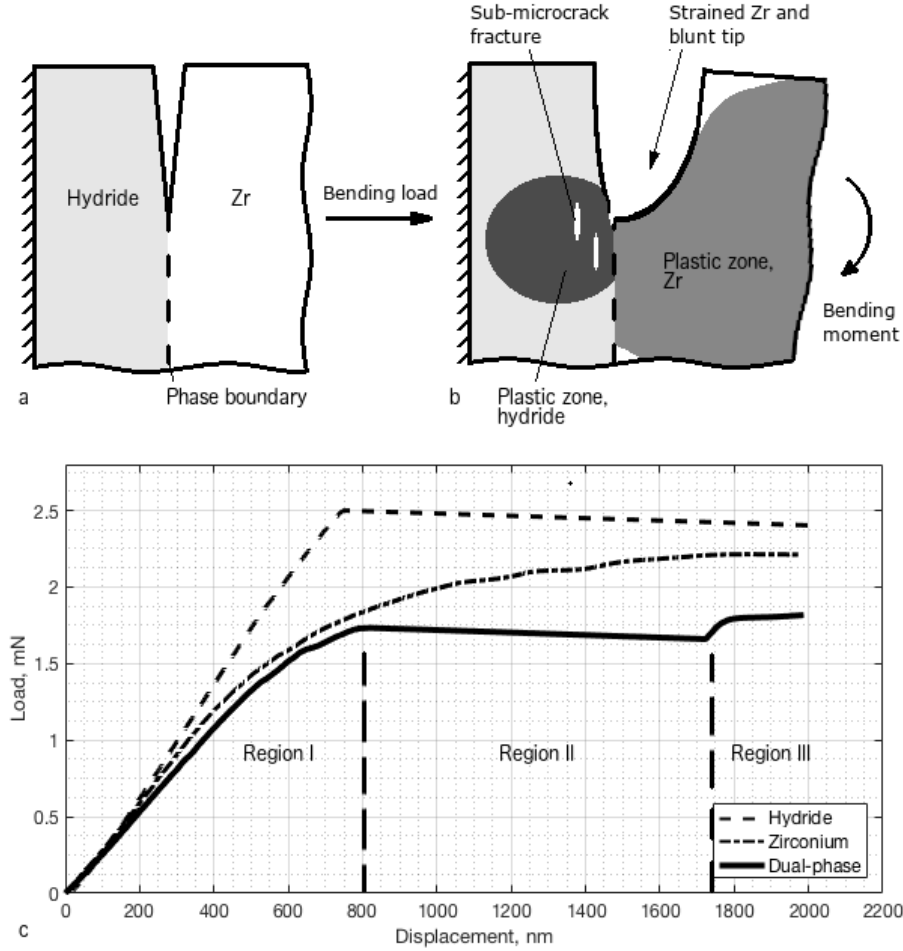


Figure 7.37 Illustration of the deformation process in a dual-phase microcantilever. a) Undeformed specimen. The symmetric plane of the notch is the Zr/hydride boundary plane. b) Deformed specimen. The main crack advance is hindered since the work done by the external bending moment is mainly dissipated for large-scale plastic deformation of the α -Zr. The stresses that intensified near the notch tip develop a plastic zone for the hydride in which nucleation and propagation of microcracks are possible. The formation of microcracks could result in stress redistribution. See Figure 7.16 to Figure 7.18. c) Experimental load-displacement curves for three types of specimens. This figure is generated by GIMP.

The yield zone radius of the hydride is approximately $r_{p,h} = \frac{1}{2\pi} \left(\frac{K_{IC}}{\sigma_{y,h}} \right)^2 = 0.5 \mu\text{m}$ ahead of the notch tip where $\sigma_{y,h}$ is the measured yield strength of the hydride at micron-scale (~ 1100 MPa). Since brittle fracture is preceded by slight yielding as observed in the test,

hydride cracking could occur within $\sim 0.5 \mu\text{m}$ from the notch tip. For the Zr, the yield zone is at the scale of the whole specimen owing to its high fracture toughness ($15 \text{ MPam}^{1/2}$) [91] and its relatively low yield strength, $\sigma_{y,\text{Zr}}$ ($\sim 600 \text{ MPa}$). The substantial extent of plastic flow is evident from the SEM post-examination where an appreciable portion of the single phase Zr microcantilever had permanently deformed (Figure 7.10).

In the illustration shown in Figure 7.37b, assuming the stress field is continuous across the Zr/hydride interface, plastic deformation of the Zr would initially become dominant over hydride fracture because its yield strength is $\sim 45\text{-}80\%$ of the hydride, i.e. $\sigma_{y,\text{Zr}} < \sigma_{y,h} \sim \sigma_{f,h}$. Since the interface-notch dual-phase specimens being tested primarily consisted of a high volume fraction of the Zr, it would deform similarly to a Zr specimen in the initial elastic and plastic region (Region I) as shown in Figure 7.37c. The highly strained Zr would lead to blunting of the notch tip, originally $< 25 \text{ nm}$ in radius, impeding the propagation of the main crack advance. This localised inhomogeneous deformation of the crack tip is associated with the void appearance as indicated in Figure 7.18. Although void growth and coalescence upon further loading could lead to intergranular rupture and separation of the hard hydrides from the Zr matrix, the strain energy release rate exceeded the critical value for fracture of the associated hydride within the yield zone ($\sim 0.5 \mu\text{m}$ radius) from the notch tip (Figure 7.18e and Figure 7.37b). This occurrence of cleavage fracture corresponds to the sudden load drop as seen in Region II of the load-displacement curve (Figure 7.37c). A part of the work done by the external bending moment was dissipated to create new surfaces of the secondary microcracks; leading to localised stress redistribution hence modifying the stress intensity factor. Since the main crack advance from the notch tip was hindered, the specimen remained intact for the second cycle of strain hardening in the Zr (Region III).

The absence of crack propagation path along the Zr/hydride phase boundary is comparable with reported observations in literature. In the SEM in-situ macroscopic tensile test of bulk Zr hydride carried out by Arsene, Bai and Bompard [11], cracks always appeared inside the hydride and no fracture of the interface was observed. In another in-situ examination of macroscopic crack growth in polycrystalline Zr hydrides by Bertolino, Meyer and Ipaña [92], crack blunting and ductile fracture of the zircaloy matrix are guided by fractured hydrides located ahead the crack tip. The type of fracture in a particular hydride-rich microstructure is likely to be dependent on the complex three-dimensional stress states near the crack.

7.6 Summary

The main findings of the microcantilever tests are:

1. The α -Zr and the δ -hydride have distinct deformation properties. The $4 \times 10 \mu\text{m}$ pre-notched Zr specimens plastically deformed at 400–600 MPa without large-scale material failure whilst the hydride specimens of similar dimensions yielded slightly at 1020–1190 MPa before brittle fracture occurred. The Zr exhibits strong elastic and plastic anisotropy whilst the hydride shows isotropic deformation response.
2. The fracture toughness of the δ -hydride was measured to be $1.9 \pm 0.2 \text{ MPam}^{1/2}$. The fractured surfaces showed cleavage without clear preferential fracture plane. The fracture toughness is independent of crystallographic orientation and specimen width from 2 to $4 \mu\text{m}$.
3. Interfacial microvoids and secondary hydride microcracks were observed in the dual-phase specimens. The experiment shows no sign of intergranular cracking along the phase boundary. The specimens predominantly underwent permanent deformation to generate a moderate plastic strain without main crack propagation.

8 DISCUSSION

8.1 Formation and Microstructure of Zr Hydrides

The formation of the Zr/hydride dual-phase system was investigated through electrolytic hydriding experiment, surface examination and modelling (Sections 4.3 and 5.5). Only one crystallographic relationship, $(0001)_\alpha || (111)_\delta$ with $[11\bar{2}0]_\alpha || [1\bar{1}0]_\delta$, was observed in all investigated regions (Figure 4.25, 4.27, 4.29, 7.15 and 7.20). It is also the most commonly reported crystallographic relationship for various Zr alloys prepared under different hydriding conditions (Section 2.2.3). The observation would be attributed to the energetically favourable atomic arrangement as the hcp $(0001)_\alpha$ and the fcc $(111)_\delta$ are both closed pack planes with a small lattice mismatch. The relationship between the two phases are also characterised by the habit plane of hydride packets in literature (Section 2.2.3). However the habit plane could not be clearly observed in this study since hydride packets were lumped together on the sample edge. The microstructural feature is a direct result of unidirectional hydrogen supply. This hydriding configuration is different from most literature in which the preparation involves hydrogen homogenisation at elevated temperature. In this study, the growth direction of precipitates is identified as $\langle a \rangle_{\text{Zr}}$ (Figure 4.28) but no habit plane is reported due to aggregation of hydride packets.

