

HIGH RESOLUTION STRUCTURAL ANALYSIS OF IRRADIATED ZIRCONIUM ALLOYS

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ABSTRACT

This thesis is part of the MUZIC-3 (Mechanistic Understanding of Zirconium Corrosion) project, with the overall goal to understand the in-reactor corrosion and hydrogen pick-up mechanisms of zirconium alloys. Zirconium alloys are commonly used for fuel cladding and support structures in light water reactors but suffer from aqueous corrosion in service that can limit the operating lifetime and the effective burnup of the fuel. Understanding the mechanisms of corrosion, especially under irradiation, is thus of great importance for the development of accurate, physically based lifetime prediction models for cladding materials, and providing information for the design of new corrosion-resistant alloys.

Acceleration of the corrosion rate has been widely reported as a result of exposure to in-reactor conditions, but the mechanisms of this accelerating effect are still not well understood. It has been correlated with the specific in-reactor coolant chemistry, intense γ -radiation or irradiation-induced redistribution of alloying elements, but rather little attention has been paid to the irradiation-induced degradation of the corrosion protective oxide layers. In an effort to understand such mechanisms, I have used both in-situ radiation damage techniques and direct observations of ex-reactor materials to study radiation effects in zirconium oxides formed on a range of Zr alloys.

The aqueous corrosion of zirconium follows the pathway: $\text{Zr} \rightarrow \text{h-ZrO} \rightarrow \text{ZrO}_2$. The transformation from Zr to h-ZrO is found to follow a displacive mechanism, and the suboxide grains can show different morphologies, equiaxed, plate-like or sawtooth-like, depending on the underlying α -Zr grain orientation, although no specific orientation relationships between h-ZrO and m-ZrO₂ or α -Zr and m-ZrO₂ were identified. The monoclinic-ZrO₂ oxides formed in an autoclave are observed to have a similar texture on

different alloys, with $(10\bar{4})_{\text{m-ZrO}_2}$ parallel to the metal/oxide interface regardless of the underlying α -Zr or h-ZrO orientations.

I report for the first time on the susceptibility to radiation damage of the suboxide phase which may influence the nucleation of new oxide grains and the transportation of oxidation species across the oxide/metal interface, and lead to enhanced corrosion rates. A monoclinic-to-cubic transformation of the bulk oxide is also observed by in-situ ion irradiation experiments, followed by irradiation-induced grain growth. The possibility of radiation-induced stabilisation of this cubic phase thus needs to be considered as a possible process that can occur at high burnups in reactors, and may further affect the corrosion rates. As a result of the in-reactor corrosion conditions, e.g. irradiation and water chemistries, the oxides formed in-flux are less well textured and with a more disrupted grain, which can contribute to enhanced corrosion rates in-flux.

My results also indicate that oxide nano-porosity plays an important role in the transportation of oxidising species throughout the oxide layer. The density of nano-porosity in the oxide corrosion layers has been successfully quantified for the first time as function of both depth in the oxide and exposure time, and a clear correlation is observed between the measured increase in hydrogen pickup fraction and the characterised increase in interconnected porosity in the oxide.

To complete the work in this thesis, a wide range of microstructural characterization techniques have been applied, like Focused Ion Beam, Transmission Electron Microscopy, Transmission Kikuchi Diffraction and high-resolution Secondary Ion Mass Spectrometry. The combination of these techniques has provided me with a wide range of information on microstructures and microchemistry, which is useful to the understanding of the degradation mechanisms in fuel cladding materials.

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PREFACE

The research described in this thesis was carried out by the author in the Department of Materials at the University of Oxford between October 2016 and June 2019, under the supervision of Prof. Chris R. M. Grovenor, Prof. Sergio Lozano-Perez and Prof. Angus J. Wilkinson. All of the work is original, and where the work of others is included it has been referenced and acknowledged. No part of this thesis has been submitted for any other degree at this university or elsewhere.

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TABLE OF CONTENTS

ABSTRACT	i
ACKNOWLEDGEMENTS	iii
PREFACE	v
TABLE OF CONTENTS	viii
LIST OF TABLES.....	xi
LIST OF FIGURES.....	xii
LIST OF ABBREVIATIONS	xxii
Chapter 1 Introduction	1
1.1. Nuclear Power in the UK	1
1.2. Zirconium in the Nuclear Industry	3
1.3. Objectives	6
Chapter 2 Literature Review.....	8
2.1. Autoclave Corrosion.....	8
2.1.1. Corrosion mechanisms	8
2.1.2. Weight gain	10
2.1.3. Corrosion kinetics.....	10
2.1.4. Hydrogen pick-up	14
2.2. Zirconium Oxides	19
2.2.1. Phases	19
2.2.2. Grain size and texture	22
2.2.3. Nano-porosity	24
2.3. In-reactor Corrosion	26
2.3.1. Corrosion kinetics.....	26
2.3.2. Hypotheses for enhanced in-reactor corrosion	27
2.3.3. Radiation damage in zirconium oxides	31
Chapter 3 Techniques and Instruments	36
3.1. Focused Ion Beam	36
3.2. Electron Backscatter Diffraction and Transmission Kikuchi Diffraction.....	40
3.3. Transmission Electron Microscopy	43
3.4. Scanning Transmission Electron Microscopy	46
3.5. Energy-Dispersive X-ray and Electron Energy Loss Spectroscopy	47
3.6. In-situ Irradiation in TEM	48

3.7. High-resolution Secondary Ion Mass Spectrometry	50
Chapter 4 Materials	55
4.1. As-received Alloy Characterisation	55
4.2. Corrosion Kinetics	59
4.3. Selected Samples	62
Chapter 5 EBSD, TEM and NanoSIMS Sample Preparation	66
6.1. EBSD Specimen Preparation	66
6.2. TEM Specimen Preparation	67
6.3. NanoSIMS Specimen Preparation	71
Chapter 6 Technique Development	75
6.1. Forescattered Electron Imaging of Nanoparticles in an SEM	75
6.1.1. Introduction	75
6.1.2. Materials and experimental methodologies	77
6.1.3. Results and discussion	81
6.1.4. Conclusions	91
6.2. Depth Resolution of Transmission Kikuchi Diffraction (TKD) Analysis	93
6.2.1. Introduction	93
6.2.2. Experimental methods	95
6.2.3. Results	96
6.2.4. Discussion	102
6.2.5. Conclusions	108
Chapter 7 Formation Mechanisms of Suboxide and Oxides by Aqueous Corrosion	109
7.1. Introduction	109
7.2. Materials and Experimental Methods	109
7.3. Results	110
7.3.1. Bulk oxide phases and texture analysis	110
7.3.2. Oxide/metal interface microstructure	115
7.4. Discussion	123
7.4.1. Formation mechanisms of h-ZrO suboxide	123
7.4.2. The impact of α -Zr orientation on suboxide nucleation	125
7.4.3. The effects of alloying elements on suboxide growth	129
7.5. Conclusions	131
Chapter 8 The Role of Oxide Nano-Porosity in Hydrogen Transport	133
8.1. Introduction	133
8.2. Materials and Experimental Methods	133

8.3.	Results	134
8.3.1.	Characterisation of oxide cracks.....	134
8.3.2.	Characterisation of oxide nano-porosity	139
8.4.	Discussion	145
8.5.	Conclusions	149
Chapter 9	Distributions of Deuterium in Zirconium Oxides	151
9.1.	Introduction	151
9.2.	Materials and Experimental Methods	151
9.3.	Results and Discussion	151
9.3.1.	Deuterium distributions in Zr oxides.....	152
9.3.2.	Effects of irradiation and sample preparation on deuterium distribution....	156
9.4.	Conclusions	159
Chapter 10	Irradiation Effects in Zirconium Oxides.....	161
10.1.	Introduction	161
10.2.	Materials and Experimental Methods	161
10.3.	Results and Discussion	162
10.3.1.	Characterisation of oxides formed in reactor conditions.....	162
10.3.2.	Ion-irradiation induced damage in the ZrO suboxide.....	165
10.3.3.	Ion-irradiation induced damage in ZrO ₂	171
10.4.	Conclusions	190
Chapter 11	Conclusions and Future Work	192
11.1.	Conclusions	192
11.2.	Suggestions for Future Work.....	196
References.....		197

LIST OF TABLES

Table 1.1 Nuclear power reactors operating in the UK [2]	2
Table 1.2 Nuclear power reactors planned and proposed in the UK [2]	3
Table 1.3 Composition range of alloying elements in standard Zr alloys (wt%) (Adapt from [7], courtesy of the A.N.T. International)	6
Table 2.1 Pre-transition kinetic constants of a range of zirconium alloys [18]	13
Table 2.2 Crystallographic information on Zr-hydrides	16
Table 2.3 Lattice parameters of zirconium oxide phases.....	20
Table 2.4 Formation energy of Schottky , cation and anion Frenkel defects in ZrO ₂ [136].....	32
Table 3.1 Summary of EBSD and TKD settings used in this work.....	42
Table 3.2 Crystal structures used for the EBSD and TKD analysis	43
Table 3.3 Summary of properties of oxide, suboxide and Zr metal matrix, and damage rates calculated by SRIM for 8×10^{11} ions/cm ² /s 1 MeV Kr ²⁺ ions.....	50
Table 3.4 NanoSIMS settings for in-depth and cross-sectional analysis in this work	53
Table 4.1 Distribution of second phase and matrix composition in different alloys.	57
Table 4.2 Summary of power law fittings of pre-transition constants on different alloys.....	61
Table 4.3 Study purposes and information on selected samples	65
Table 5.1 Grinding and polishing procedure for Zr alloys for EBSD analysis	66
Table 6.1 FSD collection semi-angles (mrad) as a function of detector distances	80
Table 6.2 Experimentally determined values of TKD physical depth resolution at 30 keV and mean free paths of scattering events in the corresponding materials	106
Table 10.1 TKD indexed phase fractions and grain size [366] measured at different doses.....	179

LIST OF FIGURES

Figure 1.1 Electricity generated by sources in the UK [1]	2
Figure 1.2 A schematic of Light-Water Nuclear Reactor [3]	4
Figure 1.3 An example of LWR fuel assemblies.....	4
Figure 1.4 Evolution of corrosion performance of PWR cladding materials [6]	5
Figure 2.1 Schematic of the corrosion process in zirconium alloys [11]	9
Figure 2.2 Typical oxidation kinetics of a Zr alloy [13].....	11
Figure 2.3 Zr–H phase diagram with equilibrium concentration at various ambient hydrogen partial pressure isobars [32].....	15
Figure 2.4 Distribution and morphology of hydrides in Zr alloy [33].....	15
Figure 2.5 Schematic of the influence of alloying elements on oxidation kinetics and hydrogen pick-up fraction [31].	17
Figure 2.6 Phase diagram of Zr-O [64].....	19
Figure 2.7 The dependence of tetragonal-to-monoclinic transformation on the change in strain energy, chemical energy and surface energy [77].	21
Figure 2.8 The calculated phase diagram of Zr-O [68].	22
Figure 2.9 Schematic of oxide structures on Zr alloys of (a) poor and (b) good corrosion performance (courtesy of Samuel Armson, University of Manchester)....	23
Figure 2.10 Nano-porosity and cracks in the oxide at a distance away (a) 1.6 μm and (b) 3 μm from the oxide/metal interface on a 140-day ZIRLO sample [91].	25
Figure 2.11 Corrosion kinetics of Zircaloy-4 in the reactor at 270°C [102]. Weight gain (points) and fast neutron flux exposure (lines) are indicated. The autoclave corrosion kinetics curve is shown in blue.	27
Figure 2.12 Illustrations of reactor corrosion vs autoclave corrosion in a Zr-1.0Nb alloy: (a) before irradiation, (b) reactor corrosion and (c) autoclave corrosion [101].	30
Figure 2.13 Schematic representation of some defects in an ionic compound MX. Cations M^{z+} are dark spheres, anions X^{z-} open spheres [135].	31
Figure 2.14 Evolution of point defects in UO_2 with initially 200 cation and anion Frenkel pairs randomly present on sublattices (orange and black for uranium vacancies and interstitials. Red and blue for oxygen vacancies interstitials) [139].	33

Figure 3.1 A schematic setup of a dual-beam FIB instrument .	37
Figure 3.2 A schematic setup for 3D SEM/EDX using serial sectioning with a focused ion beam instrument.....	37
Figure 3.3 An example of 3D high-resolution milling imaging (a) the sectioning volume, (b) a the milling trench and imaging region and (c) a typical cross-sectional SEM image.	39
Figure 3.4 3D visualization of matrix microstructure in a Zr-2.5Nb alloy (a) an overview of the sample volume, and view along (b) axial, (c) tangential and (d) radial direction.	39
Figure 3.5 Schematic setups for (a) conventional EBSD on a bulk sample, (b) off-axis and (c) on-axis TKD on a TEM thin foil.	41
Figure 3.6 (a) schematic diagram of a TEM column and the two basic TEM modes (b) diffraction mode and (c) imaging mode, reproduced from [204, 207].	44
Figure 3.7 An example of the morphology of nano-pores in the zirconium oxide layer under Fresnel imaging conditions. The dashed arrows identify the same features. .	45
Figure 3.8 Annular distribution of electrons after passing through a thin sample [215].	47
Figure 3.9 The IVEM and MIAMI2 in-situ irradiation facilities.	49
Figure 3.10 SRIM damage profile and residual Kr concentration in Zr thin foil irradiated by 700 KeV Kr ²⁺ ions for a fluence of 1.9x10 ¹⁶ ions.cm ⁻²	50
Figure 3.11 The CAMECA NanoSIMS50 used in this work.	51
Figure 3.12 A schematic diagram showing the principles of SIMS analysis [229]...	52
Figure 3.13 Schematic diagram of a double focusing mass spectrometer showing the electrostatic and magnetic sectors [229].	52
Figure 3.14 Schematics of NanoSIMS analysis geometries (a) in-depth analysis and (b) cross-sectional analysis on bulk samples, (c) in-depth analysis on a FIB lift-out sample.	53
Figure 3.15 (a) SEM view of a typical NanoSIMS crater and (b) an example of 3D visualization of distribution of deuterium in the zirconium oxide layer.....	54
Figure 4.1 HAADF and EDX showing the morphology and distribution of second phases in different Zr-Nb alloys, (a) Westinghouse RXA Zr-0.5Nb and (b) CNL SRA Zr-2.5Nb alloy.	56
Figure 4.2 Contoured low-indexed poles (half width 15°) of (a) Westinghouse RXA Zr-0.5Nb tube and (b) CNL SRA Zr-2.5Nb tube sample.	57

Figure 4.3 3-dimensional schematic of the dominant crystal orientation in the manufactured Zr alloys, (a) Westinghouse RXA Zr-Nb (b) CNL SRA Zr-2.5Nb alloys.	58
Figure 4.4 (a) EBSD map of Westinghouse RXA Zr-Nb sample and (b) TKD map of CNL SRA Zr-2.5Nb sample in tube format.....	58
Figure 4.5 Autoclave corrosion kinetics and hydrogen (deuterium) content as a function of exposure time for (a) commercial Zircaloy-4, (b) RXA Zr-0.5Nb and (c) SRA Zr-2.5Nb alloys and corresponding power law fits of the pre-transition regimes. (Plotting data provided by Dr. Jonna Partezana, Westinghouse, US and Dr. Heidi Nordin, CNL, Canada).....	60
Figure 4.6 Comparisons between in-flux, out-of-flux and autoclave corrosion kinetics and corresponding power law fits of the pre-transition regimes for SRA Zr-2.5Nb samples (Plotting data provided by Dr. Heidi Nordin, CNL, Canada), selected samples used in this study are highlighted by red and blue arrows.....	61
Figure 4.7 Estimated damage dose in oxides as a function of oxide depth on B74 samples.....	63
Figure 5.1 An example of polished Zr-1Nb alloy surface morphology (a) polarized light optical micrograph and (b) EBSD band contrast map.....	67
Figure 5.2 Step-by-step instructions for TEM sample preparation with FIB, (a) trenching, (b and c) lift-out and (d) thinning, reproduced with kind permission of Dr. Ben Myers, Northwestern University.	68
Figure 5.3 An example of a TEM specimen containing both zirconium oxide and metal matrix prepared using FIB (showing transparency at 5keV SEM).....	69
Figure 5.4 SEM top view of specimens for in-situ irradiation. (a) as-prepared, (b) shape of specimen with single weld exposed to irradiation after 8.4×10^{15} ions.cm ⁻² and (c) shape of specimen welded on both sides exposed to irradiation after 10^{16} ions.cm ⁻² .70	
Figure 5.5 Schematic welding geometries on a 3 mm Cu grid. (a) one-side welded geometry on the middle bar and (b) both sides welded geometry on the V-shape bar.	71
Figure 5.6 Preparation routes of site-specific radioactive samples for NanoSIMS analysis.....	74
Figure 6.1 (a) A HAADF STEM image and (b, c and d) corresponding EDX maps showing the composition and distribution of SPPs in the Zr-Nb sample. Boxes indicate larger Zr(Nb,Fe) ₂ Laves phase SPPs.....	77
Figure 6.2 In-chamber camera images of typical experimental configurations for (a) FSD imaging mode, (b) transmission Kikuchi diffraction mode.....	78

Figure 6.3 (a, c and d) Schematic views of the OPTIMUS TM head working in the FSD imaging mode identifying the key parameters; detector size, working distance (d_w), detector distance (d_d) and collection angles (β_1 and β_2). The intensity distribution of transmitted electrons shown in colour gradients is drawn schematically according to electron trajectories from Monte Carlo simulations. (b) an enlarged image showing the configurations of the OPTIMUS TM head [261].	79
Figure 6.4 Cross-sectional view of the 3D sample model and typical electron trajectories (200 electrons are shown) simulated by the Monte Carlo method.	81
Figure 6.5 Monte Carlo simulations showing (a) angular distributions of foreshattered electrons and (b) images formed at 30 kV accelerating voltage and by collecting (b-1) secondary electrons (SE), (b-2) backscattered electrons (BSE) and (b-3) foreshattered electrons (FSE) within 0-100 mrad, and (b-4) FSE over 400-500 mrad respectively.	83
Figure 6.6 (a) Monte Carlo simulations showing contrast inversions as a function of collection angles and accelerating voltages. (b) examples of simulated images using electrons scattered in the range 300-400 mrad.	84
Figure 6.7 Calculated energy distributions of transmitted electrons as a function of incident electron beam energy.	85
Figure 6.8 (a) Monte Carlo simulations showing the imaging contrast when using HAFSD to image the Nb-particle embedded in a Zr matrix as a function of FSD detector distances and accelerating voltages and (b) polynomial fitting curve of critical detector distance (d_d^*) as a function of accelerating voltages to show Z-contrast. ...	85
Figure 6.9 (a) HAFSD and LAFSD images of the same region in a Zr-Nb sample using different detector distances and acceleration voltages, (b) the measured contrast of the same particle highlighted by yellow arrows in (a) at different detector distances. ...	87
Figure 6.10 (a) a transmission Kikuchi pattern acquired at a detector distance of 20 mm and 30 keV and (b) a schematic showing the angular range of the foreshattered electrons.	88
Figure 6.11 Comparisons of the contrast of embedded Nb particles in the Zr-Nb sample imaged by (a, d) FSD in an SEM at 30 kV, $d_d = 20$ mm, (b, e) BF and HAADF STEM in a STEM at 200 kV and (c) BF TEM at 200 kV.	89
Figure 6.12 An example of LAFSD ($E_0 = 30$ keV, $d_d = 20$ mm) image showing the microstructure of Zr-2.5Nb. Features such as dislocations (red arrows) and second phase (yellow arrows) are highlighted.	90
Figure 6.13 (a, b) BF and DF images using foreshattered electrons and showing the size and distribution of Nb particles. (c, d, e and f) TKD band contrast (BC) and phase maps from scanning the same region of the Zr-Nb sample in both directions. The corresponding thickness profile of the mapped region is plotted in (a).	97

Figure 6.14 Frequency distribution of mean angular deviation (MAD) from the region highlighted by the white rectangle in Figure 6.13(e) (blue bars), and from the surrounding matrix (yellow bars) of a region of the same size.	99
Figure 6.15 The influence of overlapping phases on Kikuchi patterns. (a) and (b) are the HAFSD image and TKD phase map showing the locations from which Kikuchi patterns were acquired. (c) is a schematic cross-sectional view of the TEM foil showing possible locations of 3 selected particles. (d, e, f and g) show the details of Kikuchi patterns obtained from the locations of these 3 particles and from the surrounding matrix. Kikuchi bands from the β -Nb phase are highlighted by the red dashed lines and α -Zr by yellow dashed lines.	101
Figure 6.16 Kikuchi patterns from a Zr-Nb sample from regions of different thickness.	101
Figure 6.17 Schematic of the correlation between the depth of Nb particles in an electron transparent Zr thin foil and their visibility in TKD mapping at 30 kV	103
Figure 6.18 TKD band contrast maps scanned from opposite sides of the same region in a nano-crystalline zirconium oxide showing different grain structures.....	103
Figure 6.19 Schematic diagrams showing multiple scattering processes in a crystal contributing to the formation of Kikuchi bands (red), diffraction spots (black) and the background (blue). The fan-shaped diffuse scattering represents the intensity angular distribution of the TDS electrons.....	104
Figure 7.1 (a, d) On-axis TKD band contrast and phase maps from the whole oxide layer on the Zr-0.5Nb tube sample, (b, e) off-axis TKD band contrast and phase maps from inner part of oxide layer on the Zr-1Nb tube sample and (c, f) on-axis TKD band contrast and phase maps from the whole oxide layer on the Zircaloy-4 sheet sample.	112
Figure 7.2 Combined TKD m-ZrO ₂ texture component and band contrast map for (a) Zr-0.5Nb, (b) Zircaloy-4 and (c) Zr-1Nb alloy samples. The grains are coloured according to the angular deviation of their (104) poles from the RD. (d) Statistical angular of the frequencies of grains with the (104) poles deviating away from the RD.	113
Figure 7.3 Contoured (104) poles (half width 20°) of all the m-ZrO ₂ grains and (0002) poles (half width 10°) of the underlying α -Zr substrates viewed along the oxide growth direction for (a) Zr-0.5Nb tube, (b) Zircaloy-4 sheet and (c) Zr-1Nb tube samples.	115
Figure 7.4 Enlarged TKD maps of the oxide/metal interface region in the Zr-0.5Nb tube sample, (a) band contrast map with schematic crystalline orientation of the substrate, (b) phase map and (c) texture component maps for m-ZrO ₂ , h-ZrO and α -Zr. The grains are coloured according to their angular deviation from the RD. (d) statistics and legend showing the frequencies of angular deviations away from the RD.....	117

Figure 7.5 Contoured distributions of low index poles (half width 10°) from the α -Zr substrate, h-ZrO and adjacent m-ZrO ₂ near the oxide/metal interface in Zr-0.5Nb tube.	118
Figure 7.6 TKD maps of the O/M interface region in the Zr-1Nb sample (a) band contrast map with schematic crystalline orientation of the substrate, (b) phase map and (c) IPF Y map with the corresponding legend for h-ZrO and α -Zr, (d) texture component map where the grains are coloured according to their angular deviation from the radial direction shown in (e). (e) the frequencies of angular deviations away from the RD.	119
Figure 7.7 Contoured distributions of low index poles (half width 10°) from the α -Zr substrate, h-ZrO and adjacent m-ZrO ₂ near the oxide/metal interface in Zr-1Nb tube.	120
Figure 7.8 Selected pole figures from grain-by-grain analysis showing the orientation relationships between individual h-ZrO suboxide grains and the underlying α -Zr substrate in the (a, b) Zr-0.5Nb, (c) Zr-1Nb and (d) Zircaloy-4 samples.	121
Figure 7.9 Contoured distributions of poles (half width 5°) comparing the position of $\{0002\}_{\text{Zr}}$, $\langle 11\bar{2}0 \rangle_{\text{h-ZrO}}$ and $\{11\bar{2}0\}_{\text{h-ZrO}}$, $\langle 0002 \rangle_{\text{h-ZrO}}$ from region 12 in the Zr-0.5Nb sample. The literature [27, 35] proposed that these poles are perfectly aligned.	124
Figure 7.10 MLLS Fitted EELS spectra map showing the positions of oxide, suboxide and metal substrate on the Zr-1Nb alloy sample.	126
Figure 7.11 (a) Reconstructed atomic arrangements (single stacking plane shown) of the h-ZrO/ α -Zr interface for the Zircaloy-4 sample based on TKD phase and IPF maps. (b) pole figures of the h-ZrO suboxide and α -Zr from the region of interest. To reveal the interface atomic arrangement more clearly, I have manually adjusted the Euler angles for both phases (from $\phi_1=11.4^\circ$, $\psi=100.5^\circ$, $\phi_2=30.7^\circ$ to $\phi_1=1.3^\circ$, $\psi=90.7^\circ$, $\phi_2=28.7^\circ$) so that the α -Zr grain can be orientated with (0002) in the centre of the stereographic projection.	127
Figure 7.12 (a) Reconstructed atomic arrangements(single stacking plane shown) of the h-ZrO suboxide and α -Zr based on the TKD phase and IPF maps for the Zr-1Nb sample. (b) pole figures of the h-ZrO suboxide and α -Zr from the region of interest. To reveal the interface atomic arrangement more clearly, I have manually changed the Euler angles (from $\phi_1=77.8^\circ$, $\psi=104.1^\circ$, $\phi_2=3^\circ$ to $\phi_1=89.2^\circ$, $\psi=-89.6^\circ$, $\phi_2=59^\circ$) so that the underlying α -Zr grain can be orientated with [0002] at the centre of the stereographic projection.	128
Figure 7.13 MLLS Fitted EELS spectra maps showing the shape of suboxide grains in different alloys, (a) recrystallized Zircaloy-4 sheet (106-day corrosion, oxide thickness $\sim 2.6\mu\text{m}$), (b) recrystallized Zr-0.5Nb tube (105-day corrosion, oxide thickness $\sim 2.5\mu\text{m}$).	130

Figure 8.1 Morphologies and distributions of oxide cracks on (a) 61-day Zircaloy-4, (b) 75-day Zr-0.5Nb and (c) 165-day Zr-0.5Nb samples. The oxide/metal interfaces are indicated by dashed lines, and examples of cracks by yellow arrows.	135
Figure 8.2 Morphologies and distributions of micro-cracks and nano-porosity in the outer oxide layer on the 61-day Zircaloy-4 sample	136
Figure 8.3 Morphologies and distributions of oxide cracks on (a) 150-day, (b) 700-day and (c) 2000-day CNL Zr-2.5Nb samples. The oxide/metal interfaces are indicated by dashed lines, and examples of cracks by yellow arrows.....	138
Figure 8.4 TEM Fresnel imaging showing the distributions of nano-porosity as function of depth in the oxide on three Zr alloys; (a) 75-day Zr-0.5Nb, (b) 165-day Zr-0.5Nb and (c) 61-day Zircaloy-4. Nano-pores/pipes are highlighted by red arrows and the metal-oxide interface is highlighted by the yellow dashed line. The proposed ranges of protective and non-protective oxide is marked on top of the images.	141
Figure 8.5 Stitched Fresnel contrast ($\Delta f = -2000\text{nm}$) TEM images showing the distribution and morphologies of nano-porosity in the outer oxide layer on the 700-day Zr-2.5 sample	142
Figure 8.6 Stitched Fresnel contrast ($\Delta f = -2000\text{nm}$) TEM images showing the distribution and morphologies of nano-porosity in the inner oxide layer on the 700-day Zr-2.5 sample	143
Figure 8.7 Nano-porosity density as function of the distance from the oxide/metal interface in Zr-0.5Nb samples exposed for 75 days ($\sim 2\mu\text{m}$ oxide thickness) and 165 days ($\sim 3\mu\text{m}$ oxide thickness).	144
Figure 8.8 Ingress of water molecules into a nano-pipe of ZrO_2 and H_2 diffusion. (a) model of a nano-pipe in t- ZrO_2 with water at 550 K and 150 bar; (b) ingress of water into nano-pipes after 50 ps; (c) generation of molecular H_2 by reaction of water with vacancies in side walls; (d) diffusion of H_2 molecules into the nano-pipe of about 0.5 nm width [143].....	147
Figure 8.9 Energies of dissociation and barriers of H_2 into Zr and its suboxides [143].	148
Figure 8.10 Nano-pores and nano-pipes distribution in ZrO_2 corrosion films. (a) Schematic of the nano-pore and nano-pipes size and distribution in the oxide layer. (b) shows magnified images of nano-pores and nano-pipes in the protective oxide near the metal-oxide interface. (c) shows the proposed mechanism for H uptake.	149
Figure 9.1 High-resolution mass spectra from a deuterated zirconium sample showing the separation of $^2\text{H}^-$ and H_2^- peaks [236].....	152
Figure 9.2 Distribution of $^2\text{H}^-$ and $^{18}\text{O}^-$ in a 61-day Zircaloy-4 sample (a) 1D depth profiles, (b) the 3D deuterium distribution and (c) is a magnified image from the red box in (b) showing the interconnected pathways for deuterium.....	153

Figure 9.3 Distributions of $^1\text{H}^-$ and $^2\text{H}^-$ in a 700-day Zr-2.5Nb sample (a) 1D depth profiles, (b) the 3D deuterium distribution 153

Figure 9.4 Correlating locations of deuterium hot spots, cracks and iron-containing SPPs. (a) the SEM image of a crater bottom in the middle of the oxide layer on the 61-day deuterated Zircaloy-4 sample. (b) EDX mapping of the positions of iron-containing SPPs (magenta spots) on the crater surface in (a). (c) is an accumulated $^2\text{H}^-$ ion image from the last 40 planes (~ 20 nm thick). (d) from the last 4 planes (~ 2 nm thick). 155

Figure 9.5 Schematic of suggested hydrogen outgassing and diffusion processes during Cs^+ primary ion bombardment. Courtesy of Dr. Kexue Li..... 155

Figure 9.6 Intensity of $^2\text{H}^-/^1\text{H}^-$ ratios as a function of NanoSIMS analysis geometries (in-depth and cross-sectional) and materials. Note that the resin is only included in the cross-sectional samples. Plotting data supplied by Dr Kexue Li..... 158

Figure 10.1 TKD band contrast (left column) and texture component (middle column) maps for oxides formed on CNL Zr-2.5Nb tubes (a) In-flux, 190 days, 7.6×10^{20} n.cm $^{-2}$, (b) Out-of-flux, 185 days, (c) autoclave, 150 days and (d) autoclave, 700 days. The white arrows in (a and b) show the regions of oxidised β -Zr. The grains in the texture component maps are coloured according to the angular deviation of their $(104)_{\text{m-ZrO}_2}$ poles from the RD. $(104)_{\text{m-ZrO}_2}$ pole figures and statistics showing the frequencies of grains with the (104) poles deviating with specific angular ranges away from the RD are shown in the right column..... 163