Dense stacks of hydride precipitates with thickness $< 2 \mu\text{m}$ were found to align with $\langle a \rangle_{\text{Zr}}$ (Figure 4.19, 4.28 and 7.14). The mechanism for forming such microstructure first involves fast diffusion of small hydrogen atoms. It leads to formation of dispersed hydride nuclei followed by their preferential growth along $\langle a \rangle_{\text{Zr}}$. The dilation strain due to lattice mismatch

accompanies with radiation of dislocations into the matrix. These dislocations act as new nucleation sites for phase transformation and the process repeats. Therefore slightly misorientated hydride precipitates tend to pile up closely to form packets or clusters.

Nonetheless the sub-micron internal structure of an individual packet and how it responds to shear stresses are not fully understood. The presence of hydride/hydride grain interface as identified by EBSD is reported both in this study and in the literature (Section 2.2.4 and 4.4); among which some are hydride/hydride twin boundaries (Figure 4.27). However diffuse diffraction patterns were also seen around hydride precipitates inside a packet. Those unindexed interspace ($<0.2\ \mu\text{m}$) among precipitates could be hydride/hydride interface, a thin layer of Zr matrix, multiple hydride grains, micropores due to liberation of internal strain energy during precipitation, or other complex structure. In all cases the dislocation density is likely high since the precipitation process can generate dislocation loops (Section 2.2.4).

The internal structure of a packet is important because of its influence on the slip operation within the packet. It would also affect the plastic strain transmission across the phase boundary. Further work involving intragranular hydrides that prepared from a short duration of electrolytic hydriding (<2 hours) may be useful for investigating such structure (Section 3.2). The experimental setting would generate hydride packets of few microns in length; in which they contain densely packed precipitates of $\sim 1\ \mu\text{m}$ in length. The density of emitted dislocations is minimised in a practical sense for the shortest possible hydriding duration at low temperature to grow precipitates sufficiently large for microstructure characterisation. Lift-out foils or cross-sectional samples can be prepared depending on the characterisation technique. Intragranular hydrides are preferred due to their relatively simple structure in the

absence of Zr/Zr grain boundary and their well-understood crystallographic alignment with only one set of $\langle a \rangle_{\text{Zr}}$ in a large Zr grain.

8.2 Plastic Deformation of the δ -hydride

The δ -hydride possesses yielding ability as reported in Section 7.4.3 however the activated slip system is unclear. In a hydride packet where slightly misorientated precipitates densely align, the operation for plastic deformation can be complicated. It may involve slip within hydride precipitates and/or deformation between precipitates. Lattice rotation and dislocation generation within some large precipitates have also been observed in various experimental studies (Section 2.3.3). Further work involving mechanical tests of single-phase micropillars or short microcantilevers that consist of few hydride packets would be useful for investigation. The sample preparation presented in this study has demonstrated that it is possible to prepare a hydride film thick enough for making such microscale specimens. Dual-phase specimens are not preferred since plastic deformation would primarily occur in the α -Zr owing to its considerably lower yield strength (Table 7.5). The selection of geometry and loading configuration should allow in-plane shear stress acting on the hydride/hydride interface while tensile stress should be minimised to avoid brittle fracture. High resolution EBSD with a small step size ($<0.1 \mu\text{m}$) could be used for crystallographic orientation mapping of the multiple hydride grain structure prior to specimen fabrication. The angle between the mutual alignment plane of hydride precipitates and the loading direction would be a main independent variable in order to compare the deformation within the precipitates to that between the precipitates.

8.3 Fracture Toughness of the δ -hydride

The fracture toughness of the microscale δ -hydride ($1.9 \text{ MPam}^{1/2}$) is considerably higher than the CT-specimen testing value reported for macroscopic Zr hydrides ($1 \text{ MPam}^{1/2}$) (Section 7.4.2). The main cause is however inconclusive. The increased fracture toughness may relate to the intrinsic plasticity of the δ -hydride or arise from the extrinsic plane stress condition. It may also correlate with the hydride grain size or the sub-micron structure of the hydride packets. Nonetheless the mechanism likely differs from the ISE (Section 2.4.1) in which it involves large plastic strain. The correct interpretation of the increased fracture toughness would need more results from testing different materials and results from testing Zr hydrides at multiple scales.

8.4 Deformation Behaviours near the Zr/hydride Interface

In the dual-phase microcantilevers having the notch front situated in the α -Zr, crack tip blunting and initial stage of ductile failure occurred (DP4, Figure 7.24). These observations and the load-displacement response are very similar to the pure Zr specimens. Since the highest stress near the crack front was redistributed to about the yield strength of the Zr ($\sim 500 \text{ MPa}$), the hydrides that embedded in the free end of the dual-phase specimen experienced noticeably lower stresses than that would initiate cleavage cracking ($\sim 1300 \text{ MPa}$). Therefore the hydrides mostly underwent elastic deformation and had negligible influence on the deformation behaviour of the notch tip.

In comparison, some unique features including interfacial microvoids and secondary hydride cracks were seen in the specimens having the notch made in the δ -hydride (DP1 to DP3,

Figure 7.18 and 7.21). Microvoids nucleated to accommodate the difference in yielding rate between the two compositional phases. The continuing growth of the cavities along the notch front resulted in notch opening. However the void coalescence was insufficient to generate complete interfacial rupture along the phase boundary, instead part of the applied work was dissipated to develop secondary microcracks within the adjoining hydride. Despite these microcracks propagated downward, they were fully contained in the hydride and did not extend into the underlying Zr region. Since the notch tip was round due to microvoids development, the main crack also did not advance to the underside. Therefore those specimens underwent partial failure and remained attached to the fixed end (Section 7.5.2).

The multiple failure mechanisms observed in these specimens indicate that the transition from microscale crack growth to macroscopic behaviour might not be necessarily straightforward. The failure mode would be dependent on the complex three-dimensional stress states near the cracks and extrinsic mechanisms operated in a particular dual-phase microstructure.

9 CONCLUSIONS

A variety of techniques including OM, SEM, EBSD, XRD and EDS were applied for microstructural characterisation of hydrided zirconium thin film samples. Naturally formed microcracks and twin hydride grains were observed in the bulging δ -hydride islands. Sub-micron scale hydride precipitates densely aligned in $\langle \bar{1}\bar{1}20 \rangle_\alpha$ to form hydride packets and only one crystallographic relationship: $(0001)_\alpha || (111)_\delta$ and $[11\bar{2}0]_\alpha || [1\bar{1}0]_\delta$ was observed. The growth rate of hydrides was measured to analyse the phase transformation process. A new computational model was developed to simulate the concentration-dependent diffusion of hydrogen in the dual-phase system.

Nanoindentation and pre-notched microcantilever tests were carried out to obtain the localised micromechanical properties. The average yield strength and the nanohardness of the δ -hydride (~ 1080 MPa and 5.1 GPa) are about double that of the α -Zr (~ 500 MPa and 2.6 GPa). The percentage increase in hardness for the hydride (65%) when the indentation depth decreases from 5 μm to 0.5 μm is considerably higher than that for the Zr (37%). The crystallographic orientation exhibits strong influence on the elastic and plastic properties of the α -Zr whilst the δ -hydride possesses isotropic deformation behaviour. All 2-4 μm wide hydride microcantilevers underwent brittle fracture as indicated by cleavage observed on fracture surfaces. The fracture toughness determined by direct measurement with the aid of FEM is $1.9 \pm 0.2 \text{ MPam}^{1/2}$.

Multiple failure features were observed in the dual-phase pre-notched microcantilevers after moderate deflection. Interfacial microvoids and secondary hydride microcracks were developed near the notch front in the same specimens. The specimens underwent permanent deformation but neither the main crack nor the secondary cracks advanced to the α -Zr region.

Microscale deformation responses associated with hardening and fracture initiation are extracted for investigating the influence of hydride precipitates. The nanoindentation and the microcantilever testing methods are capable of providing precise measurements of micromechanical properties. Further study using these methods could help develop a better understanding of the relationships between local plasticity and microcrack propagation, contributing to improved models of Zr alloys performance in the hydriding environment.

APPENDIX

The Laplace's equation (Eq.5.12) shown in Section 5.4.1 can be solved by separation of variables. The equation is rewritten in spherical coordinates with azimuthal symmetry,

$$\nabla^2 \varphi = 0 \quad \text{A.1}$$

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \varphi}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial \varphi}{\partial \theta} \right) = 0 \quad \text{A.2}$$

Let $\varphi = R(r)\Theta(\theta)$ and by substituting it into Eq.A.2, we get:

$$\frac{1}{R} (r^2 R'' + 2r R') = \frac{-(\Theta'' \sin \theta + \Theta' \cos \theta)}{\Theta \sin \theta} = l(l+1) \quad \text{A.3}$$

where l is a constant. First we solve the radial function, R , which is an Euler differential equation. Let $r = e^\xi$ and from the chain rule, we get:

$$\frac{dR}{dr} = \frac{dR}{d\xi} \frac{d\xi}{dr} = e^{-\xi} \frac{dR}{d\xi} \quad ; \quad \frac{d^2 R}{dr^2} = e^{-2\xi} \left(\frac{d^2 R}{d\xi^2} \right) - e^{-2\xi} \left(\frac{dR}{d\xi} \right) \quad \text{A.4}$$

Substituting Eq.A.4 into Eq.A.3, an ordinary differential equation forms as:

$$R'' + R' - Rl(l+1) = 0 \quad \text{A.5}$$

By applying the characteristic equation method, the solution to the radial function is:

$$R = \eta_1 r^l + \eta_2 r^{-(l+1)} \quad \text{A.6}$$

where η_1 and η_2 are constants.