Figure 10.2 In-situ TEM images showing the microstructure of oxide, suboxide and metal substrate in the Zr-0.5Nb alloy (A-9) at different damage levels: (a) pre-irradiation (b) 10^{14} ions/cm ^{2} , the corresponding damage levels in dpa are also shown on the right, (c) pre-irradiation HAADF STEM image and (d) O/Zr atomic ratio map from EELS analysis of the region followed during in-situ irradiation. 166

Figure 10.3 HRTEM images and FFTs from the O/M interface regions on Zr-0.5Nb samples (A-9), (a) pre-irradiation, (b) irradiated at 293 K to 1.9×10^{16} ions.cm $^{-2}$ and (c) irradiated at 50 K to 4×10^{15} ions.cm $^{-2}$ 166

Figure 10.4 (a) low magnification bright field TEM image showing the m-ZrO $_2$, h-ZrO suboxide and α -Zr(O $_{\text{Sat}}$) after irradiation to 8.4×10^{15} ions/cm ^{2} (13dpa in h-ZrO) on Zr-0.5Nb alloy (A-9). (b) HRTEM and FFT from the region of m-ZrO $_2$ identified in (a). (c and d) HRTEM and FFT from the identified regions of α -Zr(O $_{\text{Sat}}$) and h-ZrO suboxide..... 167

Figure 10.5 HRTEM analysis after irradiation to 8.4×10^{15} ions/cm ^{2} showing the occurrence of amorphization only in the h-ZrO grain on the Zr-0.5Nb alloy (A-9). 168

Figure 10.6 HAADF STEM images from the same area of (a) pre-irradiation and (b) post-irradiation samples, Zr-0.5Nb alloy (A-9). (c) Comparison of oxygen

concentrations in the suboxide grains pre- and post-irradiation calculated from EELS spectra acquired	168
Figure 10.7 BF TEM images and corresponding SAD patterns showing the microstructural evolution of the oxide on Zr-0.5Nb sample (A-16) under 700 keV Kr ⁺⁺ irradiation at 293K (a) 0 dpa, (b) 3 dpa (5.6x10 ¹⁵ ions.cm ⁻²) and (c) 10 dpa (1.9x10 ¹⁶ ions.cm ⁻²).	172
Figure 10.8 Electron diffraction profiles of (a) simulated crystals and (b) experimental patterns after specimens are irradiated by 700 keV Kr ⁺⁺ at 293 K to different damage levels; pre-irradiation, 5.6x10 ¹⁵ ions.cm ⁻² (3 dpa) and (c) 1.9x10 ¹⁶ ions.cm ⁻² (10 dpa)	174
Figure 10.9 Two examples of SADs acquired at different tilt angles, (a) Tx=3°, Ty=-1.8°, (b) Tx=-7.6°, Ty=3.5° and (c) the BF TEM image showing the corresponding SAD region from the oxides on the Zr-0.5Nb sample (A-16), 1.9x10 ¹⁶ ions.cm ⁻² (10 dpa).	175
Figure 10.10 (a) Atomic-resolution HAADF STEM image from an oxide grain post-irradiation, 1.9x10 ¹⁶ ions.cm ⁻² (10 dpa), with corresponding FFT from the whole region, (b) direct measurement of lattice parameters based on the HAADF STEM images.	176
Figure 10.11 TKD pattern quality and phase maps from typical regions of in-situ irradiated oxides on the Zr-0.5Nb specimens (A-16). (a and d) 0 dpa, (b and e) 4 dpa, 7.4x10 ¹⁵ ions.cm ⁻² and (c and f) 10 dpa, 1.9x10 ¹⁶ ions.cm ⁻²	178
Figure 10.12 TKD pattern quality, phase maps and pole figures and stereographic projections (half width 5°) of the same region before and after in-situ irradiation. (a) 0 dpa, (b) 4 dpa, 7.4x10 ¹⁵ ions.cm ⁻²	179
Figure 10.13 Contoured pole maps and stereographic projections from (a) (100) and [001] monoclinic-ZrO ₂ in the pre-irradiation specimen compared to (b) (100) and [001] cubic-ZrO ₂ in the post-irradiated specimen (4 dpa, 7.4x10 ¹⁵ ions.cm ⁻²) from all the grains shown in Figure 10.12, half width 10°.	180
Figure 10.14 Fresnel contrast (±500 nm) bright field TEM images of the same region in the oxides on the Zr-0.5Nb specimen (A-16) showing distributions of voids at different in-situ irradiation doses; (a) 0 dpa, (b) 1 dpa, 1.9x10 ¹⁵ ions.cm ⁻² and (c) 10 dpa, 1.9x10 ¹⁶ ions.cm ⁻² . Examples of voids are highlighted by yellow circles in both the overfocused and underfocused images of the 10 dpa sample.	181
Figure 10.15 High-magnification HAADF image showing irradiation-induced voids and the corresponding EDX spectra from a void and an adjacent region of the matrix in the 10 dpa specimen (voids are darker in the dark field mode because the surrounding area has a higher average atomic mass).	183
Figure 10.16 Reconstructed atomic arrangements (only Zr cations are shown) in the (100) plane of (a) monoclinic-ZrO ₂ and (b) cubic-ZrO ₂ . The lattice parameters for the	

monoclinic phase are taken from [202] and for the cubic phase from experimental measurements in the current work. 184

Figure 10.17 Fresnel contrast (± 500 nm) bright field TEM images showing distributions of nano-porosity and voids in zirconia oxides formed on Zr alloys (a) 2000-day autoclave-corroded samples and (b) 2700-day in-reactor corroded sample (10^{22} n.cm⁻², ~8 dpa). Examples of grain boundary nano-porosity formed during corrosion are highlighted by yellow arrows and irradiation-induced voids in the grain interior by blue circles. 189

LIST OF ABBREVIATIONS

ADF	Annular Dark-Field
AEM.....	Analytical Electron Microscopy
AGR.....	Advanced Gas-cooled Reactor
APT.....	Atom Probe Tomography
AS	Aperture Slit
At %	Atomic Percentage
BF.....	Bright Field
BSE	Backscattered Electrons
BWR	Boiling Water Reactor
DF	Dark Field
DPA	Displacement Per Atom
EBSD	Electron Backscatter Diffraction
EDX	Energy Dispersive X-Ray
EELS.....	Electron Energy Loss Spectroscopy
ES.....	Entrance Slit
FCC.....	Face Centered Cubic
FEG.....	Field Emission Gun
FFT.....	Fast Fourier Transform
FIB	Focussed Ion Beam
FSD	Foreshattered Electron Detectors
FSE.....	Foreshattered Electrons
HAADF.....	High-Angle Annular Dark-Field
HCP.....	Hexagonal Close Packing
HPUF	Hydrogen Pick-Up Fraction
IIG	Irradiation Induced Growth
IPF.....	Inverse Pole Figure
LWR.....	Light Water Reactor
MAD	Mean Angular Deviation
MUZIC.....	Mechanistic Understanding of Zirconium Corrosion
O/M.....	Oxide/Metal

O/W.....	Oxide/Water
PKA	Primary Knock-On Atom
PWR.....	Pressurized Water Reactor
RXA	Recrystallization Annealing
SAD	Selected Area Diffraction
SE.....	Secondary Electrons
SEM	Scanning Electron Microscopy
SIMS	Secondary Ion Mass Spectrometry
SNR.....	Signal-To-Noise Ratios
SPP.....	Second Phase Particles
SRA.....	Stress Relief Annealing
STEM.....	Scanning Transmission Electron Microscopy
TDS.....	Thermal Diffuse Scattering
TEM	Transmission Electron Microscopy
TKD	Transmission Kikuchi Diffraction
TKP	Transmission Kikuchi Pattern
Wt %	Weight Percentage
XRD	X-ray Diffraction

Chapter 1 Introduction

This chapter will present an overview on the background of this project. I will start with an introduction to the UK's power policies and market. Due to the desire to have reliable, cheap and low-carbon energy supplies, the UK has commenced the construction on a new generation of light water reactors, in which zirconium alloys will be used as the fuel cladding materials. A brief introduction to zirconium alloys in the nuclear industries is then given, and this chapter will end with an overview on the objectives of this project.

1.1. Nuclear Power in the UK

In the UK, electricity is generated mainly from; fossil fuels, nuclear and renewable energy. The UK has legally binding carbon reduction commitments under the Climate Change Act 2008 to implement an 80% reduction in the 1990 level of greenhouse gas emission by 2050. Fossil fuels are not carbon clean sources of power generation but account for ~50% of the electricity generated in the UK. In order to meet the UK's carbon reduction targets and achieve an energy mix that produces less CO₂, the government must continue to investigate ways in which to make the power generation cleaner, cheaper and safer.

Figure 1.1 shows the electricity generated by different sources in the UK from 2008 to 2018, and we can see significant progress against the decarbonisation targets has been made over the time. More than 75% of the UK's electricity was produced by burning fossil fuels in 2008, which was reduced to <45% in 2018 [1]. Nuclear power is expected to play an important role in the transition to a low carbon, smarter and flexible electricity market. The UK now has 15 reactors (with a total capacity of ~8.88MWe) generating about 21% of its electricity, but almost half of this capacity is to be retired by 2025 and 14 of them will be shutdown by 2030 [2], Table 1.1. As the older nuclear plants are being retired, several

companies are planning to build a new generation of reactors to replace them, and the first one by EDF energy is expected to be connected to the UK National grid by 2026 [2]. A total of 10 new reactors has been proposed to be built in the next decade which can provide a capability of 14000 MWe, ~1.6 times the present capacities.

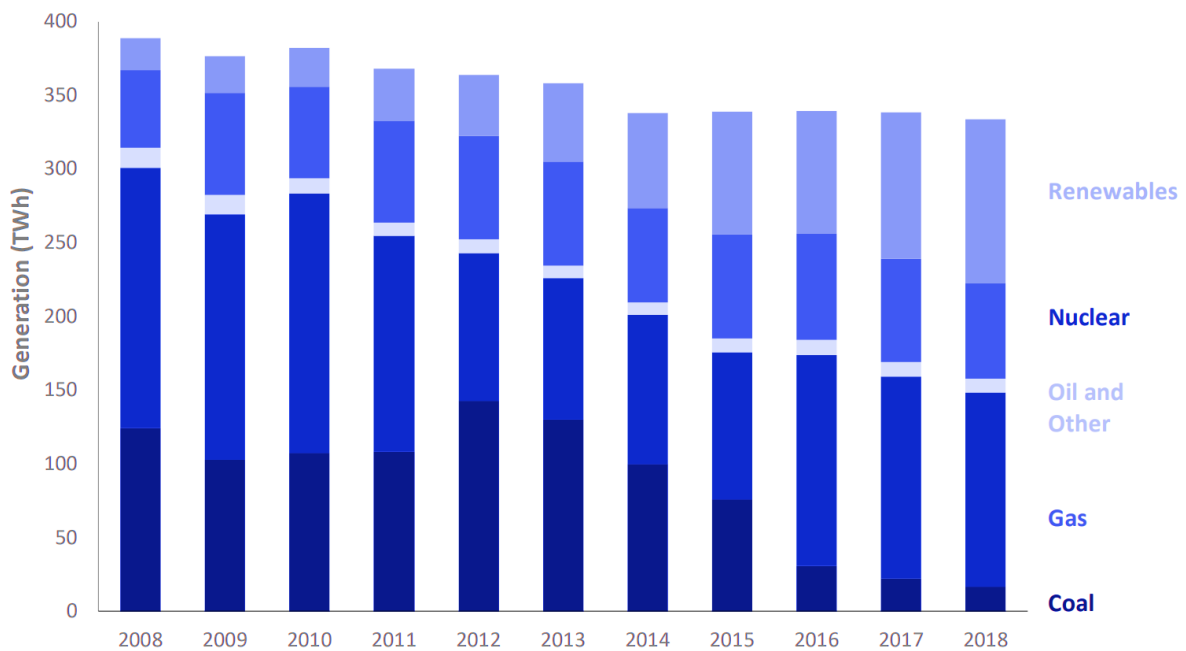


Figure 1.1 Electricity generated by sources in the UK [1]

Table 1.1 Nuclear power reactors operating in the UK [2]

Plant	Type	Present capacity (MWe)	First power	Expected shutdown
Dungeness B 1&2	AGR	2 x 520	1983 & 1985	2028
Hartlepool 1&2	AGR	595, 585	1983 & 1984	2024
Heysham I 1&2	AGR	580, 575	1983 & 1984	2024
Heysham II 1&2	AGR	2 x 610	1988	2030
Hinkley Point B 1&2	AGR	475, 470	1976	2023
Hunterston B 1&2	AGR	475, 485	1976 & 1977	2023
Torness 1&2	AGR	590, 595	1988 & 1989	2030
Sizewell B	PWR	1198	1995	2035
Total:	15 units		8883 MWe	

Table 1.2 Nuclear power reactors planned and proposed in the UK [2]

Proponent	Reactor/site	Locality	Type	Capacity (MWe)
EDF Energy	Hinkley Point C1	Somerset	EPR	1720
	Hinkley Point C2	Somerset		1720
	Sizewell C1	Suffolk		1670
	Sizewell C2	Suffolk		1670
China General Nuclear	Bradwell B1	Essex	Hualong One PWR	1150
	Bradwell B2	Essex		1150
Horizon (Suspending)	Wylfa Newydd 1&2	Wales	ABWR	2760
	Oldbury B1&B2	Gloucestershire		2760
Total	10 units		14000 MWe	

One important point is that the UK currently operates mainly old advanced gas-cooled reactors (AGR), fundamentally different from the next generation of the UK nuclear power stations, which will be light-water reactors (LWRs), Table 1.1 and 1.2. In terms of this research project, zirconium alloys are the preferred fuel cladding material in LWRs, and one of the main drivers to improve the efficiency of future reactors is to keep the fuel rods for more severe duty cycles, including longer in-core residence times to achieve higher burn-up fraction and so increase the energy extracted from the uranium fuel and reduce the amount of waste produced.

1.2. Zirconium in the Nuclear Industry

The basic principle of LWRs is the nuclear fission reaction involving a large fissile nucleus (e.g. ^{235}U , $^{235}\text{UO}_2$ and ^{239}Pu) and neutrons. By capturing neutrons, the heavy nucleus then decomposes into lighter nuclei, releasing more neutrons carrying a large amount of energy. The energy released in the fission process generates heat, some of which can be used to boil water to produce pressurized steam which will then drive a steam turbine, turn an alternator and generate electricity, Figure 1.2.

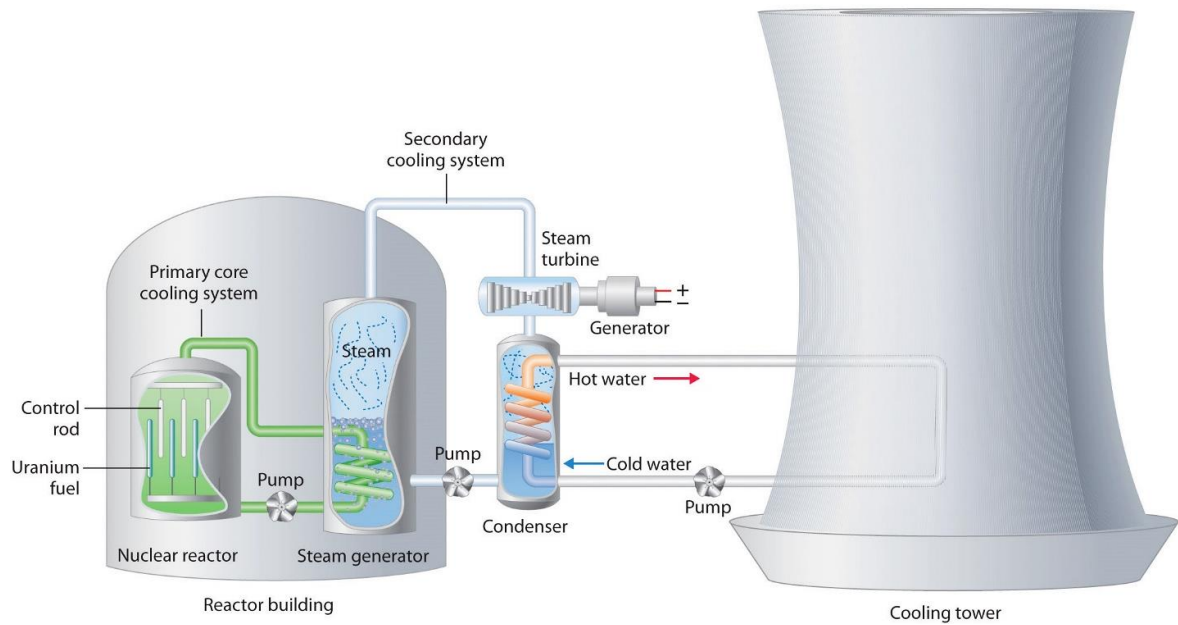


Figure 1.2 A schematic of Light-Water Nuclear Reactor (Reprinted from [3] licensed by CC BY-NC-SA 3.0).

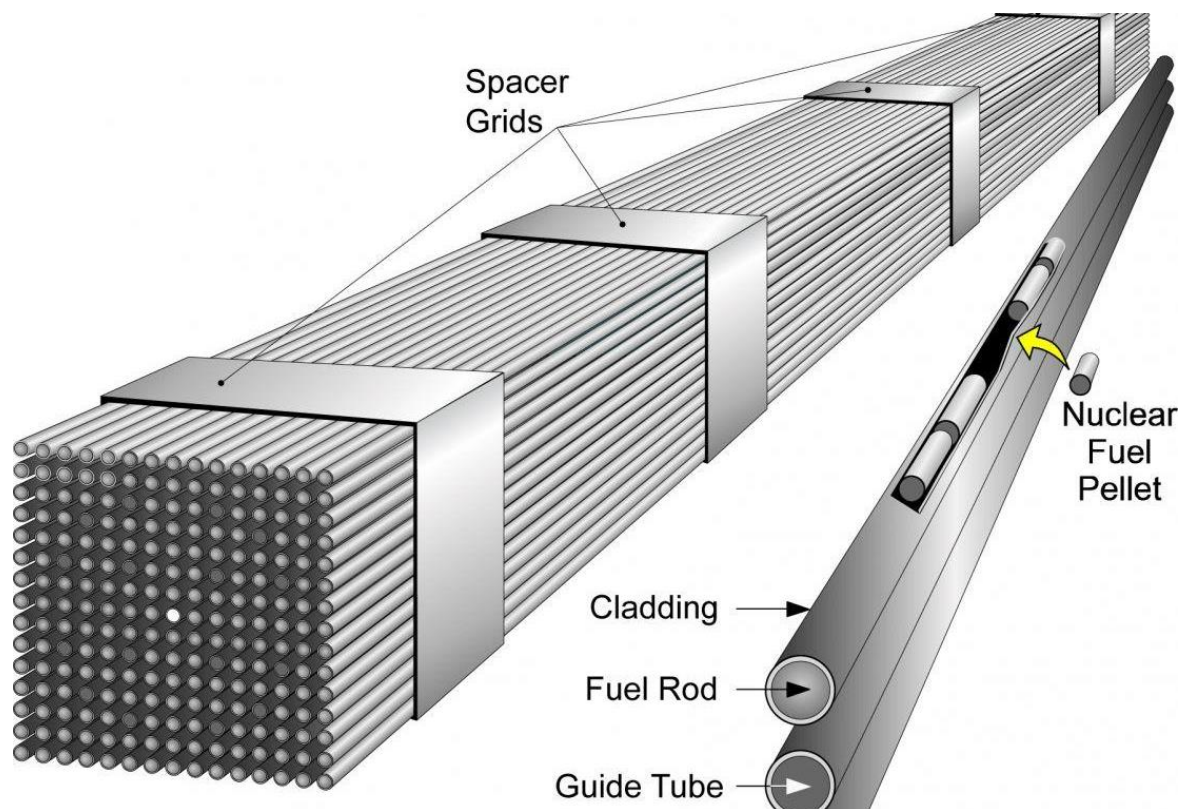


Figure 1.3 An example of LWR fuel assemblies (image downloaded from <https://www.wrvo.org/post/fitzpatrick-nuclear-power-plant-experiences-leak-within-facility>).

Zirconium alloys have been used as the cladding material in LWRs, which plays an important role as it separates the nuclear fuel and the coolant water, and hence inevitably also retains most of the radioactive fission products, Figure 1.3. The decision to choose Zr alloys as cladding material is based on an attractive combination of low thermal neutron absorption cross section, ~ 0.185 barns [4], and ‘adequate’ high-temperature corrosion resistance and reliable mechanical properties [5]. Since it was first used as cladding material in the 1950s, Zr alloys have been subject to an intense evolution, and many commercial zirconium alloys involved in different manufacturing processes and with different alloying elements such as Zircaloy-2, Zircaloy-4, ZIRLO™, M5™ and E110 have been developed, enabling a large increase in fuel duty (lifetime, temperature, surface heat flux and fast neutron fluence), Figure 1.4.

Some common LWR cladding alloys are shown in Table 1.3. All contemporary LWR fuel claddings contain 97–99% zirconium, with additional minor additions of alloying elements like Sn, Nb, Fe and Cr added to optimize the desired corrosion and mechanical properties.

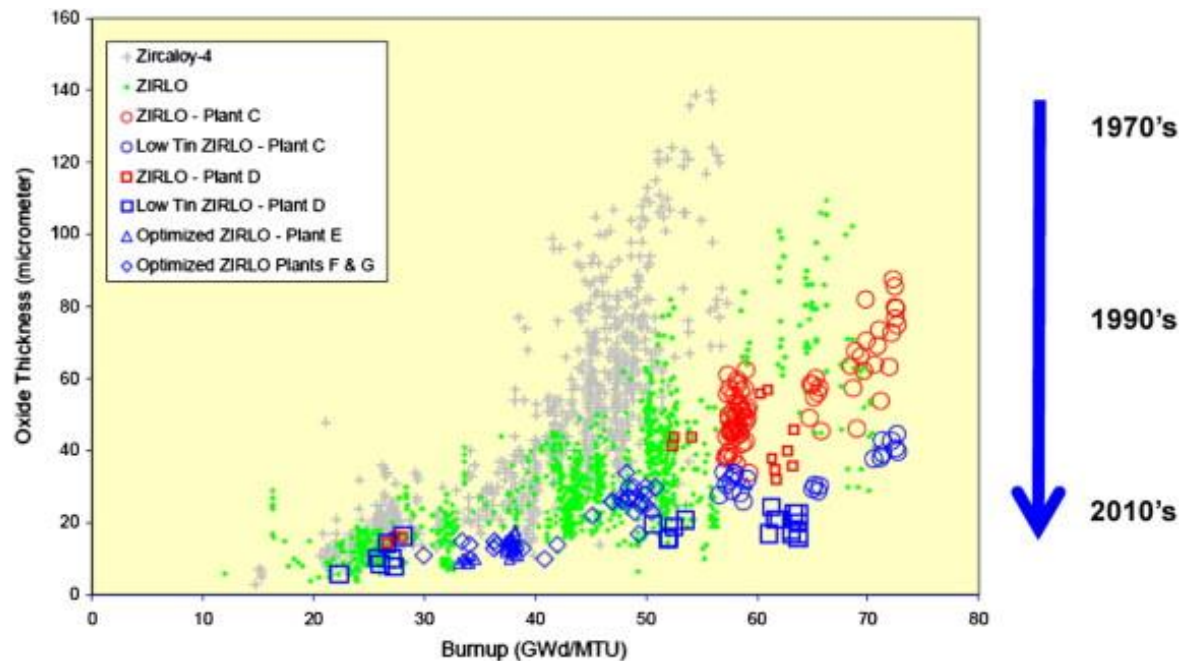


Figure 1.4 Evolution of corrosion performance of PWR cladding materials (Reprinted from [6], Copyright (2019) with permission from Elsevier).

Table 1.3 Composition range of alloying elements in standard Zr alloys (wt%) (Adapt from [7], courtesy of the A.N.T. International).

	Alloy	Sn	Nb	Fe	Cr	Ni
Zr-Sn	Zircaloy-2	1.2-1.7	-	0.07-0.2	0.05-0.15	0.03-0.08
	Zircaloy-4	1.2-1.7	-	0.18-0.24	0.07-0.13	-
	Zr-Sn	0.25	-	0.03-0.06	-	-
	Low-Sn Zircaloy-4	1.3	-	0.18-0.24	0.07-0.13	-
Zr-Nb	M5 TM	-	0.8-1.2	0.015-0.06	-	-
	E110	-	0.9-1.1	0.014	<0.003	0.0035
	E125	-	2.5	-	-	-
	Zr2.5Nb	-	2.4-2.8	<0.15	-	-
Zr-Sn-Nb	ZIRLO TM	1	1	0.1	-	-
	Low-Sn ZIRLO	0.7	1	0.1	-	-
	E635	1.3	1	0.4	-	-

1.3. Objectives

To develop new cladding alloys for higher fuel burn-ups, a model describing their degradation mechanisms, especially under irradiation, is needed. If this can be achieved then it may be possible to improve the safety and efficiency of nuclear power generation, whilst reducing the cost of nuclear power both financially and in terms of radioactive waste produced and carbon emissions saved.

In order to contribute to the understanding of the degradation mechanisms under irradiation, this project focuses on investigating the texture development and irradiation-response of zirconium oxides, and studies the possible role of oxide nano-porosity as a transport path for hydrogen through the oxide.

The literature review in Chapter 2 covers a wide range of studies on the degradation of zirconium alloys from corrosion, hydrogen pickup and irradiation damage. Most of studies of irradiation effects in the literature focus on the metal matrix of the Zr alloys, with little focus on radiation damage in the oxide layers that form on them, so my project aims to contribute to the understanding of the corrosion processes of in-service zirconium alloys with an emphasis on the study of oxide degradation under irradiation.

The oxide grown on zirconium alloys has a very complex microstructure which challenges the capabilities of techniques employed to study it. In Chapter 3, an overview is given of techniques used in the study; Focused Ion Beam (FIB), Electron Backscatter Diffraction (EBSD), Transmission Kikuchi Diffraction (TKD), Transmission Electron Microscopy (TEM), in-situ TEM and High Resolution Secondary Ion Mass Spectrometry (NanoSIMS). FIB was used extensively to prepare samples for TKD and TEM characterisation. These novel sample preparation methodologies are introduced in Chapter 5. EBSD and TKD were used to provide orientation/grain morphology information on the metal matrix and oxides, and two technical manuscripts were drafted and form the basis of Chapter 6 with the aim of contributing to the development and applications of TKD. In-situ irradiation in a TEM was used to dynamically follow irradiation-induced damage mechanisms. NanoSIMS was used to map the distribution of hydrogen/deuterium in the oxide and metal matrix.

Detailed information on the selected Zr alloys, comparison of their corrosion performance and characterisation of as-received materials are included in Chapter 4. The microstructure of the oxide has been found to directly affect the corrosion performance of zirconium alloys, and exploring the texture and morphologies of oxides formed during autoclave corrosion is the focus of Chapter 7. Based on these results, a formation mechanism for oxide/suboxide texture, and its impact on corrosion rates is proposed. In Chapters 8, 9 and 10, I have compared the oxide texture and morphologies on Zr alloys formed under in-reactor conditions with that formed in autoclaves and also from in-situ irradiation. Irradiation-induced damage in Zr oxides and its impact on corrosion rates and hydrogen pick-up are discussed based on the results. Chapter 11 summarizes the achievements and major conclusions of the work reported, and makes some suggestions for future works that could improve our understanding of the correlation between microstructures and performance of Zr alloys in service.

Chapter 2 Literature Review

2.1. Autoclave Corrosion

2.1.1. Corrosion mechanisms

Since the free energy of formation of zirconium oxide is large and negative (<-900 kJ/mol) [8], zirconium metal easily reacts with oxygen to form an oxide layer. An activity/potential gradient will then be established between the two sides of the oxide layer, oxide/water (O/W) and oxide/metal (O/M) interfaces, which further drives the transport of the species across the oxide film.

The overall corrosion reaction for Zr can be written as:



Over the years, there have been many reviews focusing on zirconium alloy corrosion [9-11]. Oxidation in the presence of a protective oxide layer can be conceptually divided into several steps, Figure 2.1, as reviewed by Couet et. al. [12]. First, oxygen in the water molecule dissociates and is adsorbed onto the oxide layer surface at an oxygen vacancy, Reactions 1 and 2. Because of the activity/potential/defect gradient, the oxygen anions diffuse across the oxide film, and when they reach the oxide/metal interface they can react with Zr metal to form new oxide, Reactions 3 and 4. The formation of this new oxide releases electrons, Reaction 3, which then migrate through the oxide by a hopping mechanism to reduce the hydrogen ions at the cathodic site, Reaction 5. Most of hydrogen atoms at the external cathode will usually recombine to form H_2 molecules and diffuse into the environment, but some atoms may migrate into the Zr matrix, where they are found either in solid solution of α -Zr or as hydride precipitates. This phenomenon is called hydrogen pick-up.