Secondly, we consider the angular function, Θ . From Eq.A.3,

$$\Theta'' + \frac{\cos\theta}{\sin\theta}\Theta' + l(l+1)\Theta = 0 \quad \text{A.7}$$

Let $q = \cos \vartheta$ and by applying the chain rule, Eq.A.7 becomes:

$$\frac{d}{dq} \left[(1 - q^2) \frac{d\Theta}{dq} \right] + l(l+1)\Theta = 0 \quad \text{A.8}$$

For a 2π periodic angular function in a physical system as shown Figure 5.3, the solution to Eq.A.8 is a Legendre polynomial of order $l = 1$, i.e. $\Theta = \cos \vartheta$ [203]. Combining it with the radial solution provided in Eq.A.5, we have the general solution:

$$\varphi(r, \theta) = (\eta_1 r + \frac{\eta_2}{r^2}) \cos \theta \quad \text{A.7}$$

For $r \leq r_\delta$ in an inclusion as shown in Figure 5.3, the concentration has to be finite when r approaches zero; therefore the coefficient η_2 is zero. The same condition applies to the system without an inclusion; assuming the effective medium is sufficiently large such that the influence from inclusions can be neglected, then η_2 is zero for $r \geq r_m$.

REFERENCES

- [1] “Energy, electricity and nuclear power estimates for the period up to 2050, 2015 edition.” IAEA, 2015.
- [2] C. R. F. Azevedo, “Selection of fuel cladding material for nuclear fission reactors,” *Eng. Fail. Anal.*, vol. 18, no. 8, pp. 1943–1962, Dec. 2011, doi: 10.1016/j.engfailanal.2011.06.010.
- [3] C. E. Coleman and D. Hardie, “The hydrogen embrittlement of α -zirconium-A review,” *J. less-Common Met.*, vol. 11, no. 3, pp. 168–185, 1966.
- [4] D. O. Northwood and U. Kosasih, “Hydrides and delayed hydrogen cracking in zirconium and its alloys,” *Int. Met. Rev.*, vol. 28, no. 2, pp. 92–121, 1983, doi: 10.1179/095066083790411759.
- [5] IAEA, “Delayed hydride cracking in zirconium alloys in pressure tube nuclear reactors-Final report of a coordinated research project 1998-2002. IAEA-TECDOC-1410,” 2004.
- [6] T. P. Weihs, S. Hong, J. C. Bravman, and W. D. Nix, “Mechanical deflection of cantilever microbeams : A new technique for testing the mechanical properties of thin films,” *J. Mater. Res.*, vol. 3, no. 5, pp. 931–942, 1988.
- [7] S. Wurster, C. Motz, and R. Pippan, “Characterization of the fracture toughness of micro-sized tungsten single crystal notched specimens,” *Philos. Mag.*, vol. 92, no. 14, pp. 1803–1825, May 2012, doi: 10.1080/14786435.2012.658449.
- [8] D. O. Northwood, “The Development and Applications of Zirconium Alloys,” *Mater. Des.*, vol. 6, no. 2, pp. 58–70, 1985.
- [9] K. L. Murty and I. Charit, “Structural materials for Gen-IV nuclear reactors: Challenges and opportunities,” *J. Nucl. Mater.*, vol. 383, no. 1–2, pp. 189–195, Dec. 2008, doi: 10.1016/j.jnucmat.2008.08.044.
- [10] H. Numakura, Y. Minonishi, and M. Koiwa, “ $\langle -1-123 \rangle \{10-11\}$ slip in zirconium,” *Philos. Mag. A*, vol. 63, no. 5, pp. 1077–1084, May 1991, doi: 10.1080/01418619108213938.
- [11] S. Arsene, J. B. Bai, and P. Bompard, “Hydride embrittlement and irradiation effects on the hoop mechanical properties of pressurized water reactor (PWR) and boiling-water reactor (BWR) ZIRCALOY cladding tubes: Part I. Hydride embrittlement in stress-relieved, annealed and recrystallized ZIRCA,” *Metall. Mater. Trans. A*, vol. 34, no. 3, pp. 553–566, 2003, doi: 10.1007/s11661-003-0093-1.
- [12] G. Bertolino, G. Meyer, and J. Perez Ipiña, “Degradation of the mechanical properties of Zircaloy-4 due to hydrogen embrittlement,” *J. Alloys Compd.*, vol. 330–332, pp. 408–413, 2002.
- [13] M. Grange, J. Besson, and E. Andrieu, “Anisotropic behavior and rupture of hydrided ZIRCALOY-4 Sheets,” *Metall. Mater. Trans. A*, vol. 31A, no. March, pp. 679–690, 2000.
- [14] S. Lin, M. Hamasaki, and Y. Chuang, “The effect of dispersion and spheroidization treatment of δ zirconium hydrides on the mechanical properties of Zircaloy,” *Nucl. Sci.*

- Eng.*, vol. 71, no. 3, pp. 251–266, 1979.
- [15] H. E. Weekes *et al.*, “In situ micropillar deformation of hydrides in Zircaloy-4,” *Acta Mater.*, vol. 92, pp. 81–96, 2015.
 - [16] J. Xu and S.-Q. Shi, “Investigation of mechanical properties of ϵ -zirconium hydride using micro- and nano-indentation techniques,” *J. Nucl. Mater.*, vol. 327, no. 2–3, pp. 165–170, May 2004, doi: 10.1016/j.jnucmat.2004.02.004.
 - [17] M. Kuroda, D. Setoyama, M. Uno, and S. Yamanaka, “Nanoindentation studies of zirconium hydride,” *J. Alloys Compd.*, vol. 368, no. 1, pp. 211–214, Apr. 2004, doi: 10.1016/j.jallcom.2003.08.094.
 - [18] S. Yamanaka *et al.*, “Isotope effects on the physicochemical properties of zirconium hydride,” *J. Alloys Compd.*, vol. 293, pp. 908–914, Dec. 1999, doi: 10.1016/S0925-8388(99)00439-9.
 - [19] K. G. Barraclough and C. J. Beevers, “Some observations on the phase transformations in zirconium hydrides,” *J. Nucl. Mater.*, vol. 34, no. 2, pp. 125–134, 1970.
 - [20] E. S. Fisher and C. J. Renken, “Adiabatic elastic moduli of single crystal alpha zirconium,” *J. Nucl. Mater.*, vol. 3, no. 3, pp. 311–315, 1961.
 - [21] D. Lloyd, “Micromechanical investigations of zirconium and zirconium hydride,” Oxford University, 2011.
 - [22] J. Gong, T. B. Britton, M. a. Cuddihy, F. P. E. Dunne, and A. J. Wilkinson, “ $\langle a \rangle$ Prismatic, $\langle a \rangle$ basal, and $\langle c+a \rangle$ slip strengths of commercially pure Zr by micro-cantilever tests,” *Acta Mater.*, vol. 96, pp. 249–257, Sep. 2015, doi: 10.1016/j.actamat.2015.06.020.
 - [23] D. O. Northwood, I. M. London, and L. E. Bahen, “Elastic constants of zirconium alloys,” *J. Nucl. Mater.*, vol. 55, no. 3, pp. 299–310, 1975.
 - [24] Z. L. Pan, N. Wang, and Z. He, “Measurements of Elastic Modulus in Zr Alloys for CANDU Applications,” in *The 11th International Conference on CANDU Fuel*, 2010.
 - [25] J. E. Bailey, “Electron microscope studies of dislocations in deformed zirconium,” *J. Nucl. Mater.*, vol. 7, no. 3, pp. 300–310, 1962.
 - [26] R. G. Ballinger, G. E. Lucas, and R. M. Pelloux, “The effect of plastic strain on the evolution of crystallographic texture in zircaloy-2,” *J. Nucl. Mater.*, vol. 126, pp. 53–69, 1984.
 - [27] E. J. Rapperport, “Room temperature deformation in zirconium,” *Acta Metall.*, vol. 7, pp. 254–260, 1959.
 - [28] F. Xu, R. a. Holt, and M. R. Daymond, “Evidence for basal -slip in Zircaloy-2 at room temperature from polycrystalline modeling,” *J. Nucl. Mater.*, vol. 373, no. 2, pp. 217–225, Feb. 2008, doi: 10.1016/j.jnucmat.2007.05.052.
 - [29] A. Akhtar, “Basal slip in zirconium,” *Acta Metall.*, vol. 21, no. 1, pp. 1–11, 1973.
 - [30] A. Akhtar, “Plastic deformation of zirconium single crystals,” *Acta Metall.*, vol. 19, pp. 655–663, 1971.
 - [31] D. G. Westlake, “Cross-guide and twinning in crystals of quenched zirconium-hydrogen alloys,” *J. Nucl. Mater.*, vol. 13, no. 1, pp. 113–115, 1964.
 - [32] J. J. Kearns, “Terminal solubility and partitioning of hydrogen in the alpha phase of zirconium, Zircaloy-2 and Zircaloy-4,” *J. Nucl. Mater.*, vol. 22, no. 3, pp. 292–303,

- 1967.
- [33] Z. L. Pan, I. G. Ritchie, and M. P. Puls, "The terminal solid solubility of hydrogen and deuterium in Zr-2.5Nb alloys," *J. Nucl. Mater.*, vol. 228, no. 2, pp. 227–237, 1996.
 - [34] A. Sawatzky and C. E. Ells, "Understanding hydrogen in zirconium," in *Zirconium in the Nuclear Industry: Twelfth International Symposium*, 2000, pp. 32–48.
 - [35] G. F. Slattery, "The terminal solubility of hydrogen in zirconium alloys between 30 and 400°C," *J. Inst. Met.*, vol. 95, no. 2, pp. 43–47, 1967.
 - [36] E. Zuzek, J. P. Abriata, A. San-Martin, and F. D. Manchester, "H-Zr (hydrogen-zirconium)," *Phase Diagrams Bin. Hydrog. Alloy. ASM Int.*, pp. 309–322, 2000.
 - [37] J. S. Bradbrook, G. W. Lorimer, and N. Ridley, "The precipitation of zirconium hydride in zirconium and zircaloy-2," *J. Nucl. Mater.*, vol. 42, no. 2, pp. 142–160, 1972.
 - [38] K. G. Barraclough, "The nature of γ -phase in zirconium-hydrogen alloys," *J. less-Common Met.*, vol. 35, no. 1, pp. 177–179, 1974.
 - [39] I. O. Bashkin, V. Malyshev, and M. M. Myshlyaev, "Reversible $\gamma \rightarrow \alpha + \delta$ transformation in zirconium deuteride," *Sov. Physics. Solid State*, vol. 34, no. 7, pp. 1182–1184, 1992.
 - [40] S. Mishra, K. S. Sivaramakrishnan, and M. K. Asundi, "Formation of the gamma phase by a peritectoid reaction in the zirconium-hydrogen system," *J. Nucl. Mater.*, vol. 45, no. 3, pp. 235–244, 1972.
 - [41] D. O. Northwood, "Gamma and delta hydrides in zirconium alloys," *J. Less-Common Met.*, vol. 48, no. 1, pp. 173–175, 1976.
 - [42] B. Nath, G. W. Lorimer, and N. Ridley, "The relationship between gamma and delta hydrides in zirconium-hydrogen alloys of low hydrogen concentration," *J. Nucl. Mater.*, vol. 49, no. 3, pp. 262–280, 1974.
 - [43] L. Lanzani and M. Ruch, "Comments on the stability of zirconium hydride phases in Zircaloy," *J. Nucl. Mater.*, vol. 324, no. 2–3, pp. 165–176, Jan. 2004, doi: 10.1016/j.jnucmat.2003.09.013.
 - [44] K. E. Moore and W. A. Young, "Phase studies of the Zr-H system at high hydrogen Concentrations," *J. Nucl. Mater.*, vol. 27, no. 3, pp. 316–324, 1968.
 - [45] M. P. Puls, "Properties of bulk zirconium hydrides," in *The Effect of Hydrogen and Hydrides on the Integrity of Zirconium Alloy Components: Delayed hydride cracking*, London: Springer, 2012. doi: 10.1007/978-1-4471-4195-2.
 - [46] D. Hardie and M. W. Shanahan, "Stress reorientation of hydrides in zirconium-2.5% niobium," *J. Nucl. Mater.*, vol. 55, no. 1, pp. 1–13, 1975.
 - [47] G. J. C. Carpenter, "The dilatational misfit of zirconium hydrides precipitated in zirconium," *J. Nucl. Mater.*, vol. 48, no. 3, pp. 264–266, 1973.
 - [48] B. J. Gill, J. E. Bailey, and P. Cotterill, "The effects of hydride precipitates on the mechanical properties of zirconium-hydrogen alloys," *J. Less-Common Met.*, vol. 40, pp. 129–138, 1975.
 - [49] R. S. Daum, Y. S. Chu, and A. T. Motta, "Identification and quantification of hydride phases in Zircaloy-4 cladding using synchrotron X-ray diffraction," *J. Nucl. Mater.*, vol. 392, no. 3, pp. 453–463, Aug. 2009, doi: 10.1016/j.jnucmat.2009.04.004.

-
- [50] N. Kumar, J. Szpunar, and Z. He, "Preferential precipitation of hydrides in textured zircaloy-4 sheets," *J. Nucl. Mater.*, vol. 403, no. 1–3, pp. 101–107, Aug. 2010, doi: 10.1016/j.jnucmat.2010.06.005.
- [51] Z. Wang, U. L. F. Garbe, H. Li, R. P. Harrison, A. Kaestner, and E. Lehmann, "Observations on the zirconium hydride precipitation and distribution in Zircaloy-4," *Metall. Mater. Trans. B*, pp. 1–8, 2013, doi: 10.1007/s11663-013-9866-0.
- [52] D. O. Northwood and R. W. Gilbert, "Hydrides in zirconium-2.5 wt.% niobium alloy pressure tubing," *J. Nucl. Mater.*, vol. 78, no. 1, pp. 112–116, 1978.
- [53] V. Perovic, G. C. Weatherly, and C. J. Simpson, "Hydride precipitation In α/β zirconium alloys," *Acta Metall.*, vol. 31, no. 9, pp. 1381–1391, 1983.
- [54] M. Veleva, S. Arsene, M. Record, J. Bechade, and J. Bai, "Hydride embrittlement and irradiation effects on the hoop mechanical properties of PWR and BWR ZIRCALOY cladding tubes: Part II.," *Metall. Mater. Trans. A*, vol. 34, no. 3, pp. 567–578, 2003, doi: 10.1007/s11661-003-0093-1.
- [55] K. Une, K. Nogita, S. Ishimoto, and K. Ogata, "Crystallography of zirconium hydrides in recrystallized zircaloy-2 fuel cladding by electron backscatter diffraction," *J. Nucl. Sci. Technol.*, vol. 41, no. 7, pp. 731–740, 2004.
- [56] S. Kim, Y. Rhyim, J. Kim, and J. Yoon, "Characterization of zirconium hydrides in Zircaloy-4 cladding with respect to cooling rate," *J. Nucl. Mater.*, vol. 465, pp. 731–736, Oct. 2015, doi: 10.1016/j.jnucmat.2015.07.006.
- [57] S. Wang, F. Giuliani, and T. Ben Britton, "Microstructure and formation mechanisms of δ -hydrides in variable grain size Zircaloy-4 studied by electron backscatter diffraction," *Acta Mater.*, vol. 169, pp. 76–87, May 2019, doi: 10.1016/j.actamat.2019.02.042.
- [58] J. Li *et al.*, "Uncovering the hydride orientation-mediated hoop fatigue mechanism in a zirconium alloy cladding tube," *Int. J. Plast.*, vol. 159, p. 103440, Dec. 2022, doi: 10.1016/j.ijplas.2022.103440.
- [59] R. N. Singh, P. Stähle, L. Banks-Sills, M. Ristmanaa, and S. Banerjee, " δ -hydride habit plane determination in α -zirconium at 298 K by strain energy minimization technique," *Defect Diffus. Forum*, vol. 279, pp. 105–110, 2008.
- [60] D. G. Westlake, "The habit planes of zirconium hydride In zirconium and zircaloy," *J. Nucl. Mater.*, vol. 26, no. 2, pp. 208–216, 1968.
- [61] Y. S. Kim, Y. Perlovich, M. Isaenkova, S. S. Kim, and Y. M. Cheong, "Precipitation of reoriented hydrides and textural change of α -zirconium grains during delayed hydride cracking of Zr-2.5 %Nb pressure tube," *J. Nucl. Mater.*, vol. 297, pp. 292–302, 2001.
- [62] R. Birch, S. Wang, V. S. Tong, and T. B. Britton, "The effect of cooling rate and grain size on hydride microstructure in Zircaloy-4," *J. Nucl. Mater.*, vol. 513, pp. 221–225, Jan. 2019, doi: 10.1016/j.jnucmat.2018.11.011.
- [63] Z. Zhao *et al.*, "Characterization of zirconium hydrides and phase field approach to a mesoscopic-scale modeling of their precipitation," *J. ASTM Int.*, vol. 5, no. 3, pp. 1–20, 2008.
- [64] J. E. Bailey, "Electron microscope observations on the precipitation of zirconium hydride in zirconium," *Acta Metall.*, vol. 11, no. 4, pp. 267–280, 1963.