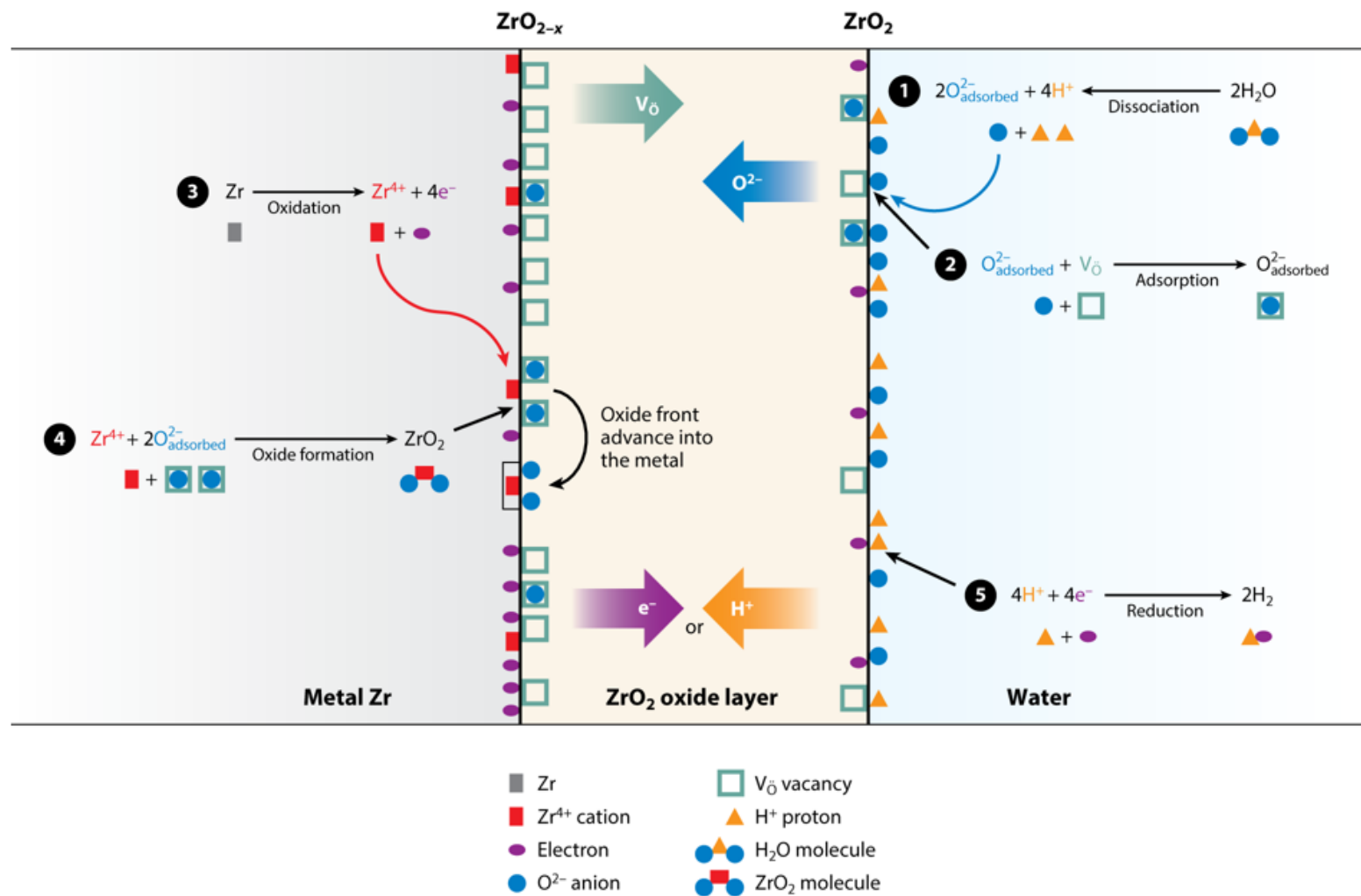


Figure 2.1 Schematic of the corrosion process in zirconium alloys (Republished with permission of Annual Reviews, Inc, from [11]; Copyright (2019) permission conveyed through Copyright Clearance Center, Inc.).

2.1.2. Weight gain

Because most oxygen absorbed by the metal forms an oxide, the weight gain (gained mass per unit area, mg/dm²) provides a measure of the thickness of the oxide scale and the degree of corrosion, allowing a convenient comparison of the kinetic behaviour of different alloys. Assuming that all oxygen that enters the layer reacts with Zr to form oxide, the weight of oxygen (W_O) required to form 1 cm³ of ZrO₂ will be,

$$W_O = 1 \text{ cm}^3 \times 5680 \frac{\text{mg}}{\text{cm}^3} (\text{theoretical density of ZrO}_2) \times \frac{m_{O_2}}{m_{ZrO_2}} = 1477 \text{ mg} \quad \text{Equation (2.2)}$$

The volume of 1 cm³ ZrO₂ equals 10² dm² × μm, thus one can conclude that 1 μm thickness of oxide formed is equivalent to a weight gain of 14.77 mg/dm².

2.1.3. Corrosion kinetics

The typical corrosion kinetics for Zr and its alloys in water are usually described as having two regimes; a sub-parabolic or cubic oxidation rate pre-transition regime and a post-transition regime with approximately linear rate [13]. The post-transition regime can be further distinguished as several periods of corrosion that reproduce the pre-transition regime, as shown in Figure 2.2. The kinetic transition usually occurs at an oxide thickness of 2 to 3 μm in Zr-Sn alloys [11]. Generally the metal and its alloys become covered with a friable grey oxide after transition instead of the black adherent film before transition [13-15]. Besides the macroscopic difference in colour, there are microstructural differences (oxide grain size, phases, cracking etc.) between the periodic oxide layers [15, 16].

The weight gain curves in the pre-transition regime can be fitted to the power law :

$$w = Kt^n \quad \text{Equation (2.3)}$$

where w is the weight gain (mg/dm²), K is a pre-exponential factor and t is the exposure time in days.

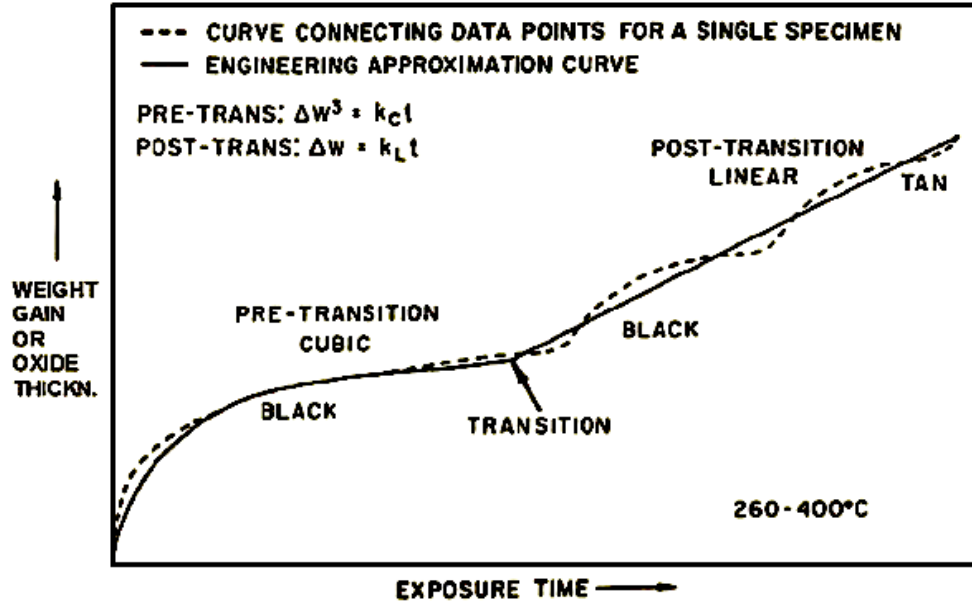


Figure 2.2 Typical oxidation kinetics of a Zr alloy (Reproduced, with permission from [13], copyright ASTM International, 100 Barr Harbor Drive, West Conshohocken, PA 19428).

If we assume the rate-limiting step during the corrosion processes is the diffusion of oxygen ions through the oxide layer, a parabolic scaling law ($n=1/2$) describing the oxide thickness as function of temperatures and corrosion time can be achieved. The characteristic equations have been presented by Olander and Motta [17]. Given that the oxygen concentration at the oxide/water interface is kept constant at C_w , and C_M is the oxygen concentration at the oxide/metal interface, a diffusion flux of oxygen through an oxide layer of thickness δ results from the concentration gradient $C_w - C_M$. According to Fick's law, the oxygen flux in such a layer is:

$$J = \frac{D_0}{\delta} (C_w - C_M) \quad \text{Equation (2.4)}$$

where D_0 is the oxygen diffusion coefficient in the oxide layer (cm^2/s).

The number of oxygen atoms diffused through an unit sample area in an increase of time (dt) can be expressed as Jdt . These oxygen atoms can lead to the increase of oxide thickness by $d\delta$ at the concentration C_M . Thus this condition can be expressed as:

$$Jdt = C_M d\delta \quad \text{Equation (2.5)}$$

Substituting Fick's law for the flux,

$$\frac{d\delta}{dt} = \frac{J}{C_M} = \frac{D_0}{\delta} \frac{(C_W - C_M)}{C_M} \quad \text{Equation (2.6)}$$

This equation can be integrated to yield,

$$\delta = K_P t^{1/2} \text{ where } K_P = \sqrt{\frac{2D_0(C_W - C_M)}{C_M}} \quad \text{Equation (2.7)}$$

The parabolic scaling constant K_P is a function of both temperature and the oxide microstructure.

Yilmazbayhan [18] reported the pre-exponential factors and the exponent n for various zirconium alloys by fitting weight gain data as function of exposure time, Table 2.1. The average n values for each series of alloys ranged from 0.18 to 0.45. Pure zirconium rarely shows protective corrosion with immediate transition or breakaway [14], while Zr-0.5X (X=Fe, Cr, Cu, Sn) alloys exhibit one transition and then breakaway [19]. Most commercial zirconium alloys (ZIRLO™, M5™, Zircaloy-4, Zr-2.5Nb etc.) exhibit multiple transitions before breakaway [11]. The ideal performance would be if the alloys could maintain protectiveness for indefinite periods and show no transitions or breakaway behaviour.

Hillner [13] proposed based on oxidation data on Zircaloy-2 and Zircaloy-4 that the pre-transition corrosion kinetics are cubic ($n=1/3$) and post-transition are linear with respect to time. Empirical relationships by Hillner [13] were proposed to be valid in the temperature range from 533 K to 673 K, as shown in the following equations.

$$\text{Pre – transition region: } w^3 = 6.36 \times 10^{11} e^{-13636/T} \times t \quad \text{Equation (2.8)}$$

$$\text{Post – transition region: } w = 1.12 \times 10^8 e^{-12529/T} \times t \quad \text{Equation (2.9)}$$

$$\text{Weight gain to transition: } w_t = 7.53 \times 10e^{-553.6/T} \quad \text{Equation (2.10)}$$

$$\text{Time to transition: } t_t = 6.73 \times 10^{-7} e^{11975/T} \quad \text{Equation (2.11)}$$

Table 2.1 Pre-transition kinetic constants of a range of zirconium alloys [18] (Copyright © 2005 by The Minerals, Metals & Materials Society. Used with permission.)

Alloy group	Alloy	Temp.(°C)	K	n	Avg. K	Avg. n
Zr-Fe-Cr	Zr-0.2Fe-0.1Cr	580	10.20	0.20	9.89	0.21
	Zr-0.2Fe-0.1Cr	720	10.20	0.20		
	Zr-0.4Fe-0.2Cr	580	9.78	0.21		
	Zr-0.4Fe-0.2Cr	720	9.39	0.22		
Zr-Cr-Fe	Zr-0.5Cr	360	non-protective		10.94	0.19
	Zr-0.5Cr-0.2Fe	360	11.50	0.17		
	Zr-1.0Cr	360	9.73	0.21		
	Zr-1.0Cr-0.2Fe	360	11.60	0.18		
Zr-Cu-Mo	Zr-0.5Cu	360	13.60	0.17	14.08	0.18
	Zr-0.5Cu-0.5Mo	360	13.60	0.17		
	Zr-1.0Cu	360	15.10	0.17		
	Zr-1.0Cu-0.5Mo	360	14.00	0.21		
Zr	Sponge	360	8.50	0.20	7.56	0.22
	Crystal Bar Zr	360	6.61	0.24		
Zircaloy	Zircaloy-4	360	11.00	0.21	10.20	0.22
	Zr-4 Control	360	9.40	0.23		
Zr-Sn	Zr-0.2Sn	360	9.30	0.29	9.50	0.29
	Zr-0.4Sn	360	8.10	0.32		
	Zr-0.8Sn	360	10.00	0.27		
	Zr-1.2Sn	360	10.60	0.27		
Zr-Sn-Nb	Zr-0.4Sn-0.2Nb	360	5.92	0.43	6.52	0.41
	Zr-0.4Sn-0.4Nb	360	7.11	0.39		
Zr-Nb	Zr-0.2Nb	360	6.40	0.43	5.92	0.45
	Zr-0.4Nb	360	5.00	0.52		
	Zr-1.0Nb	360	5.90	0.45		
	Zr-1.5Nb	360	5.80	0.44		
	Zr-2.5Nb	360	6.50	0.40		

Several assumptions have been proposed to explain the deviation from parabolic corrosion, and some common explanations include the presence of inhomogeneous oxide microstructure, stress accumulation in the oxide and the doping effects induced by aliovalent alloying elements, which can affect the diffusion [10, 11, 17].

During the oxidation, high levels of compressive stresses are developed in the oxide layer due to the conversion of Zr to ZrO₂, which has a Pilling-Bedworth ratio of ~1.56. One

possible explanation for the transition phenomenon is that the compressive stress increases as the oxide thickens which results in a decreasing diffusion of oxygen and so corrosion rate [20-22]. Then at a critical point, stress induces the formation of buckling and cracks which in turn reduce the compressive stress [23-25]. At the same time, stress-stabilized metastable tetragonal oxide will transform into the equilibrium monoclinic phase [26-28], which would degrade the protective nature of the barrier layer by the formation of nano-scale cracks and pores [29, 30]. Eventually an interlinkage of porosity and cracks from the O/M to the O/W interface will be developed through the oxide, which offers easy paths for ingress of water and permit the start of a corrosion cycle [15]. The transition phenomenon is then related to the sudden oxide breakup after the stress reaches a critical value; the interlinkage of nanoporosity and cracks that can cause an overall loss of protection [11, 27, 29].

2.1.4. Hydrogen pick-up

Absorption of hydrogen into zirconium alloys can adversely affect the mechanical properties and limit the performance of these alloys by the formation of brittle hydride phases. There are four main sources of hydrogen for nuclear cladding [17]; (i) hydrogen left over in the alloys during fabrication or from residual moisture due to surface preparation, (ii) desorption of water from incompletely dried up fuel, (iii) hydrogen produced by (n, p) reactions in the cladding, (iv) hydrogen ingress from corrosion in the coolant water. The hydrogen contents from the first three sources are usually smaller than from the fourth. A quantity called the hydrogen pick-up fraction (HPUF) is often used to describe the ingress of hydrogen from corrosion. The HPUF is defined as the ratio of hydrogen in the cladding to the hydrogen generated by the corrosion reaction [31],

$$\text{HPUF} = \frac{H_{\text{absorbed}}}{H_{\text{generated}}} \quad \text{Equation (2.12)}$$

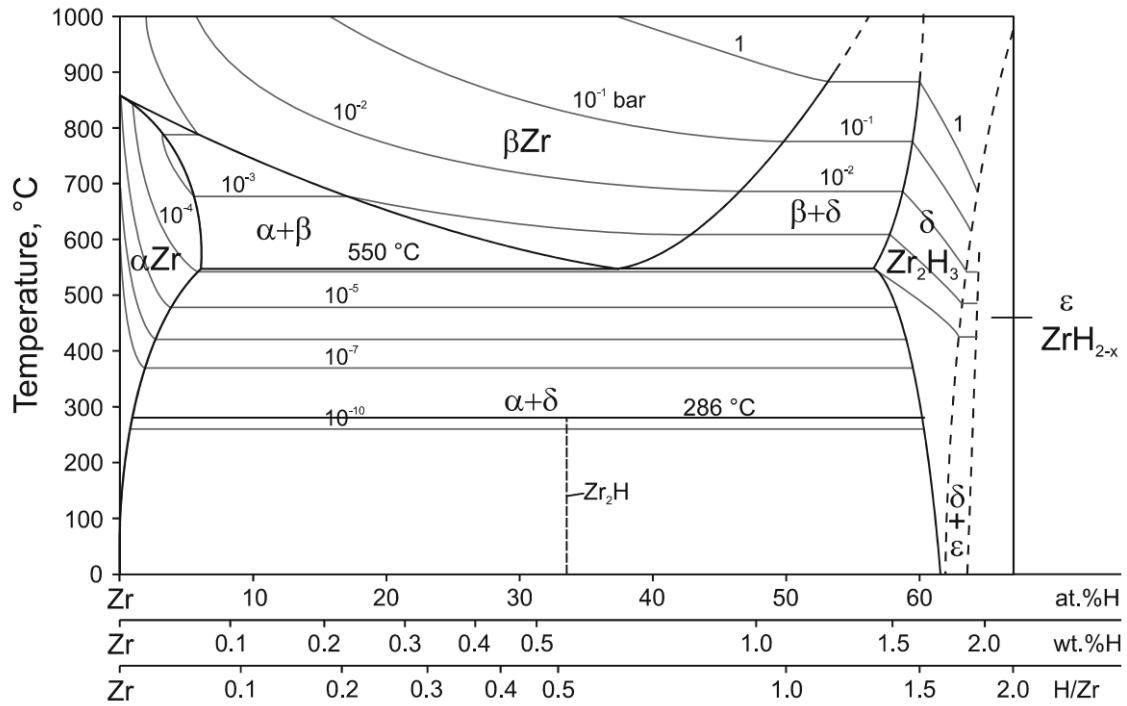


Figure 2.3 Zr–H phase diagram with equilibrium concentration at various ambient hydrogen partial pressure isobars (Reprinted from [32] by permission from Springer Nature Customer Service Centre GmbH, Copyright (2019)).

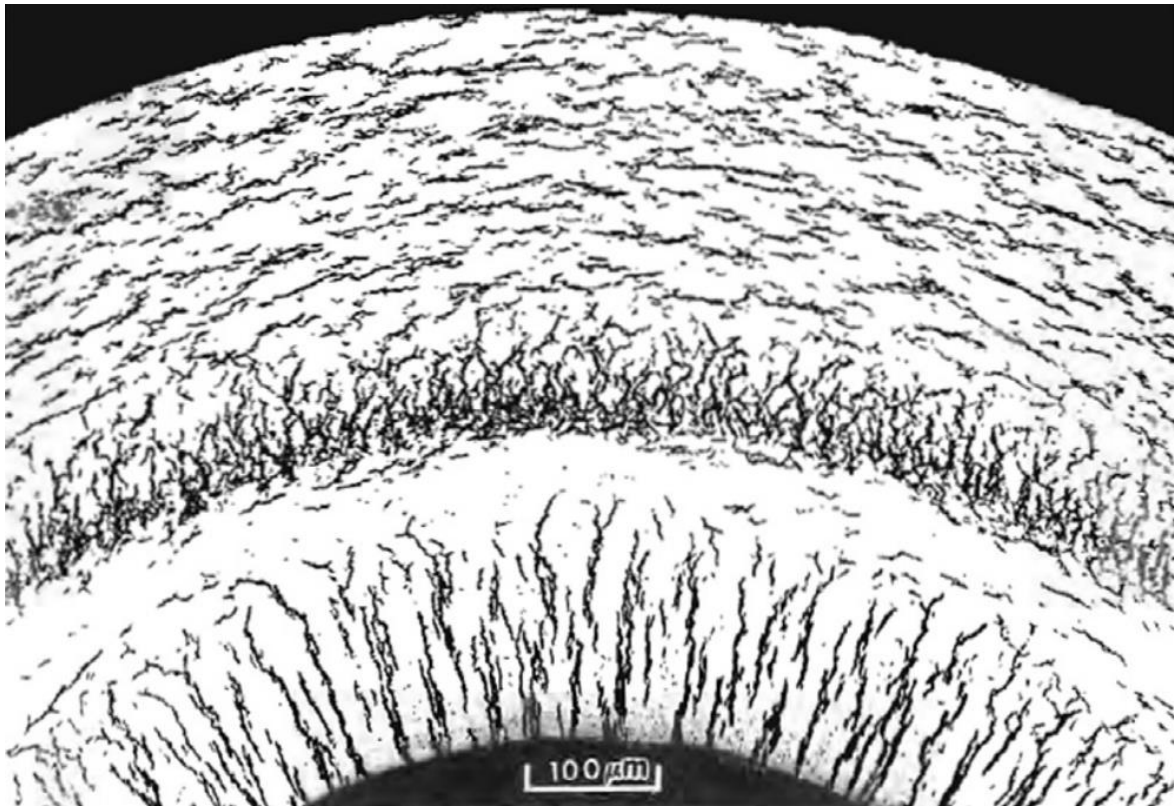


Figure 2.4 Distribution and morphology of hydrides in Zr alloy (Reprinted from [33], Copyright (2019) with permission from Elsevier).

The solubility of hydrogen in zirconium is very low, Figure 2.3, and when the solubility limit is reached, hydrides will form. Due to the high diffusivity, hydrides can form not only in the vicinity of the oxide but also in the interior of the cladding tube. A micrograph showing hydrides in Zr alloy is presented in Figure 2.4. Different hydride phases are reported under different corrosion conditions, and crystallographic information on the different hydride phases is summarized in Table 2.2.

Table 2.2 Crystallographic information on Zr-hydrides

Phase	Structure	Lattice parameters (nm)			Ref
		a	b	c	
δ -ZrH _{1.66}	FCC	0.478	-	-	[34]
		0.478	-	-	[35]
		0.482	-	-	[36]
		0.484	-	-	[37]
		0.478	-	-	[37]
		0.481	-	-	[38]
		0.478	-	-	[39]
γ -ZrH	FCT	0.460	-	0.497	[34]
		0.462	-	0.489	[35]
		0.328	-	0.501	[36]
		0.324	-	0.495	[40]
		0.460	-	0.499	[37]
		0.459	-	0.497	[39]
ε -ZrH ₂	Tetragonal	0.352	-	0.445	[34]
		0.497	-	0.452	[37]
		0.497	-	0.450	[39]
		0.354	-	0.446	[36]
ζ -ZrH _{0.5}	Trigonal	0.330	-	1.029	[34]

The electrical potential gradient over the oxide layer may serve as the driving force for proton migration, which in turn determines the amount of hydrogen pick-up [11, 41, 42]. Thus, the electrical conductivity of the oxide is a key parameter controlling hydrogen pick-up. Consequently, alloying elements can influence the oxide electronic conductivity and electrical potential gradient and control the hydrogen pick-up [43]. Values of HPUF fraction

vary from alloy to alloy, and MDA (Mitsubishi Developed Alloy), ZIRLO, Zircaloy-4 and pure Zr are reported ranging from 10% to 20% [11], while values can be as high as 80% in Ni-containing alloys [44] and as low as 3% in Nb-containing alloys [45]. An inverse relationship between the rate constant of oxidation kinetics and HPUF is reported by Couet et al. [31], as shown in Figure 2.5. It was concluded that the hydrogen pick-up mechanism is linked directly to the corrosion kinetic; the more the oxidation kinetics tends towards parabolic the lower the HPUF.

Besides potential gradient, the mobility of interstitial protons is reported to be another possible factor that could influence the amount of hydrogen pick-up [41], and so external parameters such as temperature that can influence the mobility of interstitial protons will also influence hydrogen pick-up.

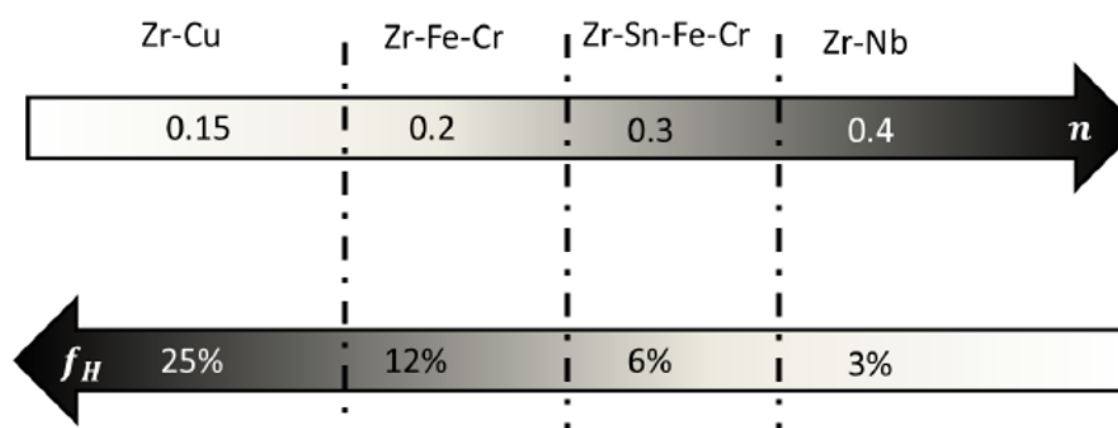


Figure 2.5 Schematic of the influence of alloying elements on oxidation kinetics and hydrogen pick-up (Reprinted from [31], Copyright (2019) with permission from Elsevier).

Understanding the fundamental mechanisms of hydrogen pick-up is important to improve the stability of structural components in-service in nuclear reactors. However, several questions are still not well answered despite the large number of publications on this subject, e.g. how hydrogen ions/molecules interact with the oxide on the metal and how hydrogen enters the metal matrix [33]. It has been proposed [46, 47] that transport of hydrogen through the oxide occurs via solid-state diffusion assisted by oxygen vacancies. Implicitly it is

assumed that the diffusing species is H^+ . On the surface of ZrO_2 in contact with water, Sato et al. [48] have demonstrated a proton migration mechanism in the form of a cooperative transfer of protons and positive charges involving intermediate water molecules as proton acceptors and donors. Such a mechanism is possible if water is present, which may not be the case close to the Zr metal-oxide interface. In both mechanisms, protons need to enter solid ZrO_2 , which may involve both overcoming an energy barrier and the availability of a sufficiently high concentration of oxygen vacancies or other defects, since the solubility of hydrogen in stoichiometric ZrO_2 without oxygen vacancies is extremely low [49]. Ploc [50] and Cox and Wong [51] pointed out the likely path of hydrogen pickup via structural flaws in the oxide film. Hence, mechanisms involving the hopping of H^+ between -OH groups or the migration of -OH groups along grain boundaries or in cracks are possible [52]. Recent studies have shown that the oxide film has a complicated microstructure containing several different types of nano-porosity [29] as discussed above. In addition to the bulk ZrO_2 oxide (mostly monoclinic and some tetragonal) a metastable ZrO suboxide may form at the metal-oxide interface [24, 53, 54]. Thus there may exist several pathways for hydrogen ingress which are activated depending on the environmental conditions.

Experimental methods such as small-angle neutron scattering [55] and thermal desorption spectroscopy [56] have been used to provide bulk-averaged hydrogen information but can not give information on the hydrogen location. Atom probe tomography (APT) [57] can measure the 3-dimensional distribution of hydrogen, but at a small scale and in limited sample volumes. To explore the experimental evidence showing the transportation pathways and trapping sites for hydrogen in the oxide layer, I have applied TEM to reveal the oxide microstructure, which is then correlated with 3-dimensional distribution of hydrogen revealed by NanoSIMS. Details are present in Chapter 8 and 9.

2.2. Zirconium Oxides

2.2.1. Phases

ZrO₂ can exist in three allotropic crystal structures, cubic (γ -ZrO₂ or c-ZrO₂), tetragonal (β -ZrO₂ or t-ZrO₂) and monoclinic (α -ZrO₂ or m-ZrO₂) as predicted by the Zr-O phase diagram, Figure 2.6. Data on the oxide phases formed on different zirconium alloys are summarized in Table 2.3. As expected from the Zr-O phase diagram, the stable phase of ZrO₂ at 300°C is the monoclinic form. However, the oxides formed under autoclave conditions are always characterized as a mixture of monoclinic and tetragonal zirconia [58-60]. The values of tetragonal phase fraction in oxides on aqueous corroded Zr alloys reported by bulk measurement techniques, laboratory and synchrotron X-ray diffraction (XRD) for example lie in the range 3–40% [22, 27, 61-63].

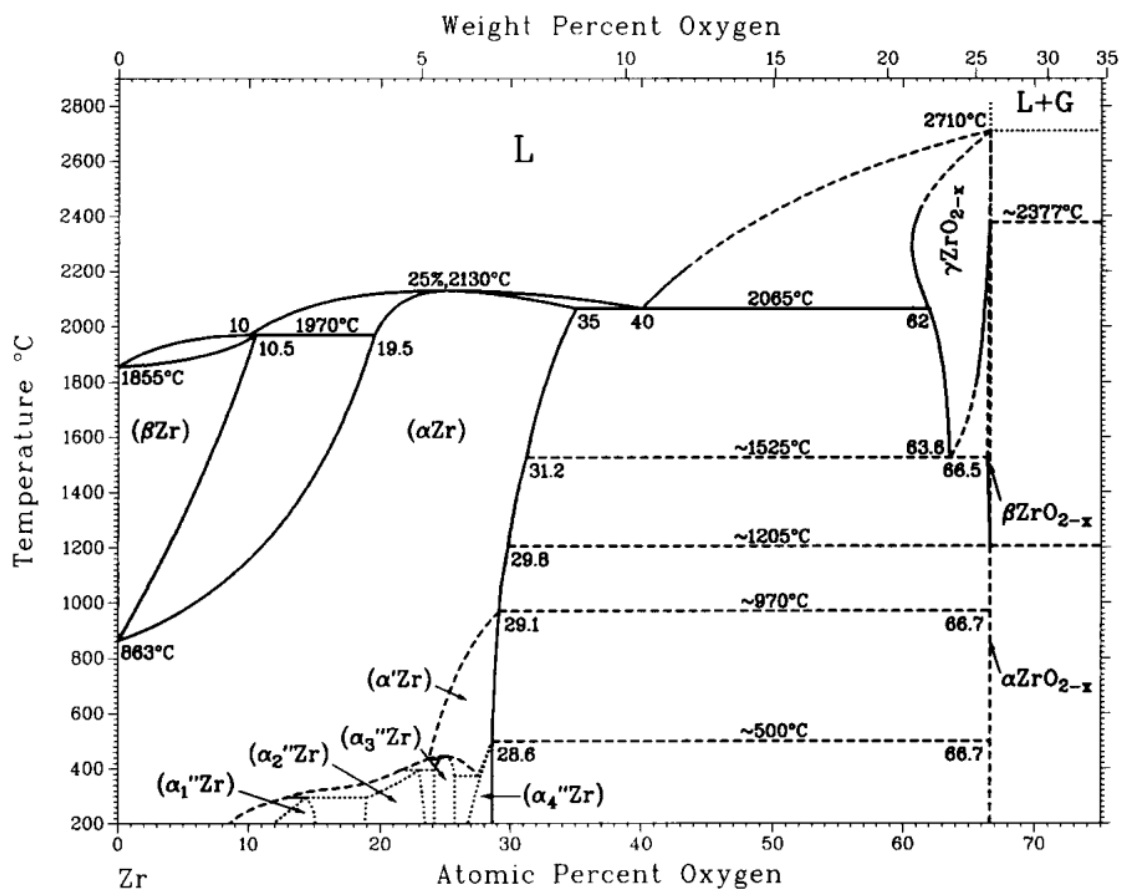


Figure 2.6 Phase diagram of Zr-O (Reprinted from [64] by permission from Springer Nature Customer Service Centre GmbH, Copyright (2019)).

Table 2.3 Lattice parameters of zirconium oxide phases

	Structure	Lattice parameter			Alloys	Ref.
		a (nm)	b (nm)	c (nm)		
ZrO ₂	Monoclinic	0.531	0.521	0.515	Zr-2.5Nb, ZIRLO	[65]
		0.522	0.528	0.541	Calculation	[66]
	Tetragonal	0.364	-	0.527	Zr-2.5Nb, ZIRLO	[65]
	Cubic	0.513	-	-	Zr-2.5Nb, ZIRLO	[65]
ZrO	Hexagonal	0.531	-	0.320	Calculation	[67]
		0.529	-	0.318	Calculation	[68]
		0.533	-	0.322	Calculation	[66]
	Cubic	0.462	-	-	Zircaloy	[69]
		0.44-0.46	-	-	Zircaloy-2	[70]
		0.463	-	-	Zircaloy-4	[71]
		0.462	-	-	Calculation	[67]
Zr ₂ O ₃	Tetragonal	0.313	-	0.574	Calculation	[68]
Zr ₂ O	Hexagonal	0.565	-	0.525	Calculation	[66]
Zr ₃ O	Rhombohedral	0.567	-	1.570	Calculation	[66]
		0.563	-	0.156	Zircaloy-4	[72]
		0.556	-	3.119	Zr-2.5Nb, ZIRLO	[65]
	Orthorhombic	0.324	-	1.221	Calculation	[67]
Zr ₆ O	Rhombohedral	0.565	-	1.564	Calculation	[66]

It has been reported that this metastable phase can be stabilized by stress [22, 73], grain size [73], oxygen vacancies [74] and alloying elements (e.g. Sn and Nb) [16, 75, 76]. The stabilization mechanisms of metastable phases in zirconium oxides has been well reviewed by Kelly and Rose [77], and the stabilisation mechanisms can be described using the thermodynamic equation,

$$\Delta W = \Delta G_C V + \Delta U_{\text{Strain}} + \Delta U_{\text{Surface}} \quad \text{Equation (2.13)}$$

where ΔW is the change in total free energy, ΔU_{Strain} is the change in strain energy and $\Delta U_{\text{Surface}}$ is the change in interface or surface energy, and V is the transformation volume. ΔG_C can be described as the change in chemical energy or the difference in chemical free energy per unit volume between the tetragonal/cubic and monoclinic phases, and is dependent on temperature and composition. Equation 2.13 has been shown schematically by Kelly and Rose [77], Figure 2.7. If at any point ΔW becomes positive, the tetragonal phase

will be stabilized, so that the further the temperature drops below the transformation temperature of $\sim 1200^{\circ}\text{C}$ the more negative ΔG_c becomes and consequently the greater ΔU_{Strain} and $\Delta U_{\text{Surface}}$ will be needed to stabilise the tetragonal phase. As oxides have high-levels of compressive stress [22, 27], the stabilisation of the tetragonal phase is favoured even at low temperatures.

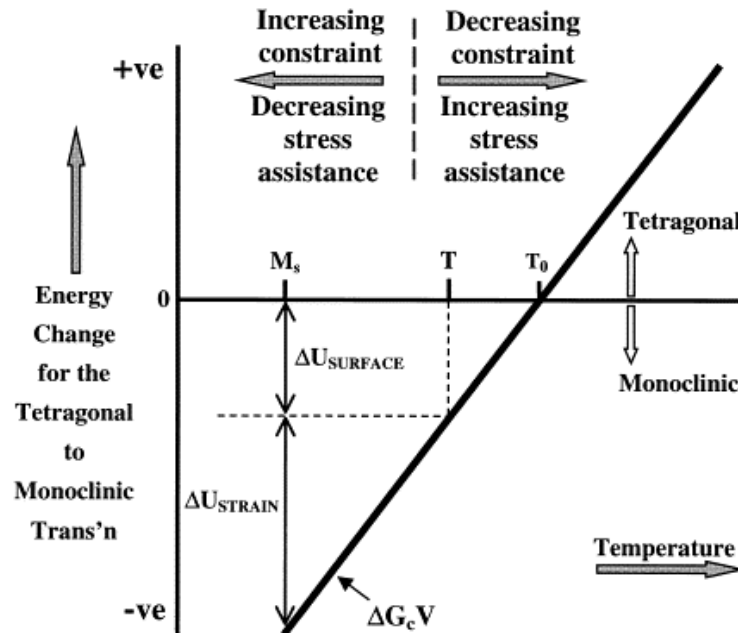


Figure 2.7 The dependence of tetragonal-to-monoclinic transformation on the change in strain energy, chemical energy and surface energy. (Reprinted from [77], Copyright (2019) with permission from Elsevier).

Recent atom probe tomography (APT), energy dispersive X-ray spectroscopy (EDS) and electron energy loss spectroscopy (EELS) studies have shown that a thin intermediate suboxide layer often forms at the Zr/ZrO₂ interface [53, 78-81]. Thermodynamic modelling shows that this ZrO suboxide phase, which is absent in the traditional Zr-O binary phase diagram, Figure 2.6, is actually an equilibrium phase over a narrow oxygen partial pressure window, Figure 2.8 [67, 68]. This ZrO was reported from an ab-initio study to have a structure similar to hexagonal ω -Zr [82, 83], with a high content of oxygen. As a relatively new phase, some key properties of zirconium suboxide are still missing in the literature, e.g. its mechanical properties and resistance to neutron/ion irradiation damage.

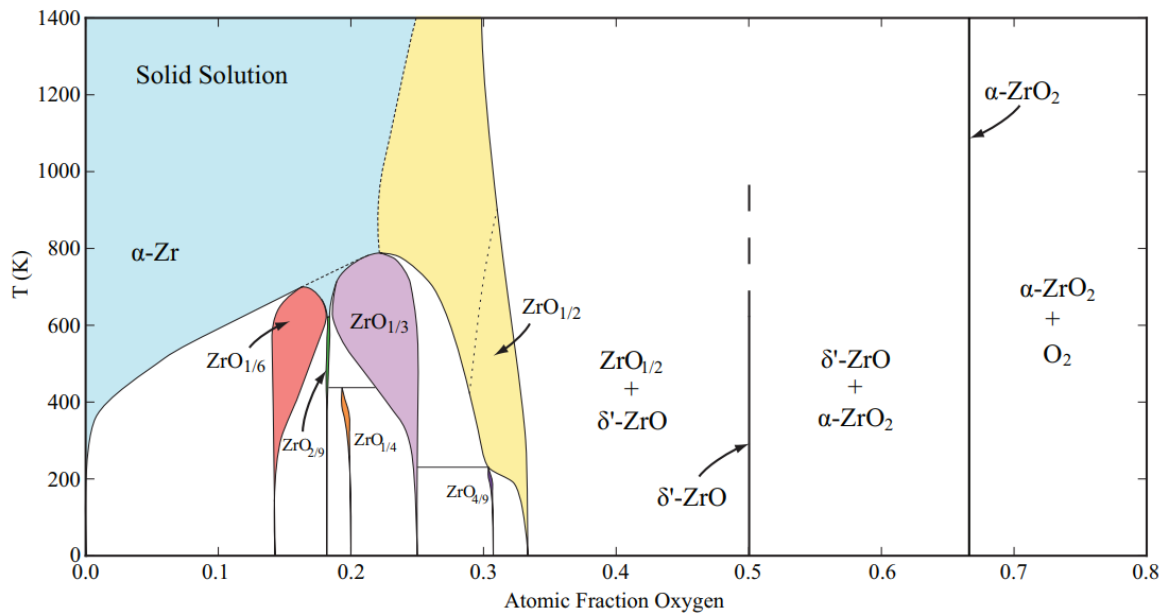


Figure 2.8 The calculated phase diagram of Zr-O (Reprinted figure with permission from [68], Copyright (2019) by the American Physical Society).

2.2.2. Grain size and texture

The improved corrosion resistance demonstrated in recently developed alloys has been correlated to a larger oxide grain size, stronger crystallographic texture in the oxide and tighter crystallographic alignment of oxide grains compared to those observed on older alloys [59], and a schematic of the oxide structure characterised on alloys showing different corrosion performance is presented in Figure 2.9. Larger oxide grains can lead to a dramatic reduction in the area of grain boundaries, thus suppressing the diffusion of corroding species [84]. The predominance of low-angle grain boundaries in highly textured oxide layers also offers only low mobility paths for diffusing species [85]. Both these effects can contribute to superior corrosion performance. A thorough understanding of texture formation in the nanoscale m-ZrO₂ grains that dominate in oxides grown by aqueous corrosion on commercial Zr alloys, and especially the orientation relationships at the oxide/metal interface, is therefore critical to understanding how to control the microstructure of the oxide layer, and further improve the performance of these alloys in service.

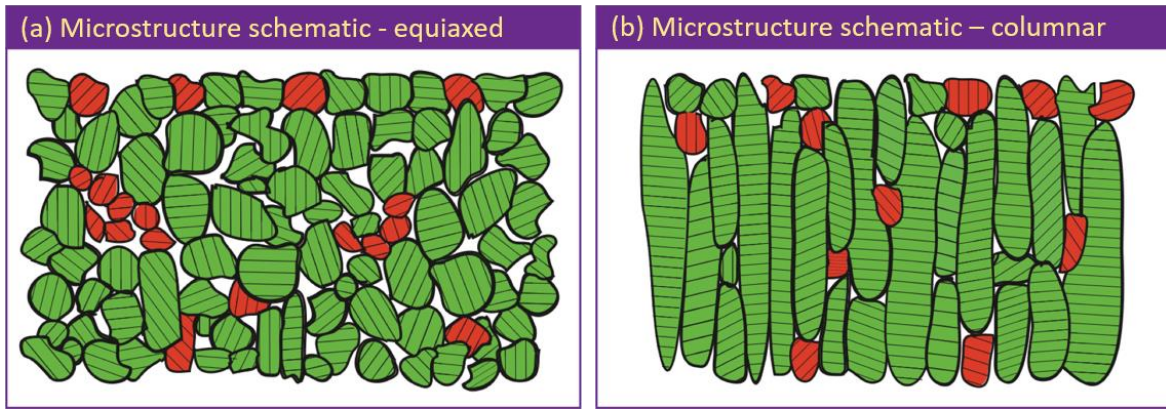


Figure 2.9 Schematic of oxide structures on Zr alloys of (a) poor and (b) good corrosion performance (courtesy of Samuel Armson, University of Manchester)

Many groups have studied the crystallographic orientation relationships between α -Zr and m-ZrO₂ using techniques such as XRD [61, 86] and transmission electron microscopy (TEM) [24, 87]. These studies revealed a strong fibre texture in m-ZrO₂ grown on Zr alloys during aqueous corrosion, with planes between $(10\bar{3})_{\text{m-ZrO}_2}$ and $(10\bar{6})_{\text{m-ZrO}_2}$ lying preferentially parallel to the sample surface. This texture is attributed to minimization of the stress associated with the metal-to-oxide transformation during oxidation [88]. X-ray diffraction techniques average over very many grains throughout the oxide, so TEM analysis has been applied to study micro-texture and grain orientations close to the α -Zr/ZrO₂ interface. However, there is little agreement on the reported orientation relationships between α -Zr and m-ZrO₂. Early observations by Ploc [89] on single α -Zr crystals suggested the epitaxial orientation relationships $(100)_{\text{m-ZrO}_2} \parallel (0001)_{\alpha\text{-Zr}}$ and $[001]_{\text{m-ZrO}_2} \parallel [11\bar{2}0]_{\alpha\text{-Zr}}$. Lin et al. [90] reported the orientation relationship to be $(010)_{\text{m-ZrO}_2} \parallel (0001)_{\alpha\text{-Zr}}$ on a Zr-Nb alloy, and the $(020)_{\text{m-ZrO}_2} \parallel (10\bar{1}1)_{\alpha\text{-Zr}}$ relationship was proposed by Motta et al. [19] based on synchrotron diffraction results. Recent high-resolution transmission electron microscopy (HRTEM) observations on the oxide/metal interface in different alloys suggested several other orientation relationships; including $(111)_{\text{m-ZrO}_2} \parallel (10\bar{1}0)_{\alpha\text{-Zr}}$ on Zircaloy-4 [87], and $(200)_{\text{m-ZrO}_2} \parallel (10\bar{1}0)_{\alpha\text{-Zr}}$, $(111)_{\text{m-ZrO}_2} \parallel (11\bar{2}0)_{\alpha\text{-Zr}}$ and $(011)_{\text{m-ZrO}_2} \parallel (11\bar{2}0)_{\alpha\text{-Zr}}$ on ZIRLO [24].

These results suggest that instead of a unique relationship either several orientation relationships are formed during the transformation from metal-to-oxide or that the local orientation relationships at the metal/oxide interface are not responsible for the formation of the bulk oxide texture. In addition, it is necessary to take the suboxide into consideration when considering how orientation relationships are formed at the metal/oxide interface.

2.2.3. Nano-porosity

As described in Section 2.1, the oxide nano-porosity and cracks play an important role in affecting the overall corrosion behaviour of Zr alloys. A lot of studies have reported on cracks or porosity in zirconium oxide films and their potential roles in corrosion and hydrogen pick-up [9, 15, 29, 30]. An example of oxide nano-porosity is shown in Figure 2.10. Ploc [50] divided these cracks or porosities into three main types: flake, ribbon and stress cracks. Flake porosity existing in isolation is seen predominantly at oxide grain boundaries, but with corrosion time can become interconnected to ribbon porosity (or nano-pipes) over hundreds of nanometers and can run towards the oxide/metal interface. Stress cracks are roughly periodic and parallel to the oxide/metal interface, linked to the large compressive stresses generated in the oxide by the volume expansion created by the Pilling–Bedworth ratio of ~ 1.56 characteristic of the oxidation of zirconium alloys [10, 15]. More recently, Ni [91] has carried out systematically microscopic characterisation of oxide nano-porosity and cracks on different alloys after different corrosion time and found the density of interconnected porosity is observed to increase towards the oxide surface and evolve over corrosion time. At the oxide/metal interface region, isolated pores of 1-3nm are frequently observed [29]. In the post-transition oxide, the location of interconnected porosity is observed much closer to the oxide/metal interface compared with the pre-transition sample.

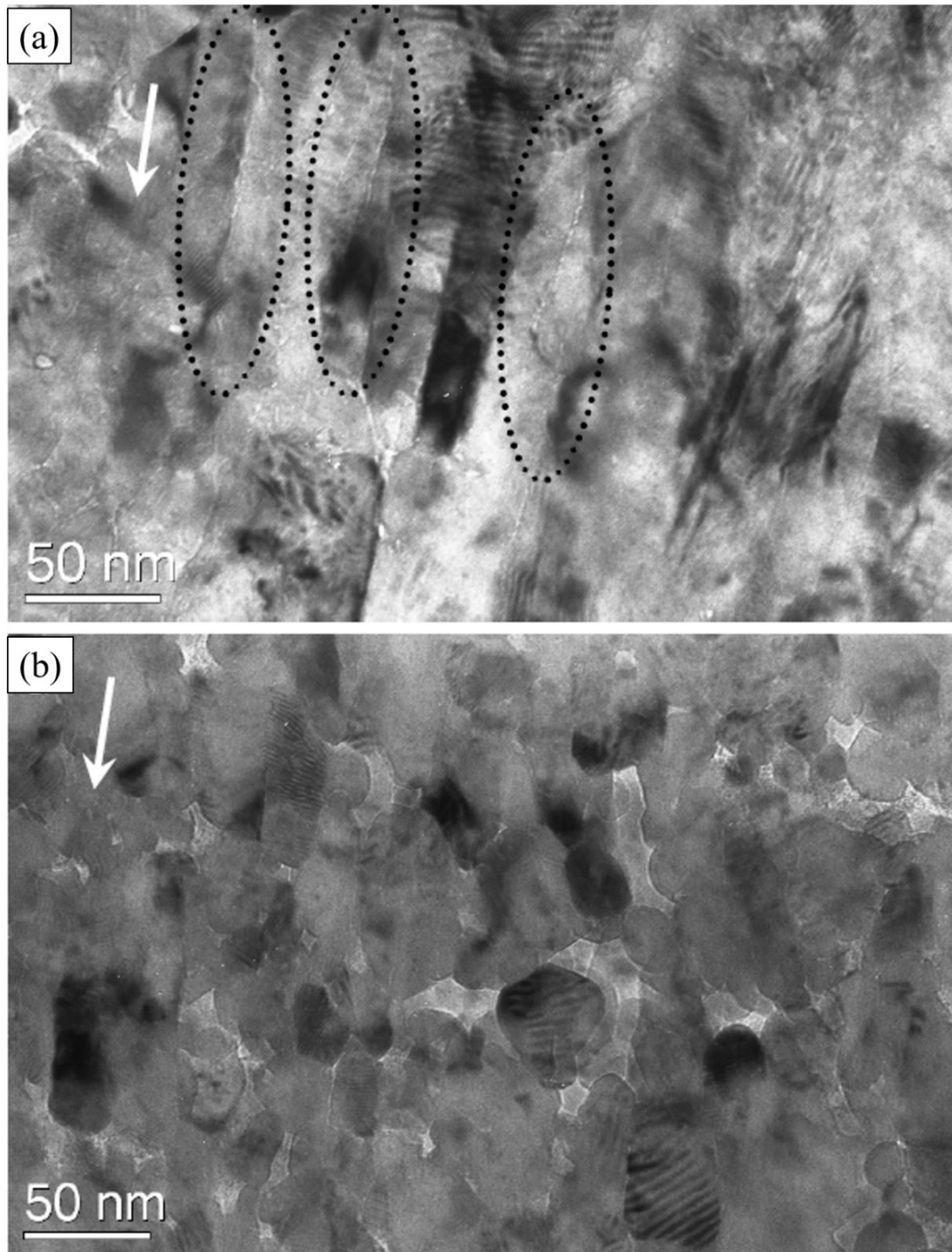


Figure 2.10 Nano-porosity and cracks in the oxide at a distance away (a) 1.6 μm and (b) 3 μm from the oxide/metal interface on a 140-day ZIRLO sample (Reproduced figure from [91] with permission from Dr .Na Ni, the copyright holder).

The formation of nano-porosity is possibly a result of oxide creep under the compressive stresses [92]. The compressive stresses introduce strains along the oxide growth direction which are difficult to accommodate by dislocation glide as too few slip systems are likely to

be active at the typical oxidation temperatures [93]. Therefore creep is a possible mechanisms to provide the required strain [25]. If the grain boundary sliding is slower than the creep process, for instance due to the segregation of foreign atoms in the grain boundaries or an impingement on quadruple points of the grain boundary networks, then voids or porosity can develop [91]. The formation of nano-porosity can also be a result of the volume changes induced by the tetragonal-to-monoclinic transformation [28, 77, 94].

Although the roles of nano-porosity in the transportation of oxidising species were proposed many years ago, there is still lack of direct experimental evidence in the literature, which will be discussed in Chapter 8 and 9.

2.3. In-reactor Corrosion

2.3.1. Corrosion kinetics

In section 2.1, a review is given regarding corrosion and hydrogen pick-up mechanisms in an aqueous environment in the absence of radiation. In nuclear reactors, the cladding materials are subjected to radiation-induced damage caused by a high flux of fast neutrons. In the complex reactor environment, the neutron irradiation and fission fragments affect simultaneously the metal matrix and the oxide, and can also lead to radiolysis in the cooling water, and this combination may lead to significantly enhanced corrosion behaviour .

Figure 2.11 shows the comparison of corrosion kinetics of Zircaloy-4 in the reactor and in the autoclave, and it is obvious that the complex reactor environment, especially the irradiation, can lead to significantly enhanced corrosion behaviour. Acceleration of corrosion rates by up to factors of 40 has been reported as a result of exposure to in-reactor conditions [95-97, 102].

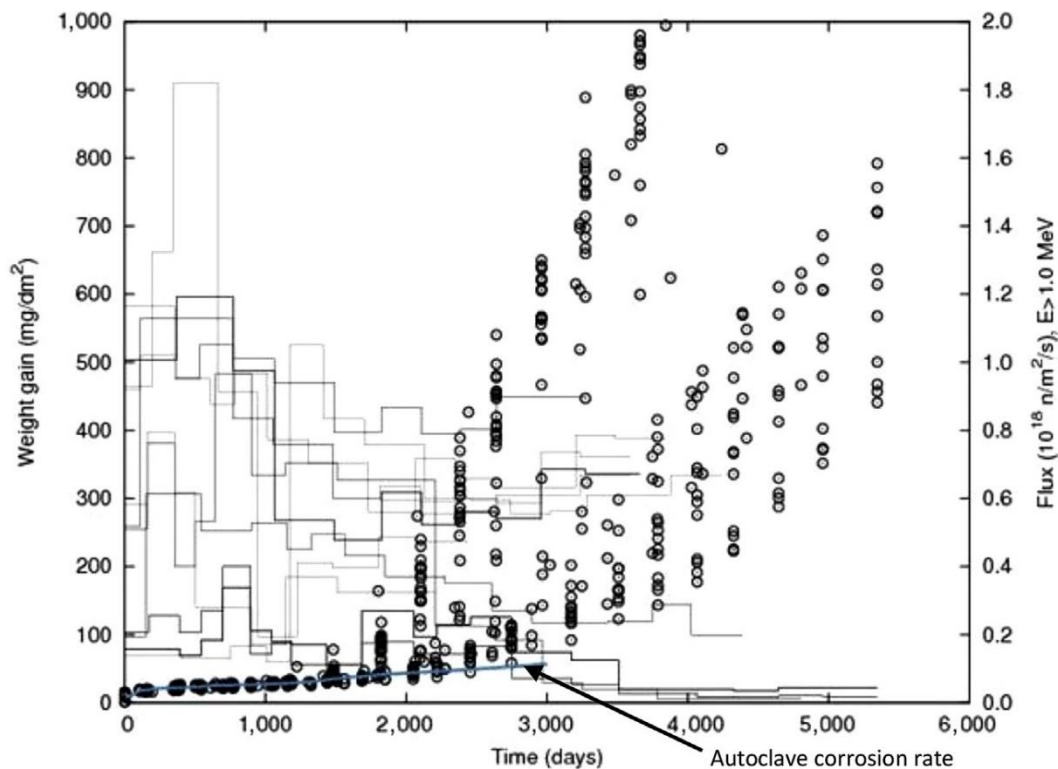


Figure 2.11 Corrosion kinetics of Zircaloy-4 in the reactor at 270°C. Weight gain (points) and fast neutron flux exposure (lines) are indicated. The autoclave corrosion kinetics curve is shown in blue. Reproduced, with permission from [102]. copyright ASTM International, 100 Barr Harbor Drive, West Conshohocken, PA 19428.

In comparison with Zircaloy-4, some Zr-Nb alloys (like M5 and E110) show much better resistance to the irradiation-accelerated corrosion under PWR conditions, especially at high burn-ups [98, 99]. Whereas low tin Zircaloy-4 reached about 90 μm in oxide thickness, the oxide layer on M5 remains below 20 μm at burn-ups of ~ 70 GWd/t in a PWR [98]. The dramatic difference is supposed to be related to the combined effects induced by different types and content of alloying elements, SPPs, oxide microstructures and hydride precipitation and their response to irradiation [98-103]. Some of the hypotheses on the mechanisms leading to in-reactor accelerated corrosion are summarized in section 2.3.2.

2.3.2. Hypotheses for enhanced in-reactor corrosion

Hypotheses for the enhanced in-reactor corrosion behaviour can be illustrated using Figure 2.12. First, irradiation can change the microstructures and microchemistry of the base alloy,

as it has been widely reported [104-107]. In Zr alloys one of the most common defects produced during irradiation are dislocation loops, and these are observed under both neutron and ion irradiation [108-110]. The evolution of dislocation loops can lead to anisotropic growth of the cladding, known as irradiation induced growth [111, 112] and this dimensional instability may further lead to enhanced corrosion rates. Irradiation-induced hardening can make the base alloy less able to accommodate oxide growth stresses which can then lead to faster stress accumulation in the oxide and result in earlier transition behaviour [113]. In addition, the microchemical evolution of Zr alloys under both neutron and ion irradiation has been widely reported [114-119]. The redistribution of alloying elements may affect corrosion by a doping effect on oxide conductivity or by affecting oxide nucleation [9, 11, 120, 121].

Different oxide microstructures can be formed on Zr alloys in a reactor and an autoclave [101, 103, 122, 123] as shown schematically in Figure 2.12. Recent corrosion tests using in-situ proton irradiation also showed accelerated corrosion kinetics [120] that matched the in-reactor kinetics at high burnups (after four cycles in PWRs [96]), and the oxide morphology formed in-reactor and under proton irradiation is similar, with a large volume fraction of cracks and fine pores present throughout the thickness of the oxide. With similar corrosion kinetics and damage rates (proton irradiation at 4.4×10^{-7} dpa/s versus neutron irradiation at 2.8×10^{-8} to 7.8×10^{-7} dpa/s [124, 125]), the O/M interface region formed in-reactor and under ion irradiation corrosion experiences similar cumulative damage levels and again have shown comparable oxide grain morphologies, an abundance of small, randomly oriented equiaxed grains [120, 123, 126, 127]. More recently, Garner et al. [103] used scanning precession electron diffraction analysis in TEM and observed a more heterogeneous microstructure in reactor-formed oxides after 3 cycles, with reduced columnar grain growth compared with autoclave formed oxides. Under irradiation, these nucleation and growth

processes can be disrupted by high concentrations of defects generated at the O/M interface [103, 123, 127]. In particular, any increase in local porosity [15, 29], and the resulting reduced cohesion between grains, may contribute to acceleration of the corrosion rate. The different oxide structures formed in-reactor conditions can be a result of irradiation effects on nucleation and growth processes, but we should also consider the possibility of direct radiation damage to the oxides once formed. There is much less reported work on the effects of radiation damage on the oxide scales formed during corrosion in service. One reason is that the Zr oxide already has a very complicated nanoscale structure, which will depend on the application of state-of-the-art microscopes like in-situ TEM and TKD. Results generated from this project on irradiation damage in Zr oxide will be presented in Chapter 10.

The other hypotheses for enhanced in-reactor corrosion performance of Zr alloys are based on the effects of coolant chemistry and radiolysis, the dissolution of oxide films and heat flux which are discussed in [128-133] .

Corrosion of recrystallised Zr-1.0Nb

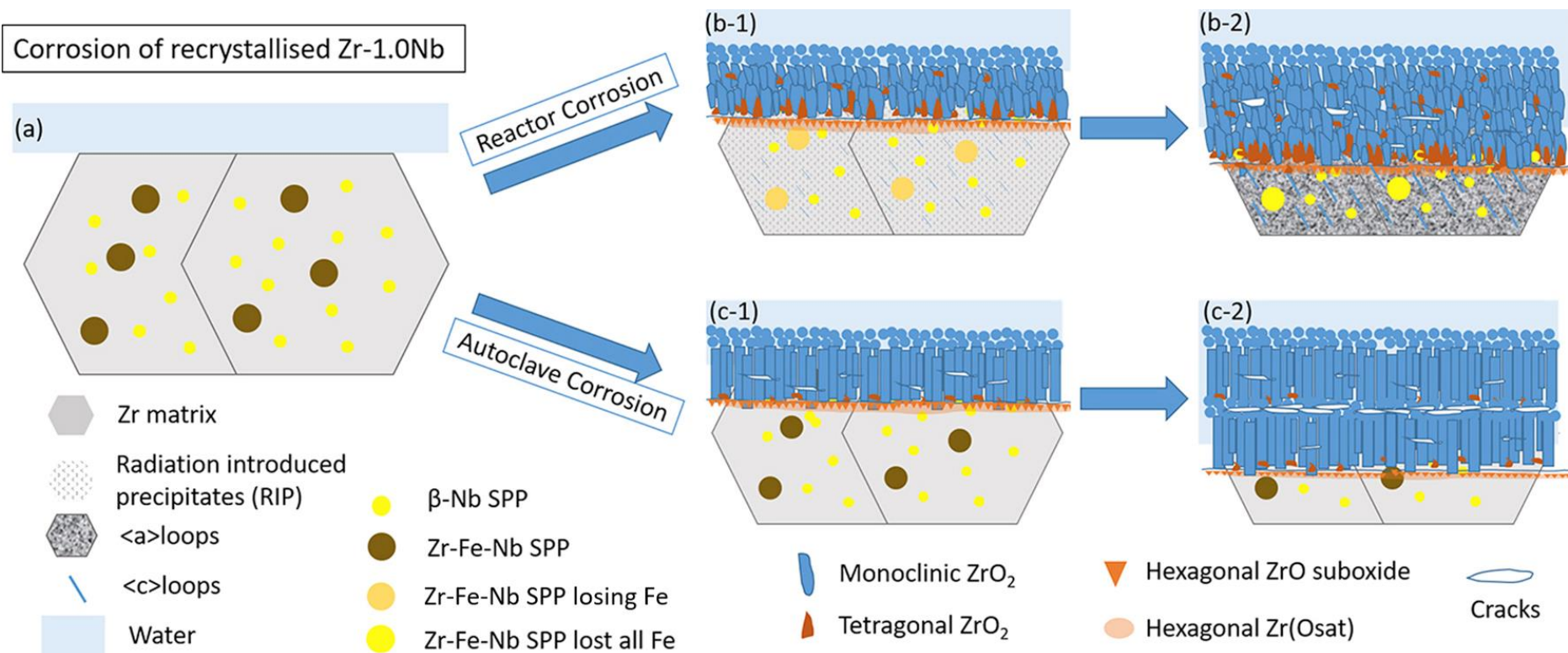


Figure 2.12 Illustrations of reactor corrosion vs autoclave corrosion in a Zr-1.0Nb alloy: (a) before irradiation, (b) reactor corrosion and (c) autoclave corrosion (Reprinted from [101], Copyright (2019) with permission from Elsevier).

2.3.3. Radiation damage in zirconium oxides

Point defects and their reactions in non-metallic materials are more complex than those in metallic materials [134, 135]. Figure 2.13 shows a schematic of an ionic compound with many possible defects; e.g. dislocations, vacancies and interstitials. To conserve the electroneutrality of the stoichiometric crystal, if a charged point defect is formed, a complementary point defect with opposite effective charge must be formed. Two possible types of point defect structures are termed as Schottky and Frenkel defects.