-
- [65] G. J. C. Carpenter, J. F. Watters, and R. W. Gilbert, "Dislocations generated by zirconium hydride precipitates in zirconium and some of its alloys," *J. Nucl. Mater.*, vol. 48, no. 3, pp. 267–276, Oct. 1973, doi: 10.1016/0022-3115(73)90023-8.
- [66] G. J. C. Carpenter and J. F. Watters, "An in-situ study of the dissolution of γ -zirconium hydride in zirconium," *J. Nucl. Mater.*, vol. 73, no. 2, pp. 190–197, 1978.
- [67] C. E. Ells, "Hydride precipitates In zirconium alloys (A review)," *J. Nucl. Mater.*, vol. 28, no. 2, pp. 129–151, 1968.
- [68] O. N. Pierron, D. a. Koss, A. T. Motta, and K. S. Chan, "The influence of hydride blisters on the fracture of Zircaloy-4," *J. Nucl. Mater.*, vol. 322, no. 1, pp. 21–35, Oct. 2003, doi: 10.1016/S0022-3115(03)00299-X.
- [69] G. Dundulis, R. Karalevičius, R. Janulionis, and A. Grybenas, "Modelling of the Zr-2 . 5Nb alloy properties with hydrides," *Mechanika*, vol. 2(64), pp. 1392–1207, 2007.
- [70] M. R. Louthan and R. P. Marshall, "Control of hydride orientation in zircaloy," *J. Nucl. Mater.*, vol. 9, no. 2, pp. 170–184, 1963.
- [71] C. E. Ells, "The stress orientation of hydride in zirconium alloys," *J. Nucl. Mater.*, vol. 35, no. 3, pp. 306–315, 1970.
- [72] H. E. Weekes, N. G. Jones, T. C. Lindley, and D. Dye, "Hydride reorientation in Zircaloy-4 examined by in situ synchrotron X-ray diffraction," *J. Nucl. Mater.*, vol. 478, pp. 32–41, Sep. 2016, doi: 10.1016/j.jnucmat.2016.05.029.
- [73] S. Yamanaka *et al.*, "Thermal and mechanical properties of zirconium hydride," *J. Alloys Compd.*, vol. 293, pp. 23–29, Dec. 1999, doi: 10.1016/S0925-8388(99)00389-8.
- [74] R. L. Beck, "Research and development of metal hydrides. Summary report AT(33-3)-3," 1960.
- [75] K. G. Barraclough and C. J. Beevers, "Some observations on the deformation characteristics of bulk polycrystalline zirconium hydrides. Part 1: the deformation and fracture of hydrides based on the δ -phase," *J. Materials Sci. Sci.*, vol. 4, no. 6, pp. 518–525, 1969.
- [76] M. Kuroda, K. Yoshioka, S. Yamanaka, H. Anada, F. Nagase, and H. Uetsuka, "Influence of precipitated hydride on the fracture behavior of zircaloy fuel cladding tube," *J. Nucl. Sci. Technol.*, vol. 37, no. 8, pp. 670–675, 2000, doi: 10.1080/18811248.2000.9714942.
- [77] Z. L. Pan and M. P. Puls, "Internal friction peaks associated with the behaviour of hydrogen in Zr and Zr–2.5Nb," *Mater. Sci. Eng. A*, vol. 442, no. 1, pp. 109–113, Dec. 2006, doi: 10.1016/j.msea.2006.02.211.
- [78] M. P. Puls, S.-Q. Shi, and J. Rabier, "Experimental studies of mechanical properties of solid zirconium hydrides," *J. Nucl. Mater.*, vol. 336, no. 1, pp. 73–80, 2005, doi: 10.1016/j.jnucmat.2004.08.016.
- [79] T. Kubo and Y. Kobayashi, "Effects of δ -hydride precipitation at a crack tip on crack propagation in delayed hydride cracking of Zircaloy-2," *J. Nucl. Mater.*, vol. 439, no. 1–3, pp. 202–211, 2013.
- [80] S.-Q. Shi and M. P. Puls, "Criteria for fracture initiation at hydrides in zirconium alloys I . Sharp crack tip," *J. Nucl. Mater.*, vol. 208, no. 3, pp. 232–242, 1994.
- [81] E. Darby, M. Martin, and D. Scarth, "Delayed hydride cracking in zirconium alloys- a review of mechanisms, assessment criteria and current developments," in *TAGSI/FESI*

- Symposium Structural Integrity of Nuclear Power Plant*, 2013, pp. 1–19.
- [82] J.-H. Huang and S.-P. Huang, “Effect of hydrogen contents on the mechanical properties of Zircaloy-4,” *J. Nucl. Mater.*, vol. 208, no. 1, pp. 166–179, Jan. 1994, doi: 10.1016/0022-3115(94)90208-9.
 - [83] S.-Q. Shi and M. P. Puls, “Fracture strength of hydride precipitates in Zr-2.5Nb alloys,” *J. Nucl. Mater.*, vol. 275, no. 3, pp. 312–317, 1999.
 - [84] J. B. Bai, “Effect of hydriding temperature and strain rate on the ductile-brittle transition in β treated Zircaloy-4,” *J. Nucl. Sci. Technol.*, vol. 33, no. 2, pp. 141–146, 1996.
 - [85] C. E. Coleman and D. Hardie, “The hydrogen embrittlement of zirconium in slow-bend tests,” *J. Nucl. Mater.*, vol. 19, no. 1, pp. 1–8, 1966.
 - [86] K. W. Lee and S. I. Hong, “Zirconium hydrides and their effect on the circumferential mechanical properties of Zr–Sn–Fe–Nb tubes,” *J. Alloys Compd.*, vol. 346, pp. 302–307, 2002.
 - [87] M. P. Puls, “Fracture initiation at hydrides in zirconium,” *Metall. Trans. A*, vol. 22, p. 2327, 1991.
 - [88] S. Arsene, J. Bai, and P. Bompard, “Hydride embrittlement and irradiation effects on the hoop mechanical properties of pressurized water reactor (PWR) and boiling-water reactor (BWR) ZIRCALOY cladding tubes: Part III,” *Metall. Mater. Trans. A*, vol. 34, no. 3, pp. 579–588, 2003, doi: 10.1007/s11661-003-0093-1.
 - [89] M. Kerr, M. R. Daymond, R. a. Holt, and J. D. Almer, “Strain evolution of zirconium hydride embedded in a Zircaloy-2 matrix,” *J. Nucl. Mater.*, vol. 380, no. 1–3, pp. 70–75, Oct. 2008, doi: 10.1016/j.jnucmat.2008.07.004.
 - [90] R. Thomas *et al.*, “‘Effect of hydrides and second phase particles on strain localisation in Zircaloy-4’ in ‘Effect of proton irradiation and hydriding on strain localisation in zirconium alloys,’ PhD thesis,” University of Manchester, 2019.
 - [91] L. A. Simpson and C. D. Cann, “Fracture toughness of zirconium hydride and its influence on the crack resistance of zirconium alloys,” *J. Nucl. Mater.*, vol. 87, no. 2–3, pp. 303–316, 1979.
 - [92] G. Bertolino, G. Meyer, and J. Perez Ipiña, “In situ crack growth observation and fracture toughness measurement of hydrogen charged Zircaloy-4,” *J. Nucl. Mater.*, vol. 322, no. 1, pp. 57–65, 2003, doi: 10.1016/S0022-3115(03)00305-2.
 - [93] M. R. Vanlandingham, “Review of Instrumented Indentation,” *J. Res. Natl. Inst. Stand. Technol.*, vol. 108, no. 4, pp. 249–265, 2003.
 - [94] B. J. Briscoe, L. Fiori, and E. Pelillo, “Nano-indentation of polymeric surfaces,” *J. Phys. D. Appl. Phys.*, vol. 31, pp. 2395–2405, Oct. 1998, doi: 10.1088/0022-3727/31/19/006.
 - [95] A. Gouldstone, N. Chollacoop, M. Dao, J. Li, A. Minor, and Y. Shen, “Indentation across size scales and disciplines: Recent developments in experimentation and modeling,” *Acta Mater.*, vol. 55, no. 12, pp. 4015–4039, Jul. 2007, doi: 10.1016/j.actamat.2006.08.044.
 - [96] W. C. Oliver and G. M. Pharr, “Measurement of hardness and elastic modulus by instrumented indentation: Advances in understanding and refinements to methodology,” *J. Mater. Res.*, vol. 19, no. 01, pp. 3–20, Mar. 2004, doi:

- 10.1557/jmr.2004.19.1.3.
- [97] X. Li and B. Bhushan, "A review of nanoindentation continuous stiffness measurement technique and its applications," *Mater. Charact.*, vol. 48, pp. 11–36, 2002.
 - [98] C. Schuh, "Nanoindentation studies of materials," *Mater. Today*, vol. 9, no. 5, pp. 32–40, May 2006, doi: 10.1016/S1369-7021(06)71495-X.
 - [99] W. C. Oliver and G. M. Pharr, "An improved technique for determining hardness and elastic modulus using load and displacement sensing indentation," *J. Mater. Res.*, vol. 7, no. 6, pp. 1564–83, 1992.
 - [100] G. M. Pharr, E. G. Herbert, and Y. Gao, "The indentation size effect: a critical examination of experimental observations and mechanistic interpretations," *Annu. Rev. Mater. Res.*, vol. 40, pp. 271–292, Jun. 2010, doi: 10.1146/annurev-matsci-070909-104456.
 - [101] N. A. Fleck and J. W. Hutchinson, "A phenomenological theory for strain gradient effects in plasticity," *J. Mech. Phys. Solids*, vol. 41, no. 12, pp. 1825–1857, 1993.
 - [102] W. D. Nix and H. Gao, "Indentation size effects in crystalline materials: A law for strain gradient plasticity," *J. Mech. Phys. Solids*, vol. 46, no. 3, pp. 411–425, Mar. 1998, doi: 10.1016/S0022-5096(97)00086-0.
 - [103] H. Gao and Y. Huang, "Geometrically necessary dislocation and size-dependent plasticity," *Scr. Mater.*, vol. 48, no. 2, pp. 113–118, Jan. 2003, doi: 10.1016/S1359-6462(02)00329-9.
 - [104] W. D. Nix, "Elastic and plastic properties of thin films on substrates : nanoindentation techniques," *Mater. Sci. Eng. A*, vol. 234–236, pp. 37–44, 1997.
 - [105] J. Joost and W. D. Nix, "Measuring the elastic properties of anisotropic materials by means of indentation experiments," *J. Mech. Phys. Solids*, vol. 42, no. 8, pp. 1223–1245, 1994.
 - [106] D. E. J. Armstrong, A. J. Wilkinson, and S. G. Roberts, "Measuring anisotropy in Young ' s modulus of copper using microcantilever testing," *J. Mater. Res.*, vol. 24, no. 11, pp. 3268–3276, 2009, doi: 10.1557/JMR.2009.0396.
 - [107] E. G. Herbert, W. C. Oliver, and G. M. Pharr, "On the measurement of yield strength by spherical indentation," *Philos. Mag.*, vol. 86, no. 33–35, pp. 5521–5539, Nov. 2006, doi: 10.1080/14786430600825103.
 - [108] S. Zhang, D. Sun, Y. Fu, and H. Du, "Toughness measurement of thin films: a critical review," *Surf. Coatings Technol.*, vol. 198, no. 1–3, pp. 74–84, Aug. 2005, doi: 10.1016/j.surfcoat.2004.10.021.
 - [109] K. I. Schiffmann, "Determination of fracture toughness of bulk materials and thin films by nanoindentation: comparison of different models," *Philos. Mag.*, vol. 91, no. 7–9, pp. 1163–1178, 2011, doi: 10.1080/14786435.2010.487984.
 - [110] G. D. Quinn and R. C. Bradt, "On the Vickers indentation fracture toughness test," *J. Am. Ceram. Soc.*, vol. 90, no. 3, pp. 673–680, 2007, doi: 10.1111/j.1551-2916.2006.01482.x.
 - [111] B. R. Lawn and A. G. Evans, "A model for crack initiation in elastic/plastic indentation fields," *J. Mater. Sci.*, vol. 12, pp. 2195–2199, 1977.
 - [112] B. R. Lawn, A. G. Evans, and D. B. Marshall, "Elastic/plastic indentation damage in ceramics: The median/radial crack system," *J. Am. Ceram. Soc.*, vol. 63, no. 9–10, pp.

- 574–581, 1980.
- [113] T. Ando *et al.*, “Fracture toughness measurement of a thin-film silicon,” *Fatigue Fract. Eng. Mater. Structures*, vol. 28, pp. 687–694, 2005, doi: 10.4028/www.scientific.net/KEM.297-300.292.
 - [114] S. Zhang, D. Sun, Y. Fu, and H. Du, “Toughness measurement of ceramic thin films by two-step uniaxial tensile method,” *Thin Solid Films*, vol. 469–470, pp. 233–238, Dec. 2004, doi: 10.1016/j.tsf.2004.08.094.
 - [115] X. Li, B. Bhushan, K. Takashima, C.-W. Baek, and Y.-K. Kim, “Mechanical characterization of micro/nanoscale structures for MEMS/NEMS applications using nanoindentation techniques,” *Ultramicroscopy*, vol. 97, no. 1–4, pp. 481–94, 2003, doi: 10.1016/S0304-3991(03)00077-9.
 - [116] T. Namazu and Y. Isono, “Quasi-static bending test of nano-scale SiO₂ wire at intermediate temperatures using AFM-based technique,” *Sensors Actuators A*, vol. 104, pp. 78–85, 2003.
 - [117] E. G. Herbert, W. C. Oliver, M. P. de Boer, and G. M. Pharr, “Measuring the elastic modulus and residual stress of freestanding thin films using nanoindentation techniques,” *J. Mater. Res.*, vol. 24, no. 9, p. 2009, 2009, doi: 10.1557/JMR.2009.0360.
 - [118] R. Ballarini, R. L. Mullen, and Y. Yin, “The fracture toughness of polysilicon microdevices : A first report,” *J. Mater. Res.*, vol. 12, no. 4, pp. 915–922, 1997.
 - [119] J. R. Greer and W. D. Nix, “Size dependence of mechanical properties of gold at the sub-micron scale,” *Appl. Phys. A*, vol. 80, pp. 1625–1629, Mar. 2005, doi: 10.1007/s00339-005-3204-6.
 - [120] M. B. Lowry *et al.*, “Achieving the ideal strength in annealed molybdenum nanopillars,” *Acta Mater.*, vol. 58, no. 15, pp. 5160–5167, Sep. 2010, doi: 10.1016/j.actamat.2010.05.052.
 - [121] M. Sebastiani, K. E. Johanns, E. G. Herbert, F. Carassiti, and G. M. Pharr, “A novel pillar indentation splitting test for measuring fracture toughness of thin ceramic coatings,” *Philos. Mag.*, vol. 95, no. 16–18, pp. 1928–44, 2015, doi: 10.1080/14786435.2014.913110.
 - [122] B. Moser, K. Wasmer, L. Barbieri, and J. Michler, “Strength and fracture of Si micropillars : A new scanning electron microscopy-based micro-compression test,” *J. Mater. Res.*, vol. 22, no. 4, pp. 1004–11, 2007, doi: 10.1557/JMR.2007.0140.
 - [123] B. N. Jaya, V. Jayaram, and S. K. Biswas, “A new method for fracture toughness determination of graded (Pt,Ni)Al bond coats by microbeam bend tests,” *Philos. Mag.*, vol. 92, no. 25–27, pp. 3326–3345, 2012, doi: 10.1080/14786435.2012.669068.
 - [124] J. Gong and A. J. Wilkinson, “A microcantilever investigation of size effect, solid-solution strengthening and second-phase strengthening for $\langle a \rangle$ prism slip in α -Ti,” *Acta Mater.*, vol. 59, no. 15, pp. 5970–5981, Sep. 2011, doi: 10.1016/j.actamat.2011.06.005.
 - [125] J. Gong and A. Wilkinson, “Investigation of elastic properties of single-crystal α -Ti using microcantilever beams,” *Philos. Mag. Lett.*, vol. 90, no. 7, pp. 503–512, Jul. 2010, doi: 10.1080/09500831003772989.
 - [126] R. Ding, J. Gong, A. J. Wilkinson, and I. P. Jones, “Transmission electron microscopy