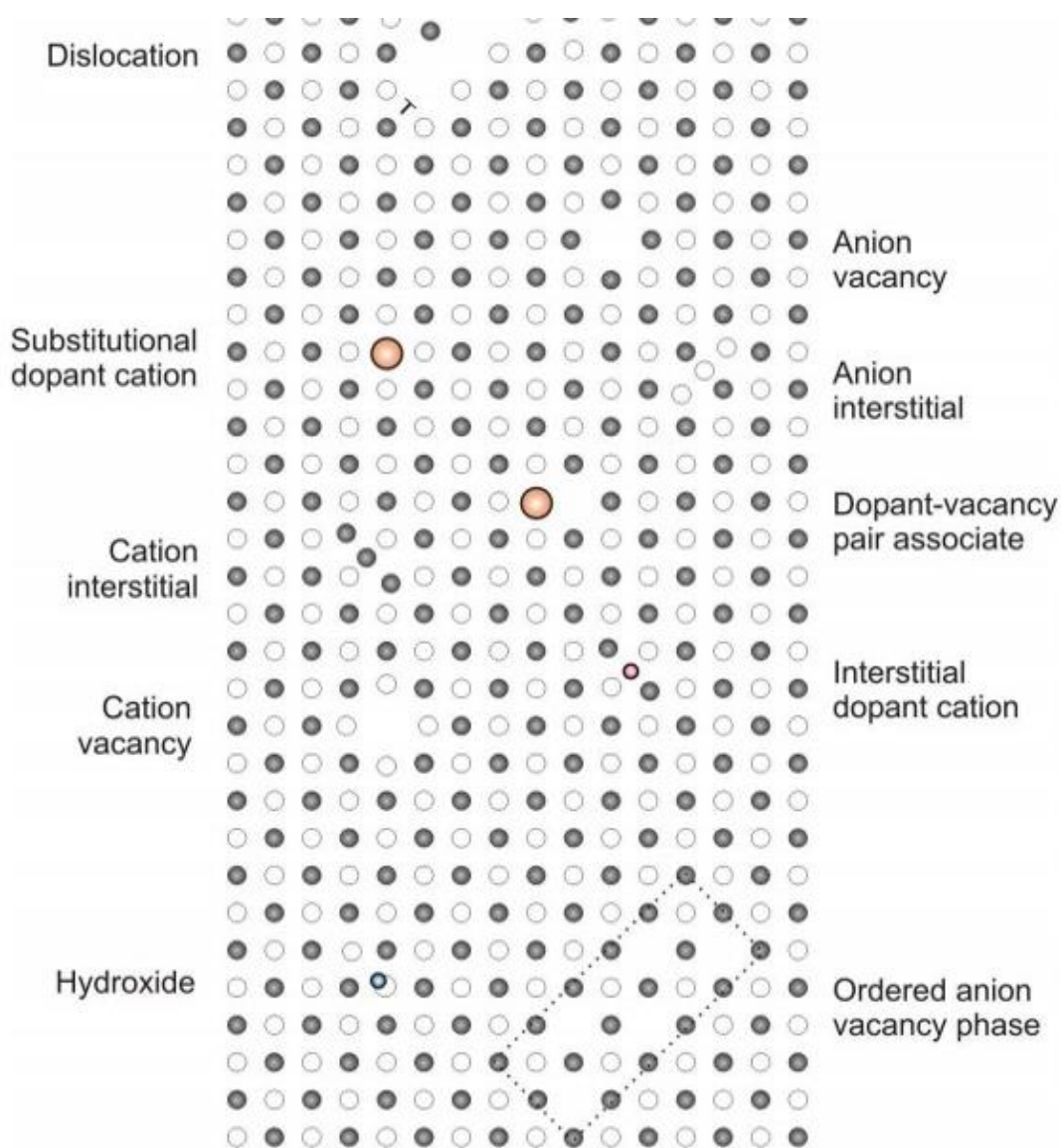


Figure 2.13 Schematic representation of some defects in an ionic compound MX. Cations M^{2+} are dark spheres, anions X^{2-} open spheres (Reproduced figure from [135] with permission from Dr .Truls Norby, the copyright holder).

In the Kröger-Vink notation, the defect reactions to form a cation and anion Frenkel pair and a Schottky defect are respectively,

$$\text{Zr}_{\text{Zr}}^{\times} = \text{V}_{\text{Zr}}^{\prime\prime\prime\prime} + \text{Zr}_{\text{i}}^{\prime\prime\prime\prime} \quad \text{Equation (2.14)}$$

$$\text{O}_{\text{O}}^{\times} = \text{V}_{\text{O}}^{\prime\prime} + \text{O}_{\text{i}}^{\prime\prime} \quad \text{Equation (2.15)}$$

$$\text{V}_{\text{Zr}}^{\prime\prime\prime\prime} + 2\text{V}_{\text{O}}^{\prime\prime} \rightarrow \text{Schottky defect} \quad \text{Equation (2.16)}$$

The formation energy of these defects [136] can thus be defined as,

$$E_{\text{f,cation Frenkel}} = E_{\text{V}_{\text{Zr}}} + E_{\text{Zr}_{\text{i}}} - 2E_{\text{ref}} \quad \text{Equation (2.17)}$$

$$E_{\text{f,anion}} = E_{\text{V}_{\text{O}}} + E_{\text{O}_{\text{i}}} - 2E_{\text{ref}} \quad \text{Equation (2.18)}$$

$$E_{\text{f,Schottky}} = E_{\text{V}_{\text{Zr}}} + 2E_{\text{V}_{\text{O}}} - 3E_{\text{ref}} + E_{\text{X}} \quad \text{Equation (2.19)}$$

where $E_{\text{V}_{\text{Zr}}}$ denotes the energy of the system containing one cation vacancy, and $E_{\text{Zr}_{\text{i}}}$ for the system with one cation interstitial. Likewise $E_{\text{V}_{\text{O}}}$ and $E_{\text{O}_{\text{i}}}$ denote the energy of a system containing one anion vacancy and interstitial respectively. E_{ref} stands for the energy of a reference system without any defect. To form a Schottky defect, an extra energy, E_{X} , is needed to remove three vacancies and deposit them in a reservoir that holds the chemical potential of ZrO_2 . Following the definitions above, Dong et al. [136] calculated the formation energies of these defects, Table 2.4. The cation Frenkel pair has a similar formation energy in the three ZrO_2 polymorphs, while $E_{\text{f, Schottky}}$ is lower than $E_{\text{f, cation Frenel}}$ and the difference increases from monoclinic to tetragonal to cubic.

Table 2.4 Formation energy of Schottky , cation and anion Frenkel defects in ZrO_2
(Reprinted from [136], Copyright (2019) with permission from Elsevier).

Crystal type	Schottky pair (eV)	Cation Frenkel pair (eV)	Anion Frenkel pair (eV)
m- ZrO_2	7.06	8.75	4.26
t- ZrO_2	3.98	8.14	3.45
c- ZrO_2	2.84	8.56	3.09

Calculations on fluorite structures such as UO_2 , ZrO_2 and CeO_2 predict that oxygen defects have significantly lower migration energies and higher mobilities than cation defects [137, 138]. For instance, the migration energies of defects in cubic- ZrO_2 calculated by Aidhy et al. [138] for $\text{Zr}_i^{\bullet\bullet\bullet}$, $\text{V}_{\text{Zr}}^{\bullet\bullet\bullet}$, $\text{O}_i^{\bullet}$ and $\text{V}_{\text{O}}^{\bullet}$ are 5.9 eV, 6.2 eV, 0.7 eV and 0.3 eV respectively. As a result, the mobile O vacancies will diffuse to the essentially immobile cation vacancies to form a Schottky defect. Figure 2.14 shows a simulation of point defect evolution in UO_2 [139], which has similar types of defect to cubic- ZrO_2 . Initially, 200 cation and anion Frenkel pairs were created on sublattices, Figure 2.14(a). As time progresses, some of the point defects annihilate by a vacancy-interstitial recombination mechanism. Most of the surviving O interstitials aggregate to form clusters. Without exception, the U vacancies and interstitials are almost immobile and do not participate in directly clustering. The authors [139] also claimed that a Schottky defect has a much lower energy than a $\text{V}_{\text{O}}^{\bullet} - \text{V}_{\text{U}}^{\bullet\bullet\bullet}$ dicluster with a distant anion vacancy, and that the system with completely separated vacancies has a much higher energy so that in the final equilibrium state vacancies in clusters or Schottky defects are extremely stable.

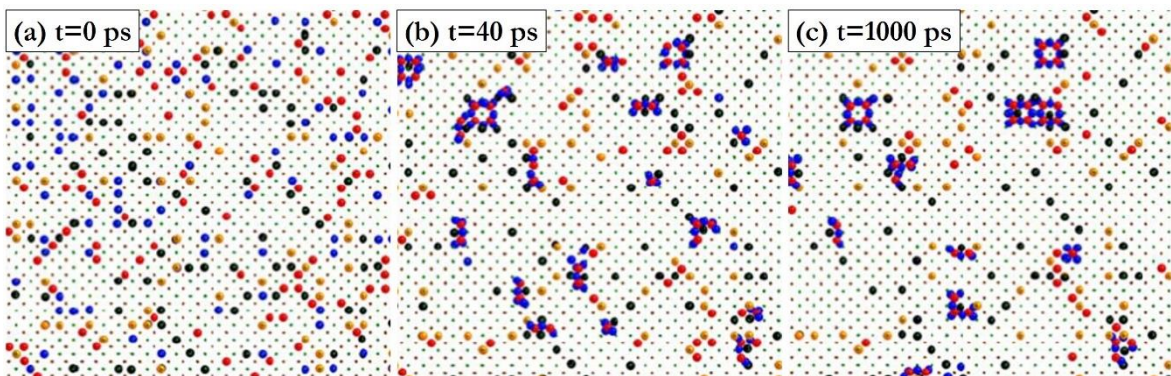


Figure 2.14 Evolution of point defects in UO_2 with initially 200 cation and anion Frenkel pairs randomly present on sublattices (orange and black for uranium vacancies and interstitials. Red and blue for oxygen vacancies interstitials). Reprinted figure with permission from [139], Copyright (2019) by the American Physical Society.

Interstitial clusters in fluorite-structured materials are a more complex defect type than vacancy clusters. Simulations [138-140] show that the interstitial clusters generally incorporate a few vacancies. In the steady state, most of the surviving interstitials will exist as isolated defects or in small clusters (the modelling indicates the largest interstitial cluster in zirconia is consistently between 3 and 4 interstitials regardless of PKA energies [140]), which may explain why in experimental studies, interstitial clusters in ZrO_2 are rarely reported [141, 142].

Under irradiation, these vacancies clusters or Schottky defects may serve as nucleation sites for irradiation-induced voids that can grow by sequestering more vacancies [104, 134]. These irradiation-induced voids or vacancy clusters can enhance the diffusion of oxidation species through an oxide layer as indicated by ab initio calculations [136, 143], which can make the oxide a faster oxygen conductor and enhance the in-reactor corrosion rates.

Both neutron and ion irradiation have been reported to lead to a high fraction of tetragonal phase in the oxide, which could be a result of radiation-induced phase transformations [103, 144-148]. Garner [103] and Gibert [149] showed that without radiation the tetragonal phase is essentially concentrated close to the metal-oxide interface, while in the neutron/proton irradiated sample, there is a significant increase in the tetragonal phase fraction distributed relatively homogeneously throughout the oxide thickness [103]. Irradiation-induced phase transformations in monoclinic zirconia have been extensively studied. A monoclinic-to-tetragonal transformation under ion irradiation has been reported by some authors [142, 145, 150-153], while others claim that the transformation is monoclinic-to-cubic [147, 154, 155], and in some cases [148] a transformation has occurred without confirming the nature of the product. Both tetragonal and cubic phases are metastable at room temperature, but can be stabilized at reactor temperature following the mechanism presented in section 2.2.

The mechanism responsible for these radiation-driven phase transitions in Zr oxide is still unclear. One of the possible hypotheses proposed by Simeone [145, 146] is that the phase transition may be a result of the local compression due to the appearance of radiation-induced interstitial clusters. The elastic energy stored in an isolated cluster can be estimated using Friedel's model [156] and transformation may happen when the size or density of these clusters is high enough so that the stored elastic energy in clusters is greater than 0.1 eV (the difference between the cohesion energies of these two phases) [145, 157]. Fabris [158] mentioned the displacement of Zr ions under radiation can lead the production of excess oxygen vacancies, and proposed that the m-to-t or m-to-c transformation is controlled by structural disorder around the oxygen vacancies, rather than by the substitutional dopant cations.

The stabilization of metastable phases, e.g. tetragonal phase, has been reported to be very important to control the corrosion performance of Zr alloys [10, 94]. When the tetragonal to monoclinic phase transformation takes place, nano-scale cracks and porosity can be created as a consequence of the ~6% volumetric change [159], and these cracks and porosity could create fast ingress routes for oxygen containing species, reducing the protective nature of the oxide film, or accelerating the rate of hydrothermal degradation [10, 11, 160, 161]. A similar volume change occurs with cubic-to-monoclinic, which can also result in the same kind of accelerated corrosion.

Chapter 3 Techniques and Instruments

This chapter gives an overview of the major microstructure and microchemistry analysis techniques used to undertake the work reported in this thesis, mainly based on Focused Ion Beam (FIB), Electron Backscatter Diffraction (EBSD), Transmission Kikuchi Diffraction (TKD), Transmission Electron Microscopy (TEM), in-situ TEM and high-resolution Secondary Ion Mass Spectrometry (NanoSIMS).

3.1. Focused Ion Beam

FIB milling was developed in the 1970s [162, 163] and has been widely applied in TEM and APT sample preparation, especially after development of the so-called lift-out method [164-171] which enables site-specific sample preparation. A schematic setup of a dual-beam FIB instrument is shown in Figure 3.1. The primary ion beam is extracted from the gallium source and then focused by a set of electrostatic lenses. When the Ga^+ beam hits the sample surface, a small amount of material is sputtered away. Because of this sputtering capability, the FIB is widely used as a micro- and nano-machining tool for sample preparation for TEM. As the primary beam rasters the outer sample surface, emitted secondary electrons can also be collected to form images, and recently some other detectors have been included in FIB-SEM systems, e.g. X-ray and backscattered electron detectors, which when combined with the milling capabilities enables so-called 3-dimensional SEM/EDX/EBSD characterisation [172-174]. 3D imaging and chemical mapping combines 2D analysis with successive serial sectioning. A schematic setup of 3D SEM/EDX using FIB serial sectioning is shown in Figure 3.2. This combination allows 3D information to be obtained on phase distribution, grain morphology and distribution of elements in a specific volume.

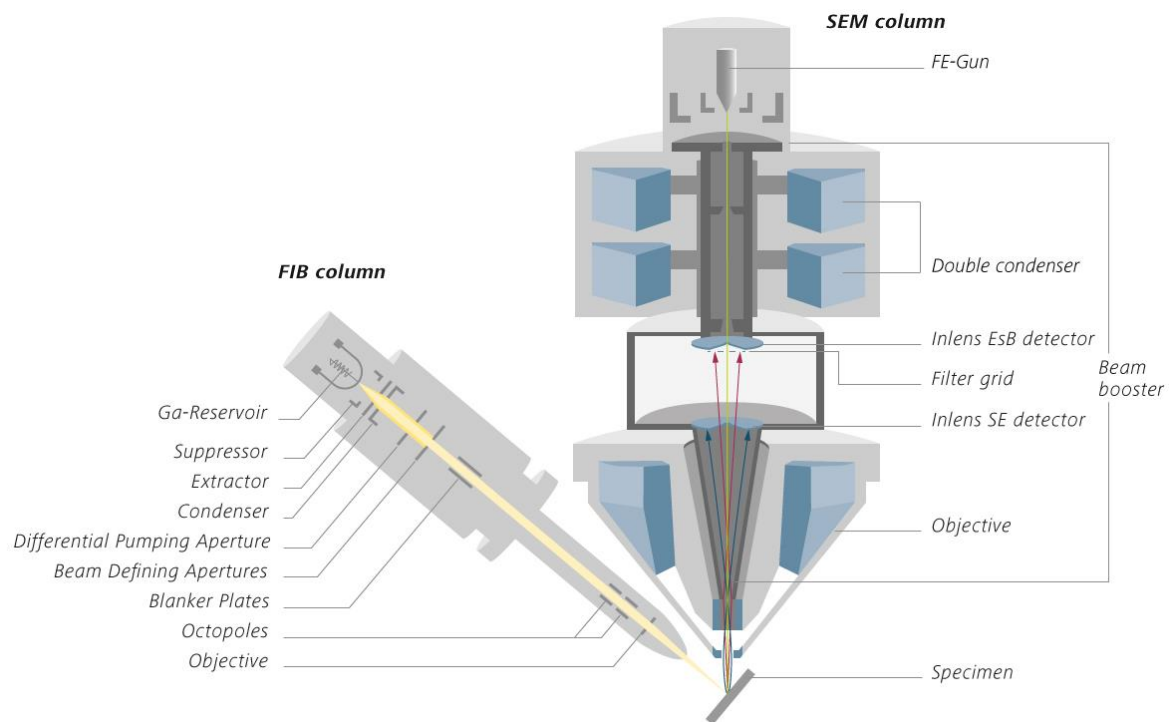


Figure 3.1 A schematic setup of a dual-beam FIB instrument (image from <https://www.zeiss.com/microscopy/int/products/fib-sem-instruments/crossbeam/crossbeam-technology.html>).

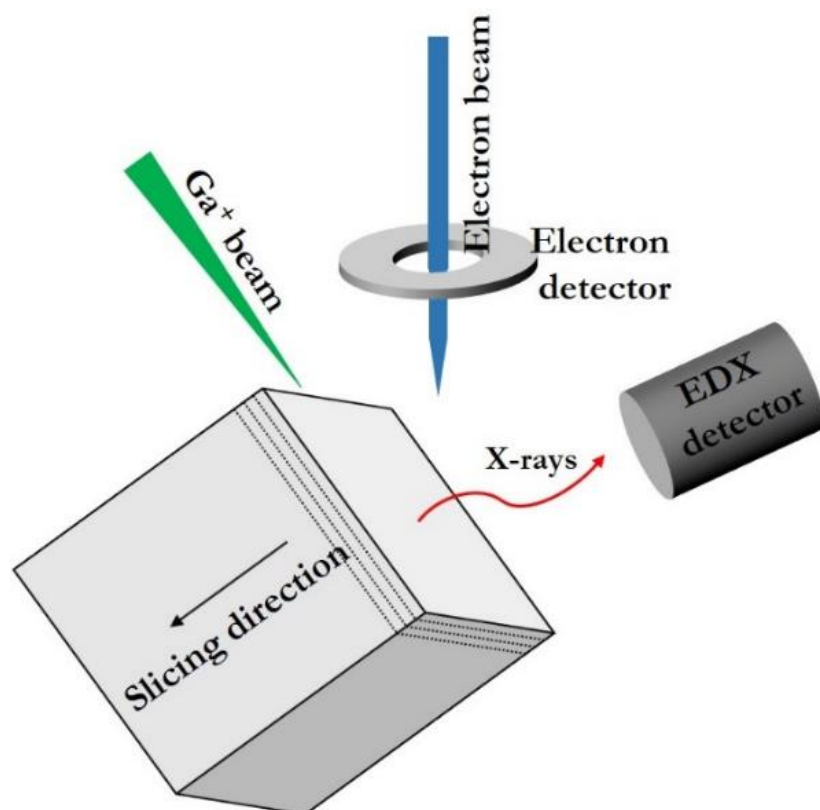


Figure 3.2 A schematic setup for 3D SEM/EDX using serial sectioning with a focused ion beam instrument.

Advanced features of the recently developed Zeiss Atlas 5 software package, e.g. auto-drift correction, auto-stigmation, auto-focus and dynamic 3D tracking algorithms, enable high resolution milling and imaging simultaneously, and allows us to analyse sample volume up to thousands of cubic micrometres with nanometre resolution in all three dimensions. An example of high-resolution 3D milling and imaging of the matrix microstructure for a Zr-2.5Nb alloy (B166) is shown in Figure 3.3. Before sectioning, a protective layer of platinum (Pt) was first deposited. Five fine lines were then milled on the top of the Pt layer using a low primary beam current (50 pA) as highlighted in Figure 3.3(c). These lines were used as markers for auto-drift correction, auto-stigmation, auto-focus and dynamic 3D tracking during the following sectioning steps. A layer of carbon was then deposited on the top of the Pt both to protect them and enhance the contrast of the markers. A trench was milled in the front of the deposited layers to a depth of 20 μm . The final cross-section surface was cleaned using a primary beam current of 700 pA, which allows an adequate image quality, Figure 3.3(b). High-resolution imaging with a pixel size of 2 nm was then acquired every 20 nm slicing thickness from the region highlighted by the yellow dotted rectangle, Figure 3.3(b). Auto-drift correction, auto-stigmation, auto-focus and dynamic 3D tracking were performed every 30s until the end of sectioning. The 3D dataset was then visualized using Avizo 9.5 software, Figure 3.4, to show the distribution of the β -phase (lighter contrast). This high-resolution milling and imaging technique has been used to reveal the tomography of zirconium alloys and oxides, e.g. the oxide/metal interface roughness, distributions of cracks in the oxide layer and distributions of second phase particles in the metal matrix.

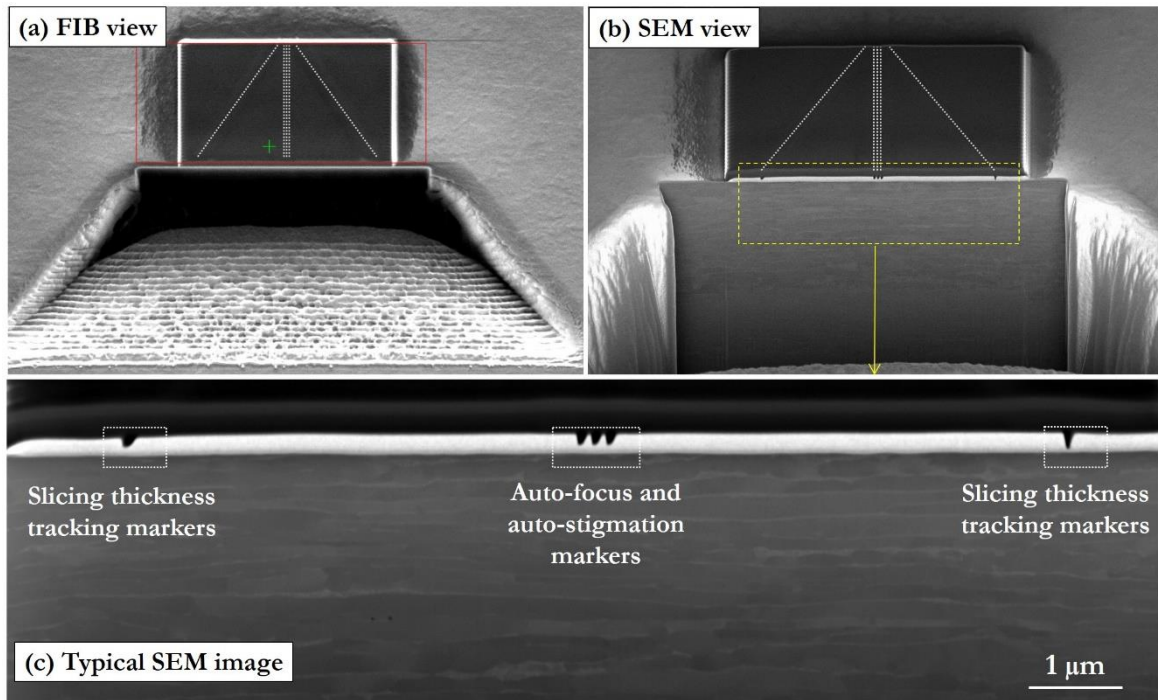


Figure 3.3 An example of 3D high-resolution milling imaging (a) the sectioning volume, (b) a the milling trench and imaging region and (c) a typical cross-sectional SEM image.

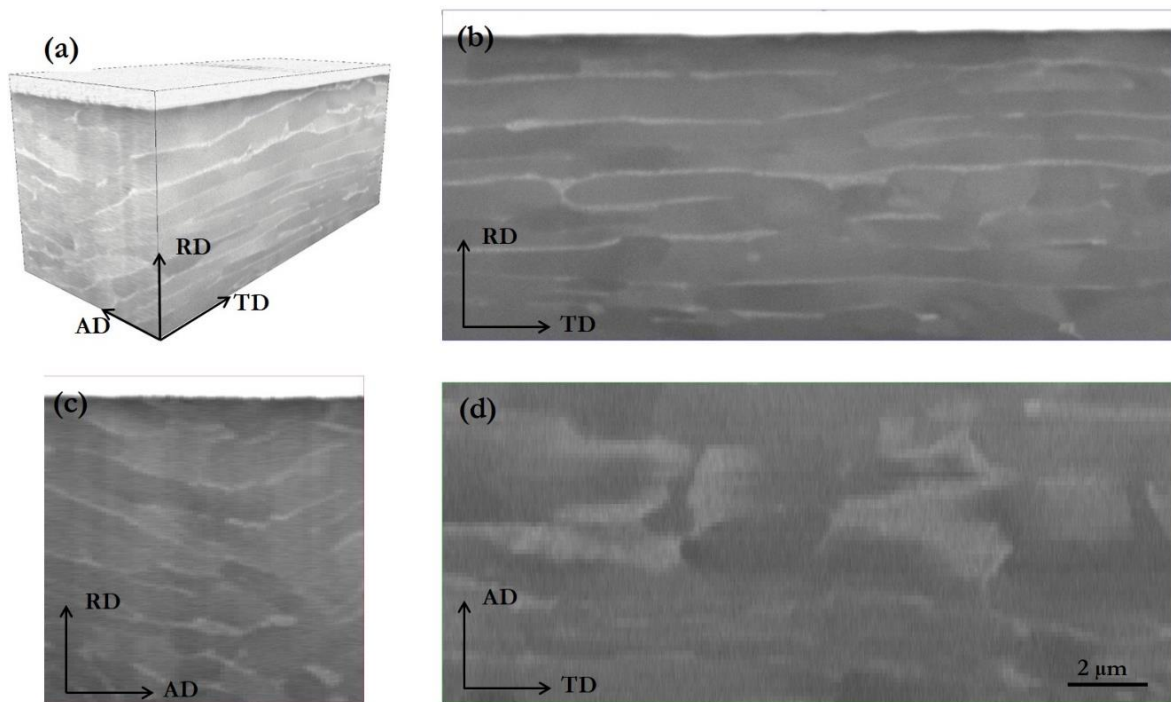


Figure 3.4 3D visualization of matrix microstructure in a Zr-2.5Nb alloy (a) an overview of the sample volume, and view along (b) axial, (c) tangential and (d) radial direction.

In this study, FIB has been used for preparation of electron transparent foils for TEM and TKD analysis, for small-volume radioactive samples for NanoSIMS analysis, and also for 3D serial sectioning and imaging. A Zeiss Crossbeam 540 FIB/SEM in the David Cockayne Centre for Electron Microscopy (DCCEM, <http://www-em.materials.ox.ac.uk>) was used on non-radioactive samples, and a FEI Helios NanoLab 600i FIB/SEM in the Materials Research Facility (MRF, <http://www.ccf.ac.uk/mrf.aspx>) at the Culham Center for Fusion Energy (CCFE) on radioactive samples. Sample preparation methodologies using FIB will be described in detail in Chapter 5.

3.2. Electron Backscatter Diffraction and Transmission Kikuchi Diffraction

EBSD has been widely used to explore microstructures in crystalline samples, revealing texture, defects, grain morphology and local deformations [175, 176]. EBSD is based on capturing and analysing Kikuchi patterns [175, 176]. When an electron beam interacts with atoms in a crystalline sample, some of the scattered electrons interacting with lattice planes at the correct diffraction angle can lead to the formation of pairs of parallel lines in the diffraction pattern, so-called Kikuchi bands [177]. These Kikuchi diffraction patterns are recorded from a phosphor screen by a CCD camera and further used for automated indexing [178-181]. Examples of Kikuchi diffraction patterns captured on the phosphor screen are shown in Figure 3.5. Kikuchi bands have a direct relation to the crystal lattice planes [182, 183]. The centre lines of each of the bands corresponds to the gnomonic projection of the lattice planes, and the width of the bands is dictated by Bragg's Law and the specimen-to-phosphor screen distance.

Three possible geometric setups are schematically shown in Figure 3.5; conventional EBSD, off-axis transmission Kikuchi diffraction (TKD) and the newly developed on-axis TKD. In conventional geometric EBSD, Figure 3.5(a), a mirror-polished bulk sample is used and

generally tilted by 70° towards the detector to increase the backscattering yield and thus the quality of the pattern obtained.

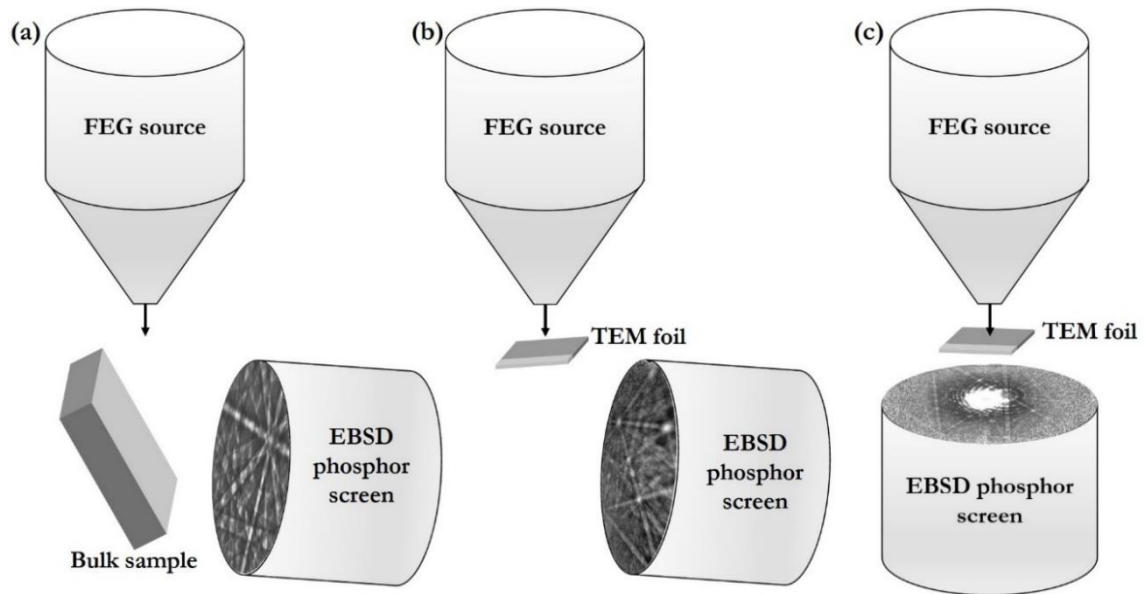


Figure 3.5 Schematic setups for (a) conventional EBSD on a bulk sample, (b) off-axis and (c) on-axis TKD on a TEM thin foil.

The combined size of the incident electron beam and the interaction volume for Kikuchi pattern formation determines the spatial resolution that can be achieved for spatially resolved orientation mapping to $\sim 20\text{-}90\text{ nm}$ [184, 185]. In the transmission geometry, Figure 3.5(b) and (c), a thin TEM foil is used instead of a bulk sample, allowing the electron beam to pass through, leading to a dramatic decrease of the interaction volume and an improvement in spatial resolution. In the on-axis configuration, Figure 3.5(c), the TEM foil is mounted with the TKD head positioned immediately beneath the sample in a transmission geometry, allowing us to acquire Kikuchi patterns directly below the sample where the signal yield is strongest and the gnomonic distortions are minimised. These features reduce the acquisition time of on-axis TKD required for diffraction patterns of similar quality by up to a factor of 50 compared with the off-axis geometry, and give a spatial resolution of few nanometers [186, 187], which has been widely utilized in the characterisation of nano-crystalline materials including oxides [187, 188], superconductors [189], metallic alloys [190, 191] and

nanoparticles [192]. Automated crystal orientation mapping in the transmission electron microscope (ASTAR) offers a spatial resolution of ~ 1 nm, and has been used successfully to map both phases and orientation in similar fine-grained microstructures [193]. However, dynamical errors are always present in ASTAR analysis, and can be a major factor limiting its angular resolution [194, 195], and overlapping grains through the thickness of the sample will result in the formation of composite diffraction patterns which can lead to deconvolution problems during the template matching process [193]. As a result, I have used the on-axis TKD technique to study the crystallography of the nanostructured materials. More information about TKD configurations can be found in [196-198].

In this thesis, conventional EBSD is used to characterize the microstructure of as-received metals with grain size of a few microns. On-axis TKD is applied to study nano-scale oxides formed on Zr alloys, and generated detailed information on the phase distributions, grain size and crystallographic orientations. TKD characterisation was carried out on a Zeiss Merlin FEG-SEM system equipped with a Bruker e-flash high resolution EBSD detector. The detailed map setting parameters used are summarized in Table 3.1. Crystallographic information for each phase used in studying phase distributions in the samples is summarized in Table 3.2. The mechanisms controlling the formation of Kikuchi bands and influencing the depth resolution in ‘on-axis’ TKD will be also discussed in Chapter 6.

Table 3.1 Summary of EBSD and TKD settings used in this work

Geometry	Sample tilt	HT (kV)	Probe Current (nA)	Detector distance (mm)	Working distance (mm)	Step size (nm)	Dwell time (ms)	Pattern resolution
EBSD	70°	20	15	18	18	100	30	320x240
Off-axis TKD*	10°	30	1.2	13	7.4	11	500	400x300
On-axis TKD	0°	30	1.5	16.5	4.4	3-5	9.3	320x240

*the off-axis TKD data courtesy of previous group member Dr. Jing Hu

Table 3.2 Crystal structures used for the EBSD and TKD analysis

Crystal structure	a(Å)	b(Å)	c(Å)	$\alpha(^{\circ})$	$\beta(^{\circ})$	$\gamma(^{\circ})$	Ref
Hexagonal Zr	3.23	3.23	5.14	90	90	120	[199]
Hexagonal ZrO	5.31	3.2	3.2	90	90	120	[68]
Cubic ZrO ₂	5.09	5.09	5.09	90	90	90	[200]
Tetragonal ZrO ₂	3.59	3.59	5.18	90	90	90	[201]
Monoclinic ZrO ₂	5.17	5.23	5.34	90	99.25	90	[202]
β -Nb	3.3	3.3	3.3	90	90	90	[203]

3.3. Transmission Electron Microscopy

Over the past 50 years TEM has become the premier technique for microstructural characterisation at the nanoscale. A schematic diagram of a TEM together with the optics of the two most basic operations, diffraction mode and imaging mode, are shown in Figure 3.6. The fundamentals of TEM have been very well described in textbooks [204-206]. A stable beam of electrons of adjustable energy is emitted from the electron gun, and then focused by a set of electromagnetic lens and apertures. The double condenser or illumination system consists of two or more lenses and one aperture. By selecting different illumination modes, a convergent or parallel illumination beam can be achieved. A convergent beam allows us to use a small bright probe to focus on a selected feature in the specimen, which is useful in analytical electron microscopy (AEM) or convergent beam diffraction. The parallel beam mode provides nearly parallel illumination at low intensity with high coherency that is useful in bright field and dark field imaging, phase contrast imaging and selected area diffraction, in Figure 3.6(b) and (c). After interacting within the thin specimen, the transmitted and forward scattered electrons are then focused by the objective lens in the imaging mode to the first intermediate image plane which subsequently acts as the object plane for the magnifying lens. Whether the viewing screen shows a diffraction pattern or an image is determined by the intermediate lens. In the diffraction mode, the intermediate lens can be focused on the diffraction pattern formed in the back focal plane of the objective lens.

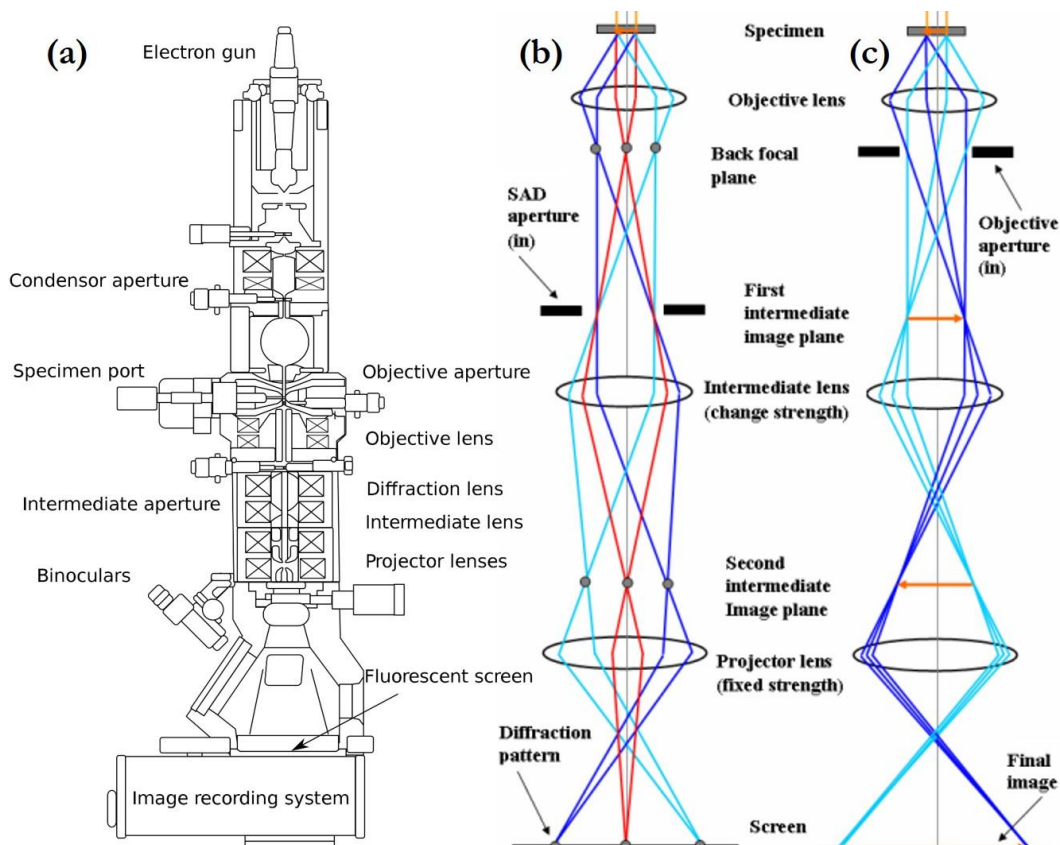


Figure 3.6 (a) schematic diagram of a TEM column and the two basic TEM modes (b) diffraction mode and (c) imaging mode. (a) is adapted from (https://commons.wikimedia.org/wiki/File:Scheme_TEM_en.svg) under the Creative Commons Attribution-Share Alike 3.0 Unported license. (b and c) are reprinted from [204] by permission from Springer Nature Customer Service Centre GmbH, Copyright (2019), and [207] with the permission from Dr. Bob Hafner.

Most of the contrast in the imaging mode is based on the non-uniform distributions of foreshattered electrons within the specimen, which is controlled by the scattering power of the atoms comprising the specimen, the number of atoms in the cross section of the sample (i.e. the specimen thickness), and the crystallinity of the sample. Fresnel contrast is an effective imaging mode to detect buried pores, and originates from the difference in the inner potential of the matrix and the cavity and depends on thickness variations in the direction of the electron beam [208]. This imaging mode can clearly reveal the morphology and distribution of nano-porosity in zirconium oxides as small as 1 nm [209], and Figure 3.7 shows an example of how nano-porosity of different types can be detected in a typical fine grained polycrystalline zirconium oxide corrosion product layer on a Zr-0.5Nb alloy imaged

under Fresnel conditions. When the image is over-focused, buried pores show dark contrast and the same defects are bright when under-focused.

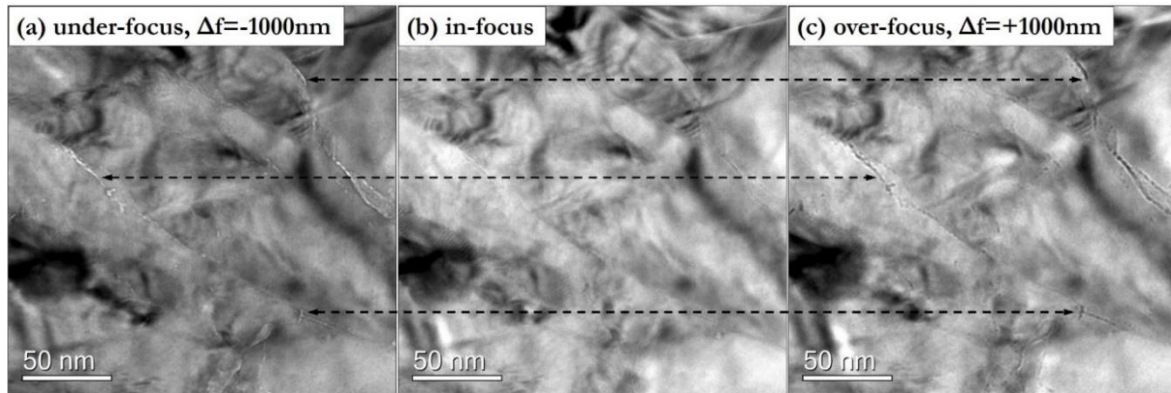


Figure 3.7 An example of the morphology of nano-pores in the zirconium oxide layer under Fresnel imaging conditions. The dashed arrows identify the same features.

State-of-art TEM analysis can be used in several different forms, such as high-resolution transmission electron microscopy (HRTEM), scanning transmission electron microscopy (STEM) and analytical electron microscopy (AEM) [210-212]. HRTEM (or HREM) is an specialized imaging mode that allows for direct imaging of the atomic structure of the sample. HRTEM usually operates under phase-contrast conditions because the information about the atomic structure of the object is contained in the phase of the elastically scattered electron waves. Phase contrast along one direction, x , for a very thin specimen can be described by the interference of two beams, the direct unscattered and diffracted beams, g :

$$I = A^2 + B^2 + 2AB\sin(2\pi g'x - \pi st)$$

where I is the intensity, A is the amplitude of the direct beam, B is a parameter related to the amplitude of the diffracted beam, and depends on s and the extinction distance for the diffraction vector $\bar{g}$; s is the excitation error which describes the deviation from exact Bragg diffraction, t is the specimen thickness and $\bar{g}' = \bar{g} + s$ along the x direction,. As a result of this equation, contrast comes from the sinusoidal oscillation in intensity along x with a periodicity of $1/\bar{g}'$. When s is set to zero, the periodicity is equal to $1/\bar{g}$ or d . In most

experimental conditions, s is much smaller than g and can be ignored. Lattice spacing information about the specimen can thus be generated from the HRTEM images. In this work, HRTEM has been used to identify irradiation-induced changes in the lattice structure of nano-crystalline zirconium oxides.

In this study, a JEOL 2100 microscope operated at 200 kV was used to carry out Fresnel contrast analysis of nano-porosity in zirconium oxides. High-resolution electron microscopy analysis was performed using a JEOL 3000F microscope operating at 300kV

3.4. Scanning Transmission Electron Microscopy

In STEM mode, instead of parallel illumination beam a convergent focused beam (with a typical spot size 0.05–0.2 nm) is used, which is then rastered over the sample so that at each point the beam is parallel to the optical axis. The signals generated point-by-point from the specimen are recorded by the detectors to form a complete image of the scanned area. Figure 3.8 shows a schematic of the annular distribution of electron scattering, where Θ and Ω are the semi-angle and solid angle of the transmitted electron beam respectively. Above a certain high angle we expect the dominant signal to be from Rutherford scattering, and the intensity of each pixel in the image will be proportional to $t\rho Z^2$, where t is the foil thickness, ρ is the density and Z is the average atomic number [213]. When the electron beam passes through the heavier material, more electrons will be scattered to higher angles compared with the lighter material. As a result, by using a high-angle annular dark-field (HAADF) detector we can collect exclusively the Rutherford scattered electrons for imaging where the contrast is directly related to the atomic number (Z-contrast image). HAADF images are widely used in this work to help identify different phases, e.g. SPPs and oxide/suboxide. It has also been found that images acquired in SEM using the ARGUSTM system are comparable with STEM and TEM images in quality [214], and by setting suitable imaging

conditions, enhanced Z or diffraction contrast can be achieved. Details on imaging using the ARGUS™ system in an SEM will be discussed in Chapter 6.

3.5. Energy-Dispersive X-ray and Electron Energy Loss Spectroscopy

When an energetic electron strikes the sample, different interactions can occur, e.g. elastic scattering, plasmon scattering, single valence electron excitation and inner shell excitations [204]. During this process, the electron loses some energy and the lost energy can be transferred to the specimen exciting secondary signals such as characteristic X-rays, Auger and secondary electrons, Figure 3.8. Collecting and analysing the characteristic X-rays and the energy lost by electrons in the undiffracted beam is the basis of energy-dispersive X-ray (EDX) and electron energy loss spectroscopy (EELS) analysis in STEM mode, and these two analytical techniques have been used to provide microchemistry information.

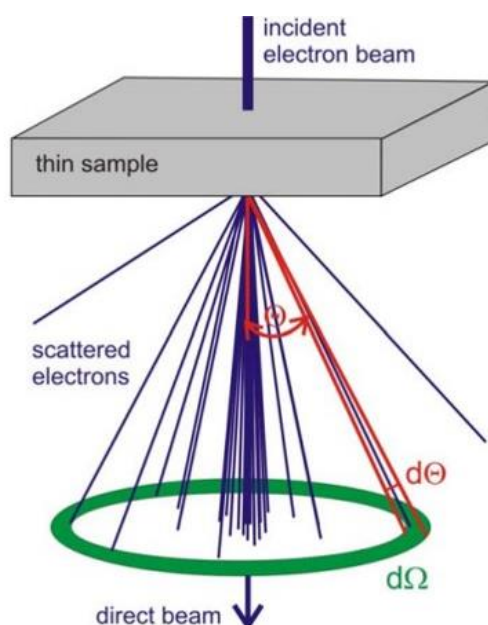


Figure 3.8 Annular distribution of electrons after passing through a thin sample (Reprinted from [215] by the permission from Dr. Frank Krumeich, ETH Zurich).

In this study, high-resolution electron microscopy and energy-dispersive X-ray (EDX) spectrometry analysis was performed using a JEOL 3000F transmission electron microscope operating at 300kV. Electron energy-loss spectroscopy (EELS) were carried out on a JEOL

ARM 200F TEM operated at 200kV with a convergence semiangle of 30 mrad and a collection semiangle of 40 mrad. The EELS spectral images were acquired in both low loss and core loss energy ranges with spatial drift corrected. For each spectrum, the zero loss peak was used for energy calibration, and principal component analysis (PCA) was carried out by using open source software HyperSpy [216].

3.6. In-situ Irradiation in TEM

In-situ TEM techniques allow researchers to study samples in real-time under heating [217, 218], cooling [219] and straining [220, 221]. In this work, TEM imaging with in-situ ion irradiation has been used to investigate site-specific microstructures at the nanoscale while the specimen is being irradiated. Ion irradiation offers several advantages over neutron irradiation, including the avoidance of radioactive hazards and the ability to access end-of-life damage levels of in-service nuclear materials in less than a day. However, there are several factors we need to take into account when trying to relate our in-situ observations to the real damage conditions in service. The different radiation species and dose rates of experimental and in-reactor conditions can lead to different size and densities of cascades, and may lead to different microstructural evolution [104]. The different sample geometry also need to be considered as the large surface areas associated with thin TEM foils may help stabilise particular structures in a way that cannot happen in bulk oxides.

Two state-of-art in-situ irradiation TEM systems were used in this work to study the response of zirconium oxides to irradiation. The first set of in-situ irradiation experiments was carried out at the Intermediate Voltage Electron Microscopy (IVEM)-Tandem Facility at Argonne National Laboratory, Figure 3.9(a). A Hitachi-9000 microscope (300 kV, LaB₆ source) was used for TEM observations, with in-situ irradiation realised by the intersection of the accelerated ion beam and electron beam at the sample stage in the TEM column. The

second set of experiments was done at the MIAMI2 facility, University of Huddersfield, UK, using a Hitachi-9500 microscope (300 kV, LaB₆ source), Figure 3.9(b).

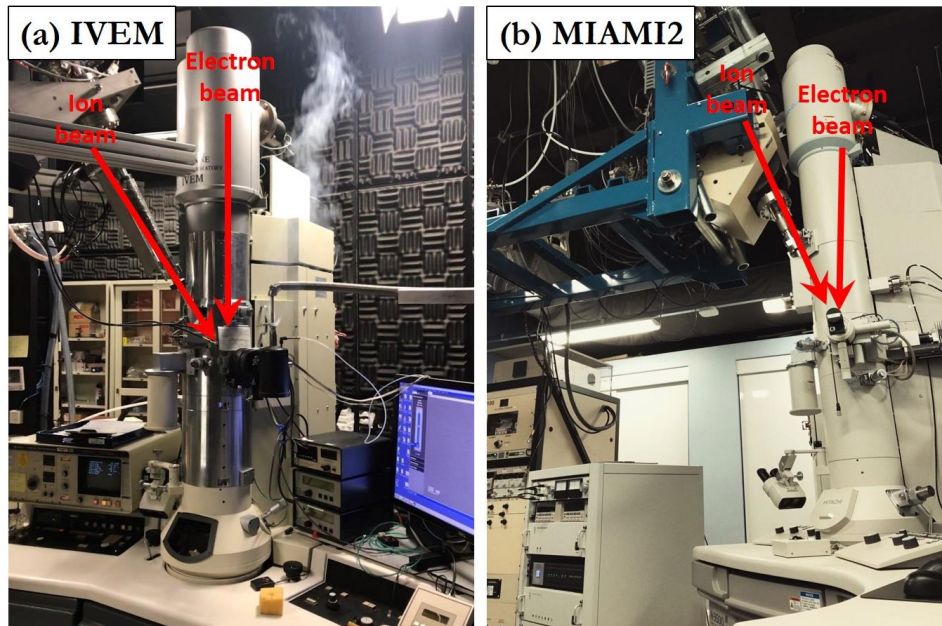


Figure 3.9 The IVEM and MIAMI2 in-situ irradiation facilities.

A flux of Kr²⁺ ions with energy of 700 KeV or 1 MeV at a rate of $\sim 10^{12}$ ions.cm⁻².s⁻¹ was used to irradiate thin TEM foils, and can provide a damage rate up to $\sim 10^{-4}$ dpa.s⁻¹ in zirconium oxide. As a comparison, in-reactor neutron-irradiation damage rates range from 10^{-8} to 10^{-7} dpa.s⁻¹ [124, 125]. The dpa rates for bulk ZrO₂, suboxide and the metal matrix were calculated using SRIM [222] by selecting the Kinchin-Pease mode as recommended by Stoller [223], and are summarized in Table 3.3. Displacement energies are set to 40 eV and 28 eV for Zr and O in h-ZrO suboxide, α -Zr(O_{Sat}) and α -Zr phases [224]. Higher displacement energies for Zr and O in m-ZrO₂ are required [225], and values of 120 eV for O and 80 eV for Zr were used in my calculation. It is worth mentioning that the damage rate calculated by SRIM is mainly based on these chemical properties, so the influences of crystal structure, dose rate and temperature are not taken into consideration. By using the high-energy flux, 700 keV for example, more than 99% of the ions will be transmitted through a typical TEM thickness of 50 nm. An example of the calculated residual Kr concentration in

a specimen irradiated by 700 keV Kr²⁺ ions for a fluence of 1.9x10¹⁶ ions.cm⁻² is shown in Figure 3.10, and the average residual Kr concentration is ~0.026 at.%.

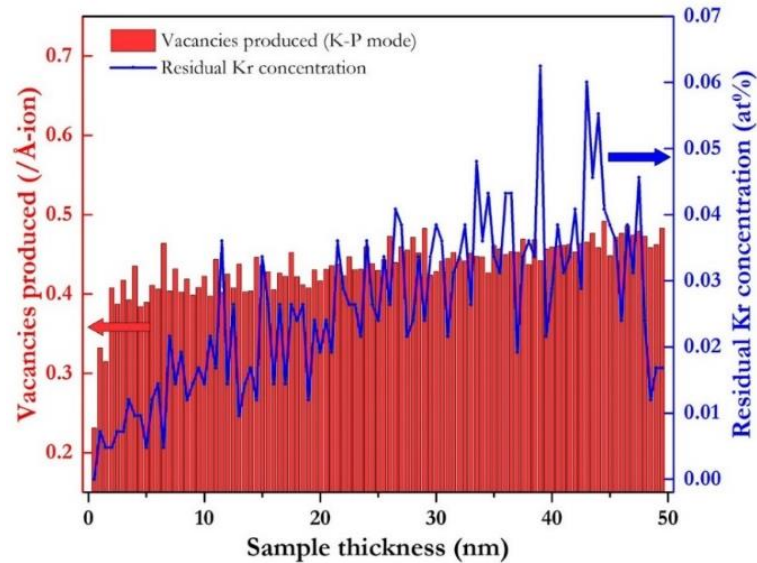


Figure 3.10 SRIM damage profile and residual Kr concentration in Zr thin foil irradiated by 700 KeV Kr²⁺ ions for a fluence of 1.9x10¹⁶ ions.cm⁻².

Table 3.3 Summary of properties of oxide, suboxide and Zr metal matrix, and damage rates calculated by SRIM for 8 x 10¹¹ ions/cm²/s 1 MeV Kr²⁺ ions

	Density (g/cm ³)	Defects/(Å-ion)	Damage rate (dpa/s)
m-ZrO ₂	5.7	0.4	3.7 x 10 ⁻⁴
h-ZrO suboxide	6.9	1.2	1.2 x 10 ⁻³
α-Zr(O _{Sat})	6.8	1.1	1.5 x 10 ⁻³
α-Zr	6.5	1	1.8 x 10 ⁻³

3.7. High-resolution Secondary Ion Mass Spectrometry

Secondary ion mass spectrometry (SIMS) is a major technique for investing a wide range of materials from semiconductors and metals to polymers and biological materials due to its combination of very high chemical sensitivity, excellent mass resolution, surface sensitivity, and good lateral and depth resolution [226-229]. SIMS is able to detect all elements (and isotopes) from hydrogen to uranium with parts of billion sensitivity from some elements, as well as being able to detect and distinguish between molecular ions [230, 231]. Benninghoven [227] gave a definition for the so-called “static limit” for SIMS analysis. If

the probability of an incident ion hitting an area twice during one measurement is below 1%, one can assume static conditions, and every impact yields signal from undisturbed surface areas. Static SIMS uses a primary ion beam with a very low current density compared with dynamic SIMS to remain within the static limit and this is the key principle of Time-of-Flight SIMS (ToF-SIMS) [232, 233]. Static SIMS can provide molecular information whereas dynamics SIMS provided mostly elemental and isotopic information because the rate of damage to the sample surface is much higher resulting in the breaking of most chemical bonds [229]. The faster erosion rate of dynamic SIMS also allows bulk analysis of the sample, including depth profiling and three-dimensional imaging. A CAMECA NanoSIMS 50 has been used in this study, as shown in Figure 3.11 with key features labelled. A schematic showing the principles of SIMS analysis is shown in Figure 3.12. When high-energy particles (e.g. O^-/O^{2-} or Cs^+ in NanoSIMS) hit the sample surface, energy is transferred to the sample by a series of elastic and inelastic collisions and only ions from the immediate surface are sputtered [227, 234], Figure 3.12. After being focused by a set of electrostatic lens and apertures, the mass- and energy- selected secondary ions are finally collected by the detectors.

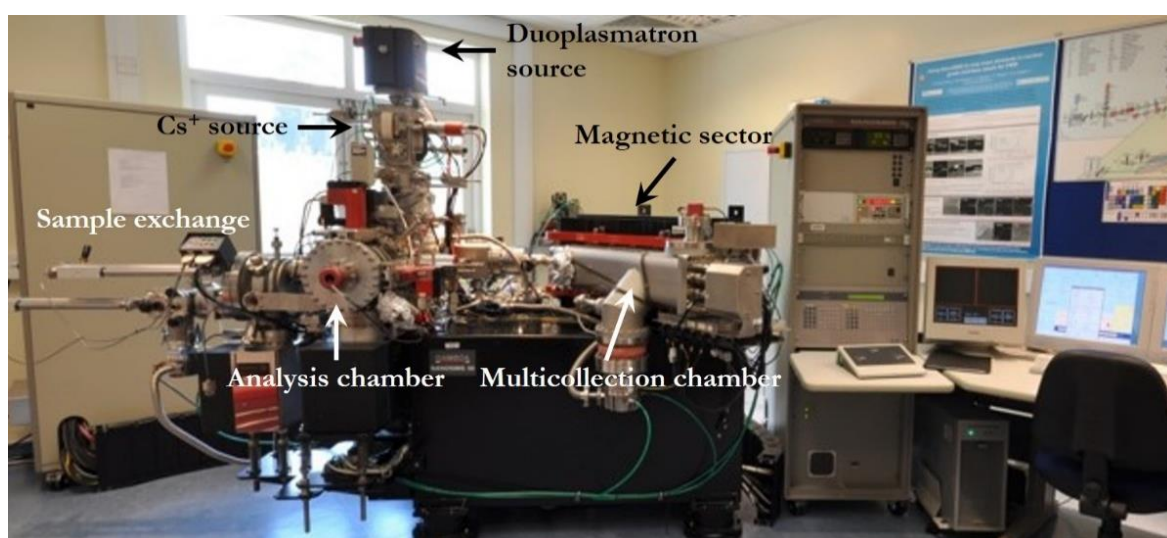


Figure 3.11 The CAMECA NanoSIMS50 used in this work.

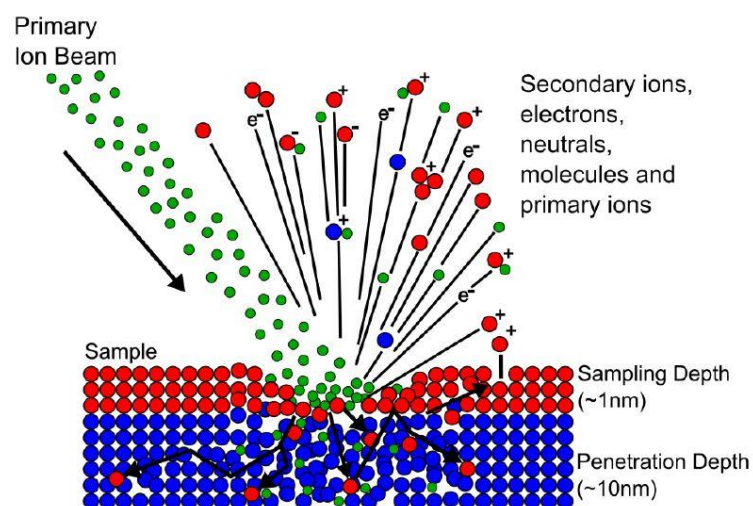


Figure 3.12 A schematic diagram showing the principles of SIMS analysis (Reprinted from [229] by permission from John Wiley and Sons, Copyright (2019)).

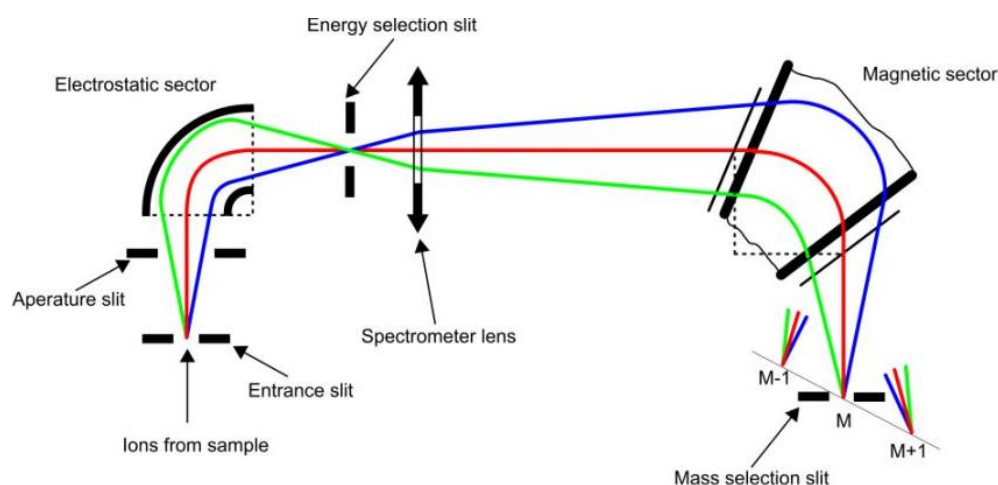


Figure 3.13 Schematic diagram of a double focusing mass spectrometer showing the electrostatic and magnetic sector (Reprinted from [229] by permission from John Wiley and Sons, Copyright (2019)).