- of deformed Ti–6Al–4 V micro-cantilevers,” *Philos. Mag.*, vol. 92, no. 25–27, pp. 3290–3314, Sep. 2012, doi: 10.1080/14786435.2012.700414.
- [127] D. E. J. Armstrong, M. E. Rogers, and S. G. Roberts, “Micromechanical testing of stress corrosion cracking of individual grain boundaries,” *Scr. Mater.*, vol. 61, no. 7, pp. 741–743, Oct. 2009, doi: 10.1016/j.scriptamat.2009.06.017.
- [128] S. Wang, S. Kalácska, X. Maeder, J. Michler, F. Giuliani, and T. Ben Britton, “The effect of δ -hydride on the micromechanical deformation of a Zr alloy studied by in situ high angular resolution electron backscatter diffraction,” *Scr. Mater.*, vol. 173, pp. 101–105, Dec. 2019, doi: 10.1016/j.scriptamat.2019.08.006.
- [129] C. Motz, T. Schöberl, and R. Pippan, “Mechanical properties of micro-sized copper bending beams machined by the focused ion beam technique,” *Acta Mater.*, vol. 53, pp. 4269–4279, 2005, doi: 10.1016/j.actamat.2005.05.036.
- [130] D. Di Maio and S. G. Roberts, “Measuring fracture toughness of coatings using focused-ion-beam-machined microbeams,” *J. Mater. Res.*, vol. 20, no. 2, pp. 299–302, 2005, doi: 10.1557/JMR.2005.0048.
- [131] F. Iqbal, J. Ast, M. Göken, and K. Durst, “In situ micro-cantilever tests to study fracture properties of NiAl single crystals,” *Acta Mater.*, vol. 60, no. 3, pp. 1193–1200, 2012, doi: 10.1016/j.actamat.2011.10.060.
- [132] T. P. Halford, K. Takashima, Y. Higo, and P. Bowen, “Fracture tests of micro-sized TiAl specimens,” *Fatigue Fract Engng Mater Struct*, vol. 28, pp. 695–701, Aug. 2005, doi: 10.1111/j.1460-2695.2005.00893.x.
- [133] S. Massl, W. Thomma, J. Keckes, and R. Pippan, “Investigation of fracture properties of magnetron-sputtered TiN films by means of a FIB-based cantilever bending technique,” *Acta Mater.*, vol. 57, pp. 1768–1776, 2009, doi: 10.1016/j.actamat.2008.12.018.
- [134] D. E. J. Armstrong, A. J. Wilkinson, and S. G. Roberts, “Micro-mechanical measurements of fracture toughness of bismuth embrittled copper grain boundaries,” *Philos. Mag. Lett.*, vol. 91, no. 6, pp. 394–400, 2011, doi: 10.1080/09500839.2011.573813.
- [135] K. Matoy *et al.*, “A comparative micro-cantilever study of the mechanical behavior of silicon based passivation films,” *Thin Solid Films*, vol. 518, no. 1, pp. 247–256, Nov. 2009, doi: 10.1016/j.tsf.2009.07.143.
- [136] K. Matoy, H. Schönherr, T. Detzel, and G. Dehm, “Micron-sized fracture experiments on amorphous SiO_x films and SiO_x/SiN_x multi-layers,” *Thin Solid Films*, vol. 518, pp. 5796–5801, Aug. 2010, doi: 10.1016/j.tsf.2010.05.114.
- [137] Y. Deng, T. Hajilou, and A. Barnoush, “Hydrogen-enhanced cracking revealed by in situ micro-cantilever bending test inside environmental scanning electron microscope,” *Philos. Trans. R. Soc. A Math. Phys. Eng. Sci.*, vol. 375, no. 0106, Jul. 2017, doi: 10.1098/rsta.2017.0106.
- [138] S. Liu, J. M. Wheeler, P. R. Howie, X. T. Zeng, J. Michler, and J. Clegg, “Measuring the fracture resistance of hard coatings,” *Appl. Phys. Lett.*, vol. 102, pp. 171907–1–4, 2013.
- [139] D. Kiener, W. Grosinger, G. Dehm, and R. Pippan, “A further step towards an understanding of size-dependent crystal plasticity: In situ tension experiments of miniaturized single-crystal copper samples,” *Acta Mater.*, vol. 56, no. 3, pp. 580–592,

- Feb. 2008, doi: 10.1016/j.actamat.2007.10.015.
- [140] B. N. Jaya, C. Kirchlechner, and G. Dehm, “Can microscale fracture tests provide reliable fracture toughness values? A case study in silicon,” *J. Mater. Res.*, vol. 30, no. 5, pp. 686–698, 2015, doi: 10.1557/jmr.2015.2.
 - [141] T. Ishitani and T. Yaguchi, “Cross-sectional sample preparation by focused ion beam : A review of Ion-sample interaction,” *Microsc. Res. Tech.*, vol. 35, pp. 320–333, 1996.
 - [142] D. Kiener, C. Motz, M. Rester, M. Jenko, and G. Dehm, “FIB damage of Cu and possible consequences for miniaturized mechanical tests,” *Mater. Sci. Eng. A*, vol. 459, no. 1–2, pp. 262–272, Jun. 2007, doi: 10.1016/j.msea.2007.01.046.
 - [143] D. J. Larson *et al.*, “Field-ion specimen preparation using focused ion-beam milling,” *Ultramicroscopy*, vol. 79, pp. 287–293, 1999.
 - [144] S. Rubanov and P. R. Munroe, “FIB-induced damage in silicon,” *J. Microsc.*, vol. 214, no. 3, pp. 213–221, 2004.
 - [145] D. Kiener, C. Motz, T. Schöberl, M. Jenko, and G. Dehm, “Determination of mechanical properties of copper at the micron scale,” *Adv. Eng. Mater.*, vol. 8, no. 11, pp. 1119–1125, Nov. 2006, doi: 10.1002/adem.200600129.
 - [146] D. Lam, F. Yang, A. Chong, J. Wang, and P. Tong, “Experiments and theory in strain gradient elasticity,” *J. Mech. Phys. Solids*, vol. 51, no. 8, pp. 1477–1508, Aug. 2003, doi: 10.1016/S0022-5096(03)00053-X.
 - [147] C. Motz, D. Weygand, J. Senger, and P. Gumbsch, “Micro-bending tests: A comparison between three-dimensional discrete dislocation dynamics simulations and experiments,” *Acta Mater.*, vol. 56, no. 9, pp. 1942–1955, May 2008, doi: 10.1016/j.actamat.2007.12.053.
 - [148] E. Tarleton, D. S. Balint, J. Gong, and A. J. Wilkinson, “A discrete dislocation plasticity study of the micro-cantilever size effect,” *Acta Mater.*, vol. 88, pp. 271–282, 2015.
 - [149] D. E. J. Armstrong, A. S. M. A. Haseeb, S. G. Roberts, A. J. Wilkinson, and K. Bade, “Nanoindentation and micro-mechanical fracture toughness of electrodeposited nanocrystalline Ni–W alloy films,” *Thin Solid Films*, vol. 520, no. 13, pp. 4369–4372, Apr. 2012, doi: 10.1016/j.tsf.2012.02.059.
 - [150] G. Sernicola *et al.*, “In situ stable crack growth at the micron scale,” *Nat. Commun.*, vol. 8, 2017, doi: 10.1038/s41467-017-00139-w.
 - [151] M. G. Mueller, V. Pejchal, G. Žagar, A. Singh, M. Cantoni, and A. Mortensen, “Fracture toughness testing of nanocrystalline alumina and fused quartz using chevron-notched microbeams,” *Acta Mater.*, vol. 86, pp. 385–395, 2015, doi: 10.1016/j.actamat.2014.12.016.
 - [152] B. S. Li, D. E. J. Armstrong, T. J. Marrow, and S. G. Roberts, “High-temperature fracture test using chevron-notched tungsten microcantilevers,” in *Nanomechanical Testing in Materials Research and Development V, Engineering Conferences International*, 2015.
 - [153] T.-L. Yau, “Corrosion of zirconium,” in *Corrosion Engineering Handbook*, CRC Press, 1996, p. 195.
 - [154] J. H. Schemel, *ASTM STP639 manual on zirconium and hafnium*. ASTM International, 1977.

-
- [155] F. C. Iglesias, B. J. Lewis, C. Desgranges, and C. Toffolon, “Clad-coolant chemical interaction,” 2015.
- [156] A. Couet, A. T. Motta, and R. J. Comstock, “Effect of alloying elements on hydrogen pickup in zirconium alloys,” in *Zirconium in the nuclear industry: 17th international symposium*, 2014, pp. 479–514. doi: 10.1520/STP154320120215.
- [157] E. Garlea *et al.*, “Hydride-phase formation and its influence on fatigue crack propagation behavior in a zircaloy-4 alloy,” *Metall. Mater. Trans. A*, vol. 41A, no. 11, pp. 2816–2828, Jul. 2010, doi: 10.1007/s11661-010-0342-z.
- [158] M. M. Nowell, R. a Witt, and B. True, “EBSD Sample Preparation: Techniques, Tips, and Tricks,” *Microsc. Microanal.*, vol. 11, no. Suppl 2, pp. 504–505, Aug. 2005, doi: 10.1017/S143192760550672X.
- [159] H. Abdolvand and A. J. Wilkinson, “Assessment of residual stress fields at deformation twin tips and the surrounding environments,” *Acta Mater.*, vol. 105, pp. 219–231, 2016, doi: 10.1016/j.actamat.2015.11.036.
- [160] A. D. Lepage, W. A. Ferris, and G. A. Ledoux, “Procedure for adding hydrogen to small sections of zirconium alloys,” *IAEA Rep. FC-IAEA-03 AECL Rep. T1.20.13-CAN-2763-03*, 1998.
- [161] B. Fultz and J. Howe, *Transmission Electron Microscopy and Diffractometry of Materials*, Fourth. Berlin, Heidelberg: Springer Berlin Heidelberg, 2013. doi: 10.1007/978-3-642-29761-8.
- [162] J. Hubbell and S. M. Seltzer, “Tables of X-ray mass attenuation coefficients and mass energy-absorption coefficients 1keV to 20MeV for elements Z=1 to 92 and 48 additional substances of dosimetric interest. NISTIR-5632.” National Inst. of Standards and Technology. Ionizing Radiation Div., 1995.
- [163] Agilent Technologies Inc., “Agilent Nano Indenter G200 data sheet, 5990-4172EN Rev.F.” pp. 1–4, 2013.
- [164] J. Hay and J. Yu, “Imaging and indenting: The pros and cons of stretching functionality,” Agilent Technilgies, 2010.
- [165] M. F. Doerner and W. D. Nix, “A method for interpreting the data from depth-sensing indentation instruments,” *J. Mater. Res.*, vol. 1, no. 4, pp. 601–609, 1986.
- [166] A. C. Fischer-Cripps, “Critical review of analysis and interpretation of nanoindentation test data,” *Surf. Coatings Technol.*, vol. 200, pp. 4153–4165, Apr. 2006, doi: 10.1016/j.surfcoat.2005.03.018.
- [167] H. Li and J. J. Vlassak, “Determining the elastic modulus and hardness of an ultra-thin film on a substrate using nanoindentation,” *J. Mater. Res.*, vol. 24, no. 3, pp. 1114–26, 2009, doi: 10.1557/JMR.2009.0144.
- [168] B. Jönsson and S. Hogmark, “Hardness measurements of thin films,” *Thin Solid Films*, vol. 114, pp. 257–269, 1984, doi: 10.1016/0040-6090(84)90123-8.
- [169] A. Iost, G. Guillemot, Y. Rudermann, and M. Bigerelle, “A comparison of models for predicting the true hardness of thin films,” *Thin Solid Films*, vol. 524, pp. 229–237, 2012, doi: 10.1016/j.tsf.2012.10.017.
- [170] R. Haswell, D. McComb, and W. Smith, “Preparation of site-specific cross-sections of heterogeneous catalysts prepared by focused ion beam milling,” *J. Microsc.*, vol. 211, pp. 161–166, 2003.