One important feature of NanoSIMS is the mass analyser in a Mauttach-Herzog configuration [227] with a 90° spherical electrostatic sector and an asymmetric magnet, shown schematically in Figure 3.13. This type of mass spectrometer allows the NanoSIMS to achieve at the same time both high ion transmission and mass resolution ($M/\Delta M > 10^4$) combined with good lateral resolution [229], ~50 nm. When the ions enter the magnetic field, they are separated according to their mass-to-charge ratios. After mass selection, the secondary ions are detected using electron multipliers which can accurately measure low intensity ion signals. Using the CAMECA NanoSIMS 50, five ions can be collected

simultaneously. This multicollection capability allows the users to determine precise isotope ratios and compare the ratios from different locations with submicron resolution.

Figure 3.14 shows schematic for different NanoSIMS analysis geometries. In the in-depth analysis, Figure 3.14(a and c), the surface oxide is firstly sputtered by the Cs^+ beam and then the underlying metal matrix. In cross-sectional analysis, Figure 3.14(b), pre-polishing is required to reveal the position of oxide layers, and NanoSIMS mapping is then carried out on the cross-sectional face. Samples that were corroded in an autoclave are not radioactive and can be directly used in NanoSIMS analysis. In-reactor samples are highly radioactive and more work is required to reduce the radioactivity within the specimen, needing more complex sample preparation. The in-depth analysis is normally used for samples with thin oxide layers ($< 3 \mu\text{m}$), and cross-sectional analysis for thicker oxide layers. Detailed methodologies developed in this work for sample preparation are introduced in Chapter 5.

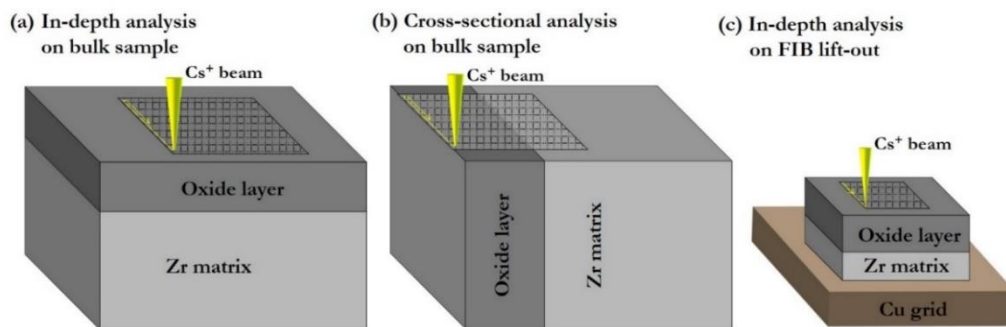


Figure 3.14 Schematics of NanoSIMS analysis geometries (a) in-depth analysis and (b) cross-sectional analysis on bulk samples, (c) in-depth analysis on a FIB lift-out sample.

Table 3.4 NanoSIMS settings for in-depth and cross-sectional analysis in this work

Analysis geometry	ES, AS	D1 (μm)	Resolution (nm)	Raster size (μm^2)	Pixels	Dwell time (μs)
In-depth	open	D1-2, 300	150–200	5×5	256×256	1000
Cross-sectional	open	D1-3, 150	100–150	8×8	512×512	1000

In this study, NanoSIMS together with SEM/FIB analysis was applied to map hydrogen distributions on a submicron scale in zirconium oxides. Detailed settings can be found in

Table 3.4. A 16 keV Cs^+ primary beam was used, and $^1\text{H}^-$ and $^2\text{H}^-$ or $^2\text{H}^-$, $^{16}\text{O}^-$ and $^{18}\text{O}^-$ secondary ions were simultaneously collected. A 3D dataset is built up by the collection of a large number of segmental 2D images. ImageJ with the OpenMIMS plugin (Harvard) [235] was used to read and analyse the NanoSIMS data, and to create deuterium depth profiles and cross-sectional views. 3D visualization of the distributions of hydrogen/deuterium is carried out using the Avizo software package, following procedures developed during this project and has been reported in a publication [236], and an example is shown in Figure 3.15. Detailed steps of the 3D reconstructions are:

- (1) Extracted stack data in ImageJ of deuterium, oxygen and secondary electron (SE) signals are saved as '*.raw' format files separately, and then loaded into Avizo.
- (2) Oxygen and secondary electron (SE) signals are smoothed by the following steps: 'Image Processing' then 'Smoothing and Denoising' and 'Median Filter'. Then data is smoothed by averaging over 3 pixels to obtain a clear 3D oxide/metal interface.
- (3) Deuterium pixels are masked by the function 'Edit New Label Field'. The pixels were separated into two groups; high-count pixels containing > 4 $^2\text{H}^-$ counts, and low-count pixels containing ≤ 4 $^2\text{H}^-$ counts.
- (4) The masking pixels are generated and showed as a 3D surface by functions 'Generate surface' and 'Show surface', sequentially.

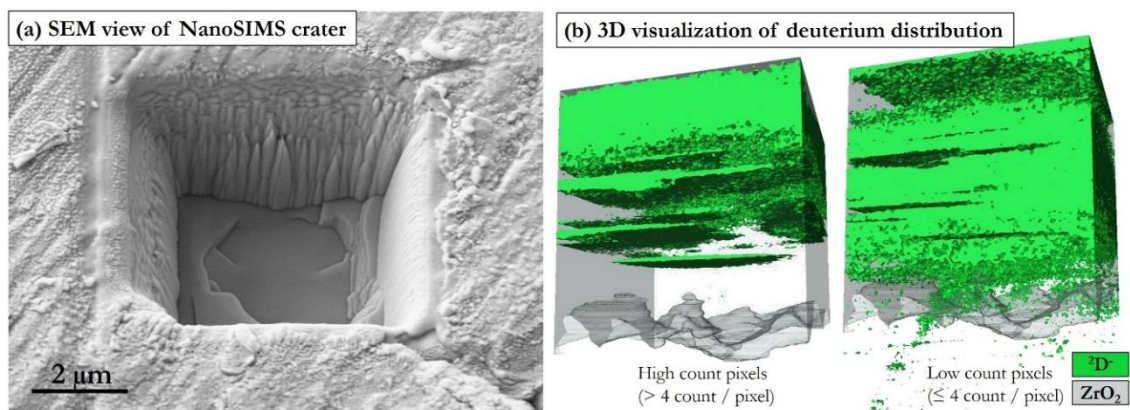


Figure 3.15 (a) SEM view of a typical NanoSIMS crater and (b) an example of 3D visualization of distribution of deuterium in the zirconium oxide layer.

Chapter 4 Materials

This chapter gives an overview of the materials used in this work, including the characterisation of as-received alloys, comparisons of corrosion kinetics and reasons for selecting the samples used in this work to progress the project. A summary of selected materials for specific study purposes is shown in Table 4.3 at the end of this chapter.

I would like to thanks Dr. Jonna Partezana, Westinghouse Electric Company and Dr. Heidi Nordin, Canadian Nuclear Laboratories for helping arranging the samples and providing the detailed sample information like fabrication processes, corrosion and hydrogen pick-up data. I would also thanks my colleagues Anna Callow and Guanze He for their help in the as-received alloy characterisation.

4.1. As-received Alloy Characterisation

Commercial Zircaloy-4 and two types of Zr-Nb alloys with different starting microstructures were provided by the Westinghouse Electric Company and by Canadian Nuclear Laboratories (CNL). As a result of the different thermo-mechanical treatments involved in the fabrication processes of Westinghouse Zircaloy-4, Zr-Nb alloys and CNL Zr-2.5Nb alloys, different grain morphologies and distributions of second phases were developed in these materials. The Westinghouse Zr-Nb alloys had a final annealing step at 560°C which leads to recrystallized equiaxed α -Zr grains, with the Nb mostly in solid solution and in small β -Nb particles homogeneously distributed inside the grains, Figure 4.1(a). Zircaloy-4 has similar grain structure as Westinghouse Zr-Nb alloys but different types of SPPs, mostly Zr(Fe,Cr)_2 Laves phase. The different content of Nb in the three Westinghouse RXA alloys (Zr-0.5Nb, Zr-1Nb) results in different number densities of SPPs, but the size is similar with an average diameter of ~50 nm. The CNL Zr-2.5Nb alloys were extruded at 815°C and then

stress relieved at 400°C for 24 hours. The microstructures of both matrix and second phases are greatly influenced by the extrusion process so that the microstructure of Zr-2.5Nb alloys includes α -Zr grains elongated in both transverse and longitudinal directions, with thin layers of β -Zr (~20 at% Nb) between the α -Zr grains, Figure 4.1(b).

Quantitative results showing number densities and total area fraction of the second phases in these alloys were analysed using ImageJ, and are shown in Table 4.1. For each of the samples, an area of at least 60 μm^2 was analysed to ensure statistical significance. APT data provided thanks to Anne Callow and Dr. Brian Setiadinata was used to quantify the matrix chemical composition, Table 4.1. The CNL SRA Zr-2.5Nb alloy has a much higher area fraction (but lower number density) of the Nb-rich phase, but the matrix composition is similar to that of the Westinghouse RXA Zr-Nb alloy. In addition, no obvious Fe-rich phases were seen in the CNL SRA Zr-2.5Nb alloys, but were frequently observed in the Westinghouse Zr-Nb alloys.

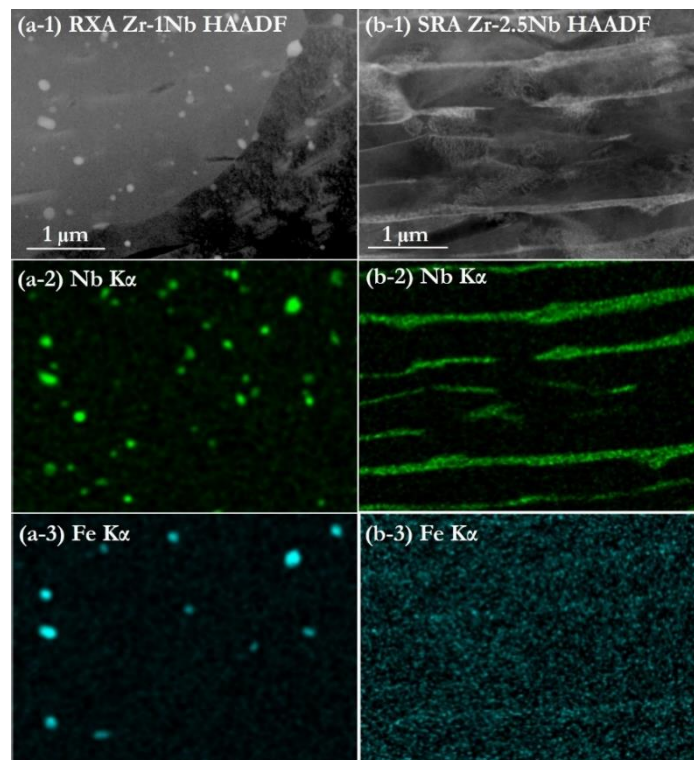


Figure 4.1 HAADF and EDX showing the morphology and distribution of second phases in different Zr-Nb alloys, (a) Westinghouse RXA Zr-0.5Nb and (b) CNL SRA Zr-2.5Nb alloy.

Table 4.1 Distribution of second phase and matrix composition in different alloys.

	Second phase number density (#/um ²)	Second phase total area Fraction (%)	Matrix composition from APT (at. %)
Westinghouse RXA Zr-0.5Nb	3.71	1.01	Zr-0.41Nb-0.013Fe
CNL SRA Zr-2.5Nb	0.72	25.43	Zr-0.45Nb-0.07Fe

APT data for matrix composition from Anne Callow and Dr. Brian Setiadinata

The texture of zirconium alloys affects its in-service performance because properties such as the yield strength, thermal and in-reactor creep strengths, fatigue and stress corrosion cracking resistance, hydride orientation and irradiation-induced growth behaviour are strong functions of texture [237, 238]. As a result of the different thermo-mechanical treatments involved in the fabrication processes of the Westinghouse RXA Zr-Nb and CNL Zr-2.5Nb alloys, they develop different preferred orientations or textures.

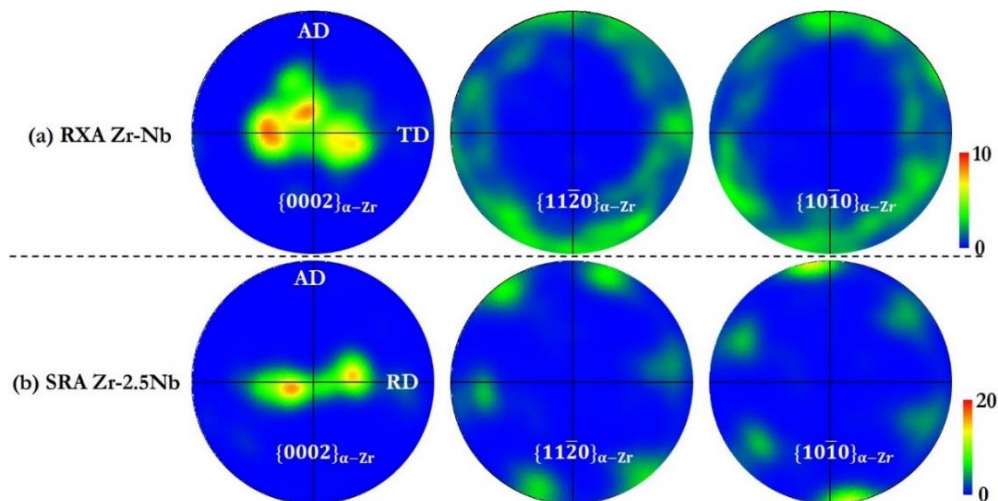


Figure 4.2 Contoured low-indexed poles (half width 15°) of (a) Westinghouse RXA Zr-0.5Nb tube and (b) CNL SRA Zr-2.5Nb tube sample.

EBSD and TKD were used to measure the texture formed in these alloys, and Figure 4.2 shows the measured pole figures for $\{0002\}_{\alpha\text{-Zr}}$, $\{11\bar{2}0\}_{\alpha\text{-Zr}}$, and $\{10\bar{1}0\}_{\alpha\text{-Zr}}$ respectively. Through the texture measurements using EBSD and TKD in this study is from relatively small regions, the preferred crystal orientations measured in these materials are similar to

those from similar materials using XRD and EBSD on large scanning regions [240, 242]. The basal pole distribution in the Westinghouse RXA Zr-1Nb sample is close to the radial direction (or corrosion direction), while in the CNL SRA Zr-2.5Nb tube sample the basal poles are distributed closer to the tangential direction (TD) and $(11\bar{2}0)_{\alpha-Zr}$ lies along the corrosion direction. More details about the texture formation in these two materials can be found in [238, 239]. Based on the texture measured in the current study and measurements on similar materials in the literature [238-240], the preferred crystal orientations in these materials are shown schematically in Figure 4.3 (AD: axial direction, TD: tangential direction, RD: radial direction.).

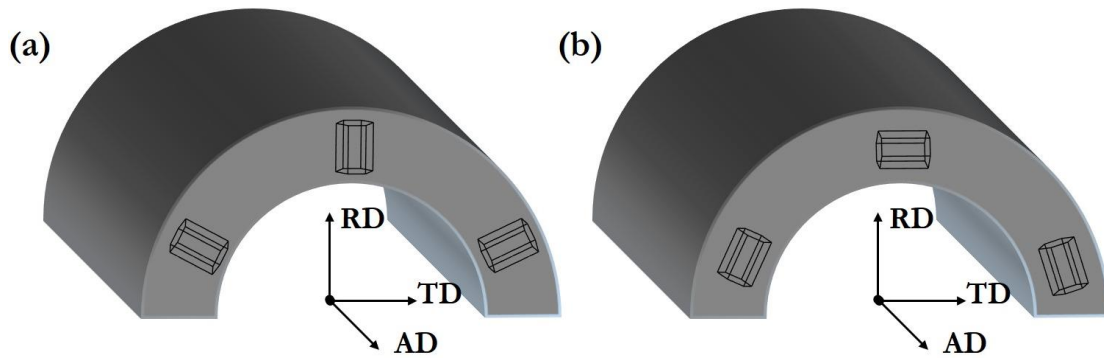


Figure 4.3 3-dimensional schematic of the dominant crystal orientation in the manufactured Zr alloys, (a) Westinghouse RXA Zr-Nb (b) CNL SRA Zr-2.5Nb alloys.

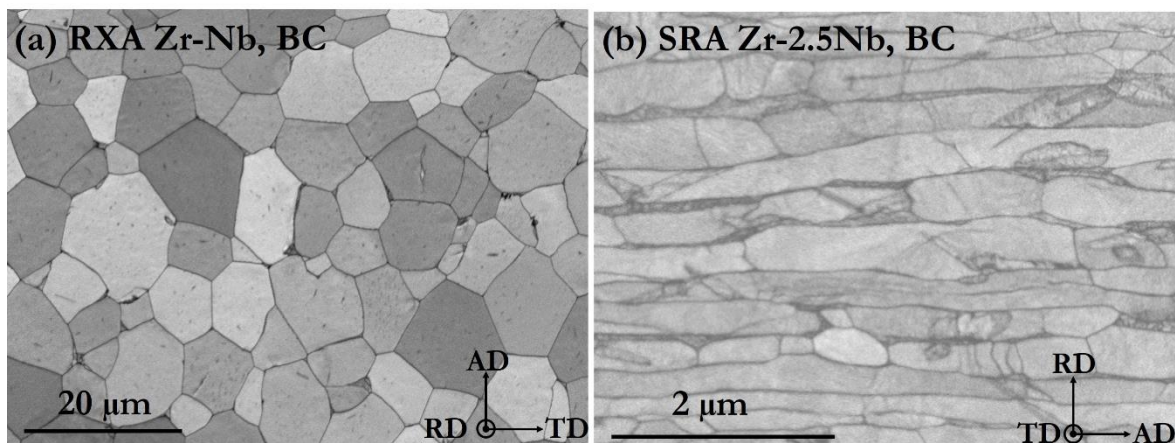


Figure 4.4 (a) EBSD map of Westinghouse RXA Zr-Nb sample and (b) TKD map of CNL SRA Zr-2.5Nb sample in tube format.

The band contrast, phase and orientation maps of the Westinghouse Zr-Nb and CNL Zr-2.5Nb alloys are shown in Figure 4.4. The Westinghouse Zr-Nb alloys had a final annealing step at 560°C which leads to recrystallized equiaxed α -Zr grains with an average diameter of $\sim 10\ \mu\text{m}$, Figure 4.4(a). Small SPPs distributed inside the grains are below the spatial resolution of bulk EBSD analysis. For CNL Zr-2.5Nb alloys, elongated α -Zr grains of length $\sim 5\ \mu\text{m}$ and width $\sim 0.5\ \mu\text{m}$ with thin layers of β -Zr between them can be seen, Figure 4.4(b), similar to the observations from STEM analysis in Figure 4.1(b). Previous papers have described the typical microstructures of these Zr-2.5Nb alloys in more detail [241-243].

4.2. Corrosion Kinetics

The commercial Zircaloy-4 and model Zr-0.5Nb alloy samples provided by the Westinghouse Electric Company were corroded in a light water autoclave at 360°C and 18 MPa for up to 225 days. Three sections of Zr-2.5Nb alloy tubes were provided by CNL, corroded under different conditions; autoclave, out-of-flux and in-flux. Here, in-flux stands for exposure to irradiation and in-reactor water chemistry in the Halden reactor, out-of-flux stands for exposure to in-reactor water chemistry but without irradiation in the Halden Reactor and autoclave stands for corrosion in a static autoclave filled with D₂O (pH=10.5, LiOD), and at 300°C and 10 MPa.

The weight gains are plotted as a function of exposure time for the different alloys in Figure 4.5. All the alloys autoclave-corroded show sub-parabolic oxidation kinetics as indicated by the power law fits, $\delta(t)=Kt^n$, with δ the oxide thickness and t the exposure time [9, 31]. The pre-transition power law fitting constants are summarized in Table 4.2. Even though corroded under different conditions (water chemistry, pressure and temperature), the autoclave-corroded Westinghouse RXA Zr-Nb alloys show a similar kinetic constant ($n=0.37$) as the CNL SRA Zr-2.5Nb alloys ($n=0.38$), but a much earlier onset of transition

to accelerated corrosion rates (~160 days in Westinghouse RXA Zr-Nb alloys vs ~700 days in CNL SRA Zr-2.5Nb alloys). From Figure 4.5, it can also be seen that the concentrations of hydrogen/deuterium absorbed in the CNL Zr-2.5Nb alloys are much lower than that in the Westinghouse Zr-Nb alloys, even at very late corrosion stages (e.g. ~17 ppm after 2000 days in CNL Zr-2.5Nb vs ~50 ppm after 225 days in Westinghouse Zr-Nb). These differences are believed to be induced by the different microstructures of these samples and the oxides that grow on them, and will be discussed below.

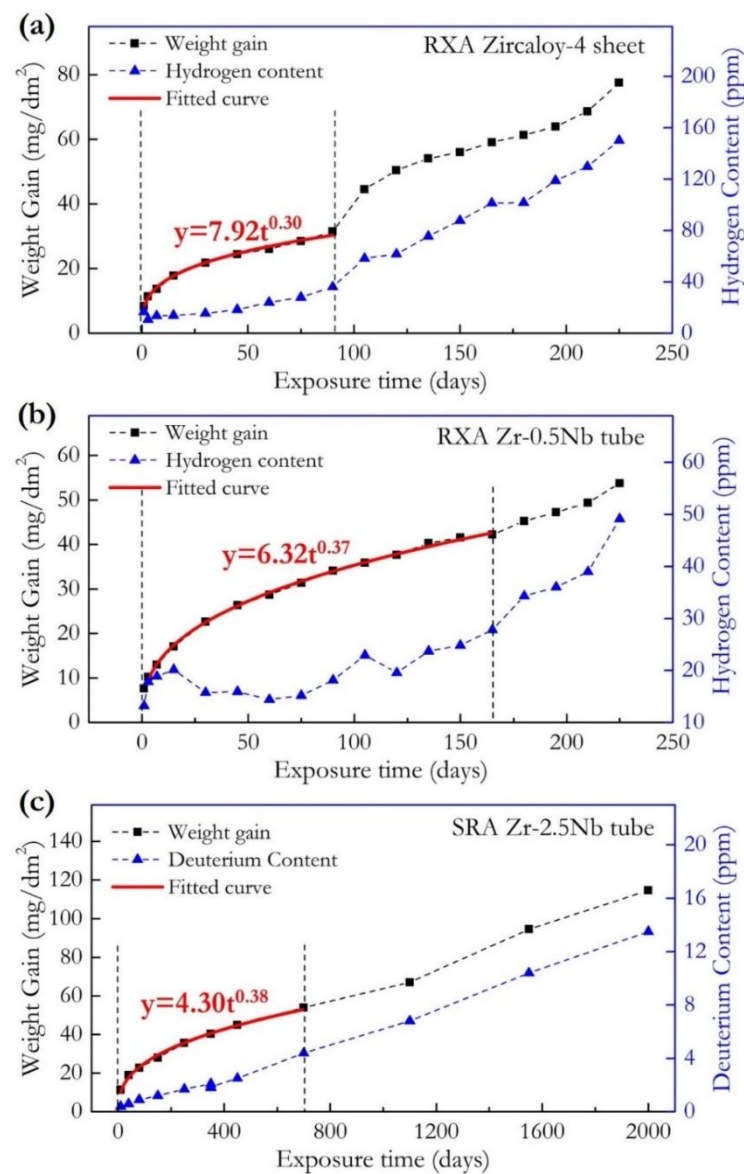


Figure 4.5 Autoclave corrosion kinetics and hydrogen (deuterium) content as a function of exposure time for (a) commercial Zircaloy-4, (b) RXA Zr-0.5Nb and (c) SRA Zr-2.5Nb alloys and corresponding power law fits of the pre-transition regimes. (Plotting data provided by Dr. Jonna Partezana, Westinghouse, US and Dr. Heidi Nordin, CNL, Canada).

Table 4.2 Summary of power law fittings of pre-transition constants on different alloys

Alloys	Corrosion conditions	K	n
Zircaloy-4	Autoclave, 360°C and 18MPa, H ₂ O	7.92±0.31	0.30±0.01
RXA Zr-0.5Nb tube	Autoclave, 360°C and 18MPa, H ₂ O	6.32±0.16	0.37±0.01
SRA Zr-2.5Nb tube	Autoclave, 300°C and 10MPa, D ₂ O	4.30±0.27	0.38±0.01
SRA Zr-2.5Nb tube	Out-of-flux, 325°C and 10MPa, D ₂ O	1.00±0.07	0.63±0.01
SRA Zr-2.5Nb tube	In-flux, 325°C and 10MPa, D ₂ O	0.22±0.09	0.93±0.06

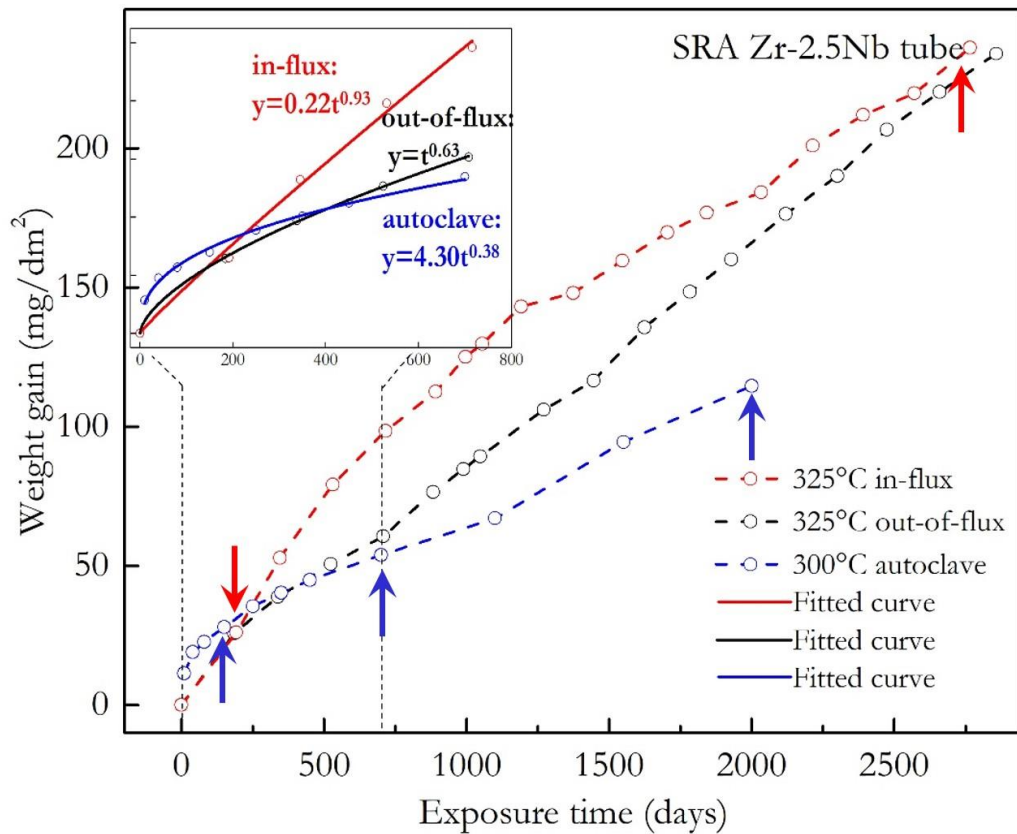


Figure 4.6 Comparisons between in-flux, out-of-flux and autoclave corrosion kinetics and corresponding power law fits of the pre-transition regimes for SRA Zr-2.5Nb samples (Plotting data provided by Dr. Heidi Nordin, CNL, Canada), selected samples used in this study are highlighted by red and blue arrows.

The corrosion kinetics of in-flux, out-of-flux and in-autoclave corroded Zr-2.5Nb alloys and the corresponding power law fitting in the pre-transition regimes are plotted in Figure 4.6. The pre-transition power law fitting constants of these samples are summarized in Table 4.2. Neither the in-flux nor the out-of-flux corrosion of these samples shows the traditional sub-parabolic kinetics in the autoclave-corroded samples studied here, and widely reported in the literature [96, 97, 102]. An approximately linear corrosion rate is seen in the in-flux

corroded samples, and the out-of-flux power law fitting constant is ~ 0.63 . Both the in-flux and out-of-flux corrosion show accelerated kinetics compared to the autoclave samples, indicating that both direct radiation effects in the alloy and its oxides and the specific in-reactor coolant chemistry can induce enhanced corrosion rates. These structure and chemistry of these samples will be studied and discussed in this work.

4.3. Selected Samples

Samples with specific exposure times were selected for microstructural characterisation and analysis. The in-reactor neutron flux for samples B56 (Zr-2.5Nb corroded for 190 days at 250°C) and B70 (Zr-2.5Nb corroded for 190 days at 325°C), and B74 (Zr-2.5Nb corroded for 2700 days at 325°C) were $\sim 4.63 \times 10^{17}$, $\sim 4.73 \times 10^{17}$ n.m⁻².s⁻¹ and $\sim 4.32 \times 10^{17}$ n.m⁻².s⁻¹ respectively. The damage dose of the metal matrix in terms of dpa can be calculated by applying a conversion factor, 1 dpa $\approx 4.1 \times 10^{24}$ n.m⁻² [244], and the corresponding damage dose is 1.85 dpa for B56, 1.89 dpa for B70 and 24.6 dpa for B74. By comparison, the calculation of damage dose in oxides is more complex because the corrosion process is ongoing, which means the freshly formed oxides at the metal/oxide interface will suffer lower damage dose than those formed earlier. The conversion factor for zirconium oxides from fluence to dpa is not available in the literature. As there are three ions in one ZrO₂ molecule, the average displacements of atom may be simplistically estimated by 1/3 of that in the zirconium matrix. Following this assumption, I have plotted the damage dose (dpa) in oxides as a function of oxide depth for B74, $\text{dpa} = 0.12d^{1.56}$, where d is the oxide depth from the oxide/metal interface, Figure 4.7. The damage dose at different depths in the oxides can be directly estimated using this equation, e.g. the damage dose is <1 dpa in the inner 4 μm of oxide layer but >8 dpa in the outer 2 μm .