-
- [171] Y. M. Soifer, A. Verdyan, M. Kazakevich, and E. Rabkin, "Nanohardness of copper in the vicinity of grain boundaries," *Scr. Mater.*, vol. 47, pp. 799–804, 2002.
- [172] S. I. Wright and M. M. Nowell, "EBSD image quality mapping," *Microsc. Microanal.*, vol. 12, pp. 72–84, 2006, doi: 10.1017/S1431927606060090.
- [173] S. D. Sitzman, G. Nolze, and M. M. Nowell, "EBSD pattern quality and its use in evaluating sample surface condition," *Microsc. Microanal.*, vol. 16, pp. 698–699, 2010, doi: 10.1017/S14319276100.
- [174] A. Aitkaliyeva, J. W. Madden, B. D. Miller, J. I. Cole, and J. Gan, "Comparison of preparation techniques for nuclear materials for transmission electron microscopy (TEM)," *J. N.*, vol. 459, pp. 241–246, 2015, doi: 10.1016/j.jnucmat.2015.01.042.
- [175] S. I. Wright, M. M. Nowell, and D. P. Field, "A review of strain analysis using electron backscatter diffraction," *Microsc. Microanal.*, vol. 17, pp. 316–329, 2011.
- [176] R. Kirchheim, "Solid solutions of hydrogen in complex materials," *Solid State Physics-Advances Res. Appl.*, vol. 59, pp. 203–292, 2004.
- [177] M. Avrami, "Kinetics of phase change. II Transformation-time relations for random distribution of nuclei," *J. Chem. Phys.*, vol. 8, no. 2, pp. 212–224, 1940, doi: 10.1063/1.1750631.
- [178] D. V. Ragone, *Thermodynamics of Materials-The MIT Series in Materials Science and Engineering*, vol. II. New York: John Wiley & Sons, 1995.
- [179] J. Stefan, "Über die Theorie der Eisbildung, insbesondere über die Eisbildung im Polarmeere [On the theory of formation of ice, in particular in the polar sea]," *Ann. Phys.*, vol. 278, no. 2, pp. 269–286, 1891, doi: 10.1002/andp.18912780206.
- [180] C. Zener, "Theory of Growth of Spherical Precipitates from Solid Solution," *J. Appl. Phys.*, vol. 20, no. 10, pp. 950–953, 1949, doi: 10.1063/1.1698258.
- [181] J. J. Kearns, "diffusion coefficient of hydrogen in alpha zirconium, zircaloy-2 and zircaloy-4," *J. Nucl. Mater.*, vol. 43, no. 3, pp. 330–338, 1972.
- [182] G. Majer, W. Renz, and R. G. Barnes, "The mechanism of hydrogen diffusion in zirconium dihydrides," *J. Phys. Condens. Matter*, vol. 6, pp. 2935–2942, 1994.
- [183] H. Wipf, B. Kappesser, and R. Werner, "Hydrogen diffusion in titanium and zirconium hydrides," *J. Alloys Compd.*, vol. 310, no. 1–2, pp. 190–195, Sep. 2000, doi: 10.1016/S0925-8388(00)00945-2.
- [184] T. Mizuno and M. Enyo, "Electrochemical kinetics and mechanism of hydrogen absorption of Ti and Zr during cathodic electrolysis," *Fac. Eng. Hokkaido Univ.*, vol. 18, no. 4, pp. 17–27, 1993.
- [185] Y. Fukai and H. Sugimoto, "Diffusion of hydrogen in metals," *Adv. Phys.*, vol. 34, no. 2, pp. 263–326, 1985.
- [186] K. Nakazato and K. Kitahara, "Site blocking effect in tracer diffusion in a lattice," *Prog. Theor. Phys.*, vol. 64, no. 6, pp. 2261–4, 1980.
- [187] R. Kirchheim, "Solubility, diffusivity and trapping of hydrogen in dilute alloys. Deformed and amorphous metals-II," *Acta Mater.*, vol. 30, pp. 1069–78, 1982.
- [188] A. H. Sihvola and I. V. Lindell, "Effective permeability of mixtures," *Prog. Electromagn. Res.*, vol. 6, pp. 153–180, 1992.
- [189] J. Jamnik, J. R. Kalnin, E. a Kotomin, and J. Maier, "Generalised Maxwell-Garnett

- equation: application to electrical and chemical transport.,” *Phys. Chem. Chem. Phys.*, vol. 8, no. 11, pp. 1310–4, Mar. 2006, doi: 10.1039/b514448p.
- [190] J. C. M. Garnett, “Colours in metal glasses and in metallic films,” *Philos. Trans. R. Soc.*, vol. 203, pp. 385–420, Jan. 1904, doi: 10.1098/rsta.1904.0024.
- [191] J. R. Kalnin, E. A. Kotomin, and J. Maier, “Calculations of the effective diffusion coefficient for inhomogeneous media,” *J. Phys. Chem. Solids*, vol. 63, pp. 449–456, 2002.
- [192] H. S. Göktürk, T. J. Fiske, and D. M. Kalyon, “Effects of particle shape and size distributions on the electrical and magnetic properties of nickel/polyethylene composites,” *J. Appl. Polym. Sci.*, vol. 50, no. 11, pp. 1891–1901, 1993.
- [193] A. Sihvola, “Dielectric properties of natural media-Mixing methods for heterogeneous and granular media,” in *Thermal Microwave Radiation: Applications for Remote Sensing*, C. Matzler, Ed. London, UK: The Institution of Engineering and Technology, IET, 2006. doi: 10.1017/CBO9781107415324.004.
- [194] Z. Hashin and S. Shtrikman, “A Variational Approach to the Theory of the Effective Magnetic Permeability of Multiphase Materials,” *J. Appl. Phys.*, vol. 33, no. 10, pp. 3125–3131, 1962, doi: 10.1063/1.1728579.
- [195] R. LeVeque, *Finite Difference Methods for Ordinary and Partial Differential Equations: Steady-State and Time-Dependent Problems*. Society for Industrial and Applied Mathematics, SIAM, 2007. doi: 10.1137/1.9780898717839.
- [196] N. Otsu, “A threshold selection method from gray-level histograms,” *IEEE Trans. Syst. Man Cybern.*, vol. 9, no. 1, pp. 62–66, 1979, doi: 10.1109/TSMC.1979.4310076.
- [197] M. Grosse, M. van den Berg, C. Goulet, and A. Kaestner, “In-situ investigation of hydrogen diffusion in Zircaloy-4 by means of neutron radiography,” *J. Phys. Conf. Ser.*, vol. 340, p. 012106, Feb. 2012, doi: 10.1088/1742-6596/340/1/012106.
- [198] H. Chan, S. G. Roberts, and J. Gong, “Micro-scale fracture experiments on zirconium hydrides and phase boundaries,” *J. Nucl. Mater.*, vol. 475, pp. 105–112, Jul. 2016, doi: 10.1016/j.jnucmat.2016.03.026.
- [199] “ASTM E1820-01 Standard test method for measurement of fracture toughness.” ASTM International, 2003.
- [200] C. D. Hardie, “Micro-mechanics of irradiated Fe-Cr alloys for fusion reactors,” DPhil, University of Oxford, 2013.
- [201] “ASTM E399-90 Standard test method for plane-strain fracture toughness of metallic materials.” ASTM International, 1997.
- [202] J. Gong and A. J. Wilkinson, “Sample size effects on grain boundary sliding,” *Scr. Mater.*, vol. 114, pp. 17–20, 2016, doi: 10.1016/j.scriptamat.2015.11.029.
- [203] R. Pandey, *Text Book of Engineering Mathematics*, 1st ed., vol. II. Word-Press, 2010.