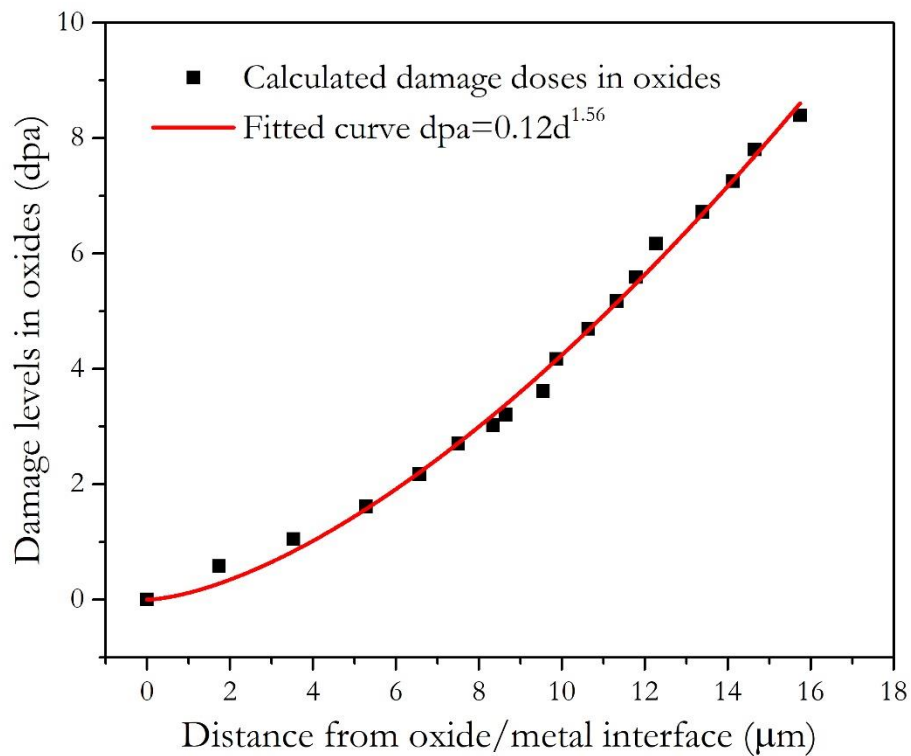


Figure 4.7 Estimated damage dose in oxides as a function of oxide depth on B74 samples.

A list of these samples and why they were selected is summarized in Table 4.3. Characterisation was carried out on all the as-received alloys (B166 for SRA Zr-2.5Nb, A-1 for RXA Zr-0.5Nb tube, N1-1 for RXA Zr-1Nb sheet and N-1 for annealed Zr-1Nb sheet) to provide information on pre-corrosion/irradiation microstructures and phase distributions. Three sets of SRA Zr-2.5Nb alloys provided by CNL were tested under different corrosion conditions as described above. 1F10 (autoclave corroded for 150 days at 300°C) and 1F1 (autoclave corroded for 700 days at 300°C) were selected to compare the morphologies of oxides formed in the pre-transition regime with the out-of-flux and in-flux samples, B56 (in-flux corroded for 190 days at 250°C), B82 (out-of-flux corroded for 185 days at 250°C), B70 (in-flux corroded for 190 days at 325°C) and B96 (out-of-flux corroded for 185 days at 325°C). B56 and B82 were corroded at the same temperature (250°C) and water chemistry for short periods and selected to compare irradiation effects at low temperatures. B70 and B96 corroded at 325°C for ~190 days were selected to study irradiation effects at higher

temperatures. B74 was corroded in-flux for 2700 days and so was heavily irradiation-damaged. By comparing the microstructures and microchemistry between B74 and the short-term corroded samples, I was aiming to study the time-dependent mechanisms controlling the enhanced corrosion rate under irradiation.

In addition, samples from the previous MUZIC-2 project were also used to study the oxide microstructure of autoclave corroded samples. Commercial Zircaloy-4 and model Zr-0.5Nb alloys at a earlier corrosion stage, and a similar model Zr-1Nb alloy at a much later stage were selected to compare the oxide microstructures. Samples corroded in heavy water were analysed by NanoSIMS aiming to reveal the mechanisms controlling the transportation of hydrogen/deuterium through the oxide layer. Detailed information on all these selected samples can be found in Table 4.3.

Table 4.3 Study purposes and information on selected samples

Study purpose	ID	Alloy	Corrosion conditions	Corrosion time (days)
Pre-corrosion/irradiation alloy characterisation (second phase distributions and grain morphology etc.)	A-1	RXA Zr-0.5Nb tube	-	-
	N1-1	RXA Zr-1Nb sheet		
	N-1	Annealed Zr-1Nb sheet	-	-
	B166	SRA Zr-2.5Nb tube	-	-
Characterisation and analysis of in-autoclave formed oxide/suboxide (porosity, grain size, grain morphology and phase distributions etc.)	Z4-7	RXA Zircaloy-4 sheet	Autoclave, H ₂ O, 360°C, 18 MPa	60 days, pre-transition
	A-9	RXA Zr-0.5Nb tube	Autoclave, H ₂ O, 360°C, 18 MPa	75 days, pre-transition
	A-16	RXA Zr-0.5Nb tube	Autoclave, H ₂ O, 360°C, 18 MPa	165 days, at transition
	X2	RXA Zr-1.0Nb tube	Autoclave, H ₂ O, 360°C, 18 MPa	540 days, post-transition
Characterisation and analysis of oxides formed in-flux and out-of-flux	1F10	SRA Zr-2.5Nb tube	Autoclave, D ₂ O, LiOD, 300°C, 10 MPa	150 days, pre-transition
	1F1	SRA Zr-2.5Nb tube	Autoclave, D ₂ O, LiOD, 300°C, 10 MPa	700 days, ~transition
	B56	SRA Zr-2.5Nb tube	In-flux, ~1.85 dpa, 250°C, D ₂ O, LiOD, 10 MPa	190 days, pre-transition
	B82	SRA Zr-2.5Nb tube	Out-of-flux, 250°C, D ₂ O, LiOD, 10 MPa	185 days, pre-transition
	B70	SRA Zr-2.5Nb tube	In-flux, ~1.89 dpa, 325°C, D ₂ O, LiOD, 10 MPa	190 days, pre-transition
	B96	SRA Zr-2.5Nb tube	Out-of-flux, 325°C, D ₂ O, LiOD, 10 MPa	185 days, pre-transition
	B74	SRA Zr-2.5Nb tube	In-flux, 325°C, D ₂ O, LiOD, 10 MPa	2700 days, post-transition
Characterisation and analysis of hydrogen/deuterium distribution in oxides	Z4-5	RXA Zircaloy-4 sheet	Autoclave, 30 days H ₂ O then 31 days D ₂ O, 360°C, 18 MPa	61 days, pre-transition
	Z4-9	RXA Zircaloy-4 sheet	Autoclave, 75 days H ₂ O then 31 days D ₂ O, 360°C, 18 MPa	106 days, post-transition
	1F10	SRA Zr-2.5Nb tube	Autoclave, D ₂ O, LiOD, 300°C, 10 MPa	150 days, pre-transition
	1F1	SRA Zr-2.5Nb tube	Autoclave, D ₂ O, LiOD, 300°C, 10 MPa	700 days, pre-transition
	1F6	SRA Zr-2.5Nb tube	Autoclave, D ₂ O, LiOD, 300°C, 10 MPa	2000 days, post-transition
	B56	SRA Zr-2.5Nb tube	In-flux, ~1.85 dpa, 250°C, D ₂ O, LiOD, 10 MPa	190 days, pre-transition
	B82	SRA Zr-2.5Nb tube	out-of-flux, 250C, D2O, LiOD, 10MPa	185 days, pre-transition

Chapter 5 EBSD, TEM and NanoSIMS Sample Preparation

The preparation of reliable specimens is of critical importance for accurate microstructure characterisation. The development of several sample preparation recipes and methodologies specifically for different characterisation techniques used in this work are described.

5.1. EBSD Specimen Preparation

The non-radioactive samples used for conventional EBSD analysis were prepared using a traditional mechanical polishing method. As a surface-sensitive technique, the diffraction signal in conventional EBSD analysis comes from the top tens of nanometres of a bulk specimen [245], and considering the need to tilt the sample up to high angles (typically 70°), it is essential to reduce the surface roughness to a minimum. This makes a specimen preparation important for acquiring good EBSD data. The advantages of using a combination of traditional mechanical polishing and argon ion beam milling have been reported [246]. A flat mirror surface is first achieved by mechanical sectioning, grinding and polishing. Residual lattice damage and contamination induced during the mechanical grinding/polishing process is then removed by subsequent low energy ion milling. Typically, the preparation can be finished in 1 hr. Step-by-step instructions for the preparation used in this work are summarized in Table 5.1, and examples of an optical micrograph and an EBSD band contrast map for a finished specimen are shown in Figure 5.1.

Table 5.1 Grinding and polishing procedure for Zr alloys for EBSD analysis

Step	1	2	3	4	5
Surface	SiC	SiC	SiC	Colloidal Suspension	PECS II Argon ion milling (beam angle: 8°, beam energy: 8keV)
Abrasive	1200	2500	4000	0.04 µm	
Polishing cloth	-	-	-	Metallographic Polishing Pad	
Coolant	water	water	water	water	
Time (mins)	5	5	10	30	5

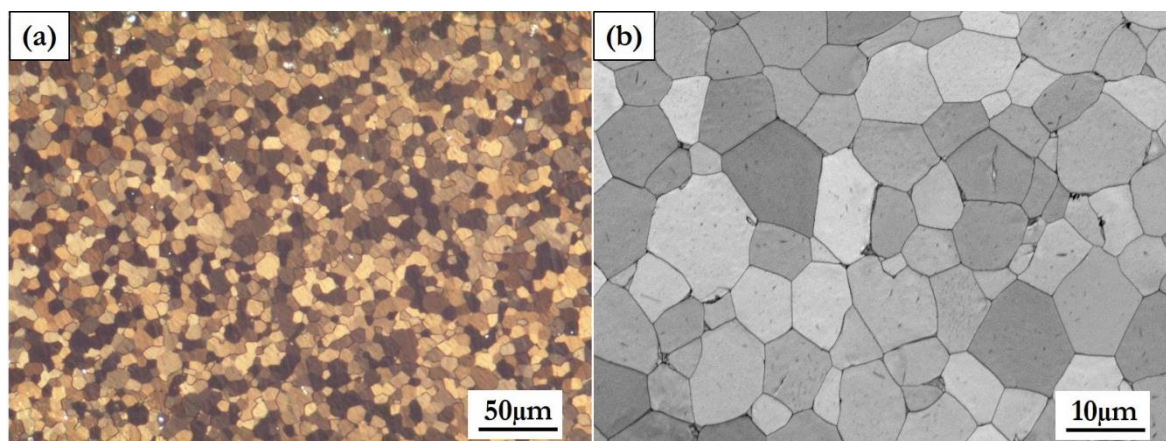


Figure 5.1 An example of polished Zr-1Nb alloy surface morphology (a) polarized light optical micrograph and (b) EBSD band contrast map.

5.2. TEM Specimen Preparation

All the specimens used in this study for (S)TEM and TKD analysis were prepared using the in-situ FIB lift-out method [167]. Detailed step-by-step instructions describing the specimen preparation using FIB are shown in Figure 5.2. A layer of Pt of $\sim 15 \times 2 \times 3 \mu\text{m}^3$ is first deposited over the region of interest to protect from possible damage induced by the 30 kV Ga^+ beam [247-249], Figure 5.2 (a-1). Trenches are subsequently milled in both sides of the Pt layer, typically $\sim 20 \mu\text{m}$ in length and $10 \mu\text{m}$ in depth, Figure 5.2 (a-2). The sample is then tilt to 0° in order to cut the bottom and the side part of the lamella, Figure 5.2(a-3). An in-situ micro-manipulator is inserted and welded to the corner of the lamella, Figure 5.2(b-1). After that, the lamellar specimen is fully detached from the bulk material, Figure 5.2(b-2). The lamella is then lifted out and positioned to touch the side of a 3 mm Cu grid by moving the micro-manipulator, Figure 5.2(c-1 and c-2). Once the sample has been welded to the Cu grid, the link with the micromanipulator can be cut as shown in Figure 5.2 (c-3). Progressive thinning with milling current of 1500-300 pA at 30 kV is performed on both sides of the foil to electron transparency, Figure 5.2(d-1 and d-2). The specimen is further thinned to a uniform thickness of $\sim 50 \text{ nm}$ using 5kV and 200 pA at 40° , Figure 5.2(d-3). With experience, this preparation can be finished in 4 hrs. In terms of the specimen size, a value $< 15 \mu\text{m}$ in

both width and depth is chosen, as it is difficult to achieve very thin specimens with large areas because bending is more likely to occur.

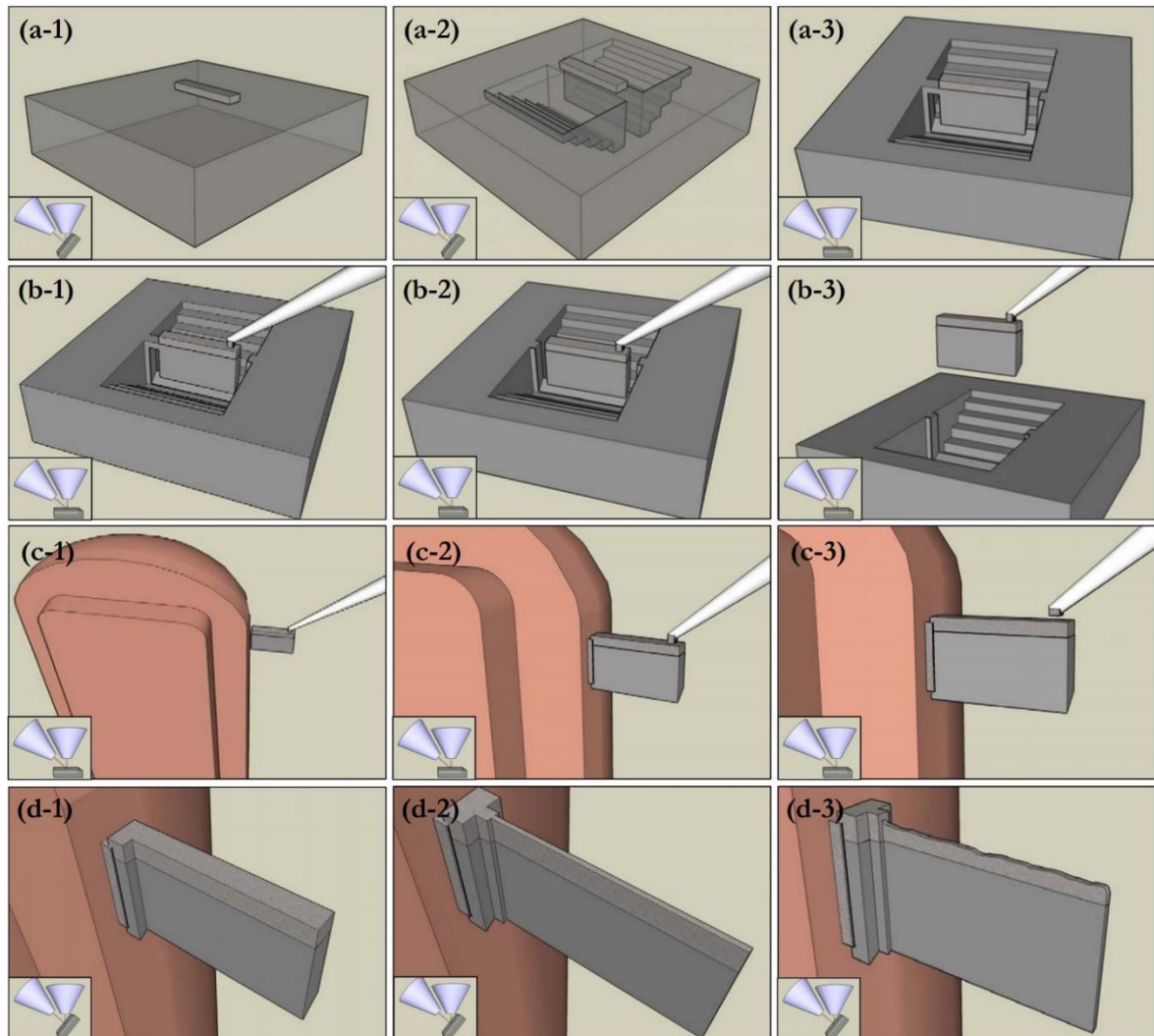


Figure 5.2 Step-by-step instructions for TEM sample preparation with FIB, (a) trenching, (b and c) lift-out and (d) thinning, reproduced with kind permission of Dr. Ben Myers, Northwestern University (from http://www.nuance.northwestern.edu/docs/epic-pdf/TEM%20Sample%20Preparation_BDM_2009_abridged.pdf).

During the final low-energy cleaning/thinning process, the sample thickness can be estimated by the transparency of the specimen imaged at 5kV. An example of a specimen prepared following the above steps is shown in Figure 5.3, exhibiting uniform electron transparency at 5 kV. The specimen thickness is also measured to be ~50 nm using electron

energy loss spectroscopy (EELS) using the t/λ method suggested by Malis et. al. [250], which is suitable for in-situ TEM, TKD and HRTEM analysis.

A considerable advantage of the FIB technique compared to classic TEM sample preparation methods, e.g. electron polishing and ion polishing, is the possibility to take out TEM samples from a local site of interest [167, 251]. This is of great importance for studying zirconium oxides, because interesting regions including oxides, the oxide/metal interface and the metal matrix can be conserved in a single FIB lamella with an almost uniform thickness, Figure 5.3. This also allows us to characterise the same region of interest in a TEM specimen through a combination of several techniques. In this work, some TEM specimens have been characterised by both STEM/EDX/EELS and TKD, and this combination allows us to obtain both crystal orientation and micro-chemistry information.

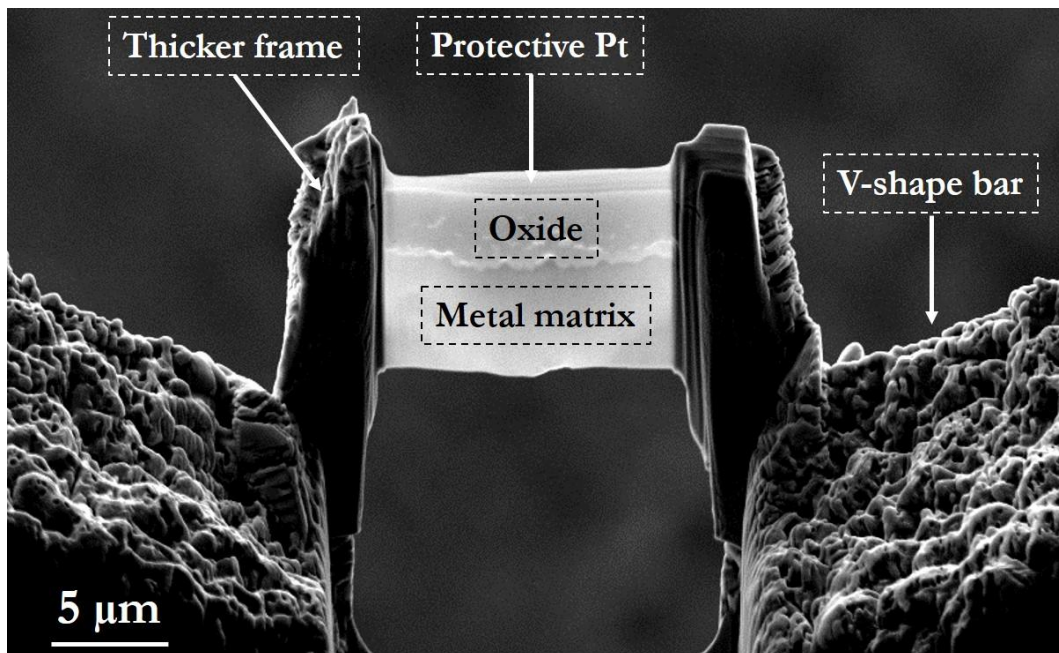


Figure 5.3 An example of a TEM specimen containing both zirconium oxide and metal matrix prepared using FIB (showing transparency at 5keV SEM).

Specimens for in-situ ion irradiation experiments were prepared using similar methodologies to those described above, but with an alternative welding strategy as stronger support/welding is needed to avoid the irradiation-induced specimen bending. Figure 5.4(a

and b) shows the shape of post-irradiation specimens supported in different geometries. When exposed to a high flux of heavy ions, the foil with only one side welded to the Cu grid bends heavily, $>20^\circ$, Figure 5.4(b).

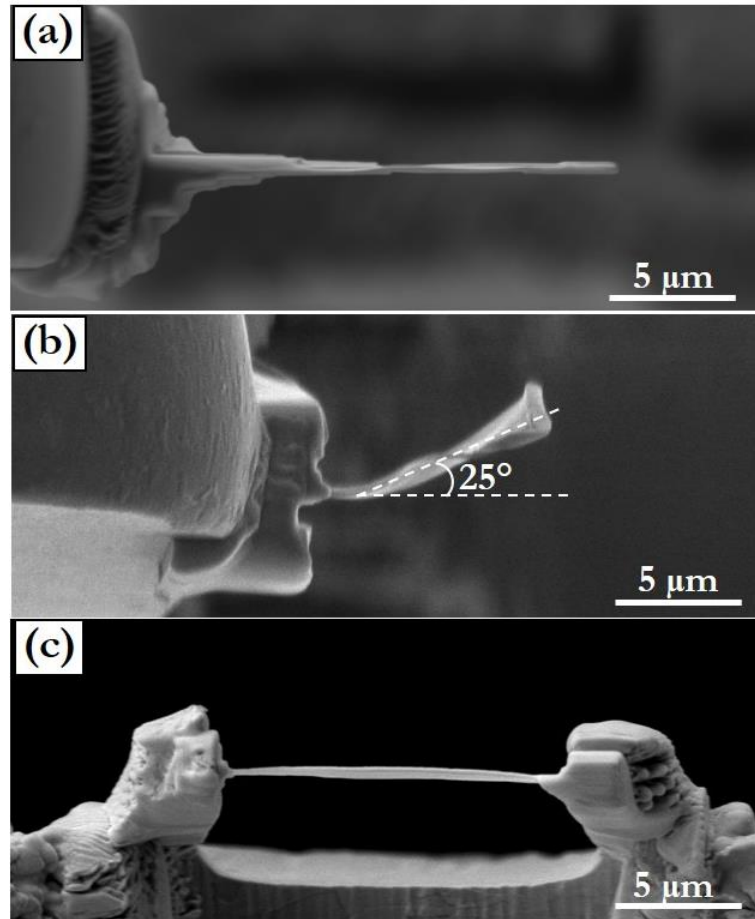


Figure 5.4 SEM top view of specimens for in-situ irradiation. (a) as-prepared, (b) shape of specimen with single weld exposed to irradiation after 8.4×10^{15} ions.cm⁻² and (c) shape of specimen welded on both sides exposed to irradiation after 10^{16} ions.cm⁻².

This bending issue is very important for in-situ experiments, as it can induce artefacts like local deformation, and make it difficult to distinguish the irradiation-induced microstructural evolution. During this project, an alternative welding strategy to improve the TEM specimen stability under in-situ irradiation was developed;

(1) When depositing the protective platinum layer, a thickness of ~ 3 µm is recommended. As most of the deposited Pt will be sacrificed during the thinning process, the remaining Pt can serve as a “frame” and reduce the bending problem.

(2) When welding the lamella to the Cu-grid, use a V-shaped location, Figure 5.5(b), instead of the traditional position in Figure 5.5(a), so the two sides of the FIB lamella are welded. During the thinning procedure, thicker frames are left intentionally to serve as strong supports and protect the foil from bending, Figure 5.3 and 5.5(b).

By welding and thinning the FIB lamella using this improved strategy, the bending issue is significantly reduced, and in-situ irradiated specimens are observed to have good geometry stability up to a high fluence, Figure 5.4(c).

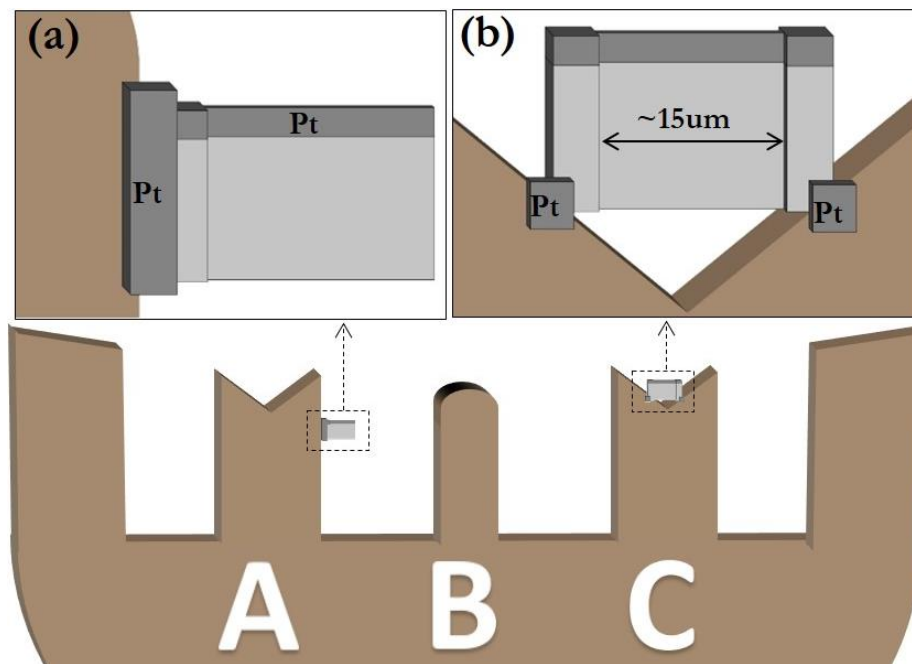


Figure 5.5 Schematic welding geometries on a 3 mm Cu grid. (a) one-side welded geometry on the middle bar and (b) both sides welded geometry on the V-shape bar.

5.3. NanoSIMS Specimen Preparation

Non-radioactive bulk samples for in-depth NanoSIMS analysis of size $7 \times 7 \text{ mm}^2$ were cut from the corroded materials using a slow speed diamond saw and loaded into the NanoSIMS without any further pre-treatment. Samples for cross-sectional NanoSIMS analysis were polished to help to identify the position of oxide layers, following similar mechanical polishing procedures to those described in 5.1 for the EBSD specimen preparation. Samples were cut into small sections that were then mounted in a 10 mm diameter embedding ring

using epoxy resin to expose the cross-section of the metal-oxide interface. The cross-sectional samples were then ground flat using silicon carbide paper down to 4000 grit and subsequently polished over several hours using only water-diluted colloidal silica. A further colloidal silica polish was performed immediately before loading samples into the NanoSIMS to remove the native oxide that forms on the polished metal surface. Both in-depth and cross-sectional bulk samples were coated with 5 nm of platinum to minimize charging from the insulating oxide layer and surrounding resin, and to provide a conducting pathway from the sample to the holder.

Radioactivity values up to 1.8×10^4 Bq were measured from the as-received in-reactor corroded samples ($\sim 4 \times 4 \times 3 \text{ mm}^3$). Because of this high activity, few characterisation facilities can be directly used on these materials, and burdensome paperwork is required for the transportation of these samples. During this project, a methodology using FIB to prepare small volumes of active samples was developed. By applying this methodology, a sample of volume $\sim 20 \times 20 \times 4 \text{ }\mu\text{m}^3$ was lifted out and welded to a 3 mm Cu grid, which is then appropriate for in-depth NanoSIMS analysis. The radioactivity of the lift-out specimen is reduced to $< 6 \times 10^4$ Bq (estimated from volumes of starting and liftout samples), which can be transported easily. A regular size of crater created during NanoSIMS in-depth analysis is $\sim 5 \times 5 \times 2.5 \text{ }\mu\text{m}^3$, indicating the activity of materials sputtered in the NanoSIMS chamber is below 2.5×10^5 Bq.

The methodology was first tested on non-radioactive samples on a Zeiss Crossbeam 540 FIB/SEM system. Images of the step-by-step process are shown in Figure 5.6 from these trial sessions. A cross-sectional polished sample was used during the trial sessions so that the oxide layer in dark-grey contrast can be seen in Figure 5.6(a). The neutron-irradiated specimens were prepared using a FEI Helios NanoLab 600i FIB/SEM in the Materials Research Facility at the Culham Center for Fusion Energy (CCFE) following similar

protocols to those shown in Figure 5.6. However, as the oxide layer is invisible in those as-received samples, an estimate of the oxide thickness was needed before starting the preparation.

(1) The bulk sample is loaded in a cross-section stub in the FIB/SEM instrument, with the sample cross-section facing the electron beam, Figure 5.6(a).

(2) Tilt the stage to 54° (52° in the FEI Helios FIB), then trench 1 is milled to a depth of 30 µm and a length of 30 µm with milling current of 65-9 nA at 30 kV, which will determine the available area of the NanoSIMS analysis, Figure 5.6(b). To reduce possible artefacts induced by FIB milling, e.g. local temperature increases, a layer of metal matrix >3 µm thick is left below the oxide layer.

(3) The under-cut process requires tilting the stage to 0°. Trench 2 and the bottom part of the lamella is milled away with milling current of 9 nA at 30 kV, Figure 5.6(c). To ensure the re-deposited material has also been removed, I repeated this procedure 3-5 times.

(4) At 0°, the micro-manipulator is inserted and carefully operated to touch one corner of the specimen, Figure 5.6(d). Once the specimen has been welded to the micro-manipulator by depositing Pt at a current of 2.5 nA, the link is subsequently milled away and the lamella is lifted out from the bulk sample, Figure 5.6(d and e).

(5) A 3 post lift-out Cu grid (Agar Scientific™) is loaded with the three bars facing the electron beam direction. At 0°, I carefully operated the micro-manipulator until the edge of the specimen touched the Cu grid Figure 5.6(f and g). After the specimen is welded to the Cu grid by depositing Pt at a current of 2.5 nA to a thickness of 2 µm, the micromanipulator can be fully detached, Figure 5.6(f and g). To reduce the possibility of the weld breaking during sample transportation, it is useful to fully weld the lift-out specimen onto the grid by depositing Pt on every side of the lift-out, Figure 5.6(i).

(6) The Cu grid with the welded specimen can then be loaded in a special NanoSIMS holder, Figure 5.6(h), for the following NanoSIMS characterisation, and an example of the post-NanoSIMS analysis crater is shown in Figure 5.6(i).

It is well known that the distribution of hydrogen in materials is sensitive to the environment [57, 252], e.g. local stress, strain and temperature. This poses a classical problem for hydrogen analysis by high-resolution techniques, and makes sample preparation a very crucial step because loss or redistribution of these easily diffusible ions/atoms/molecules is frequent, occurs rapidly and is difficult to prevent during preparation. The effects of sample preparation on the deuterium distribution in zirconium and its oxides will be discussed in detail in Chapter 8 based on the comparisons between NanoSIMS analysis on specimens prepared by different methodologies.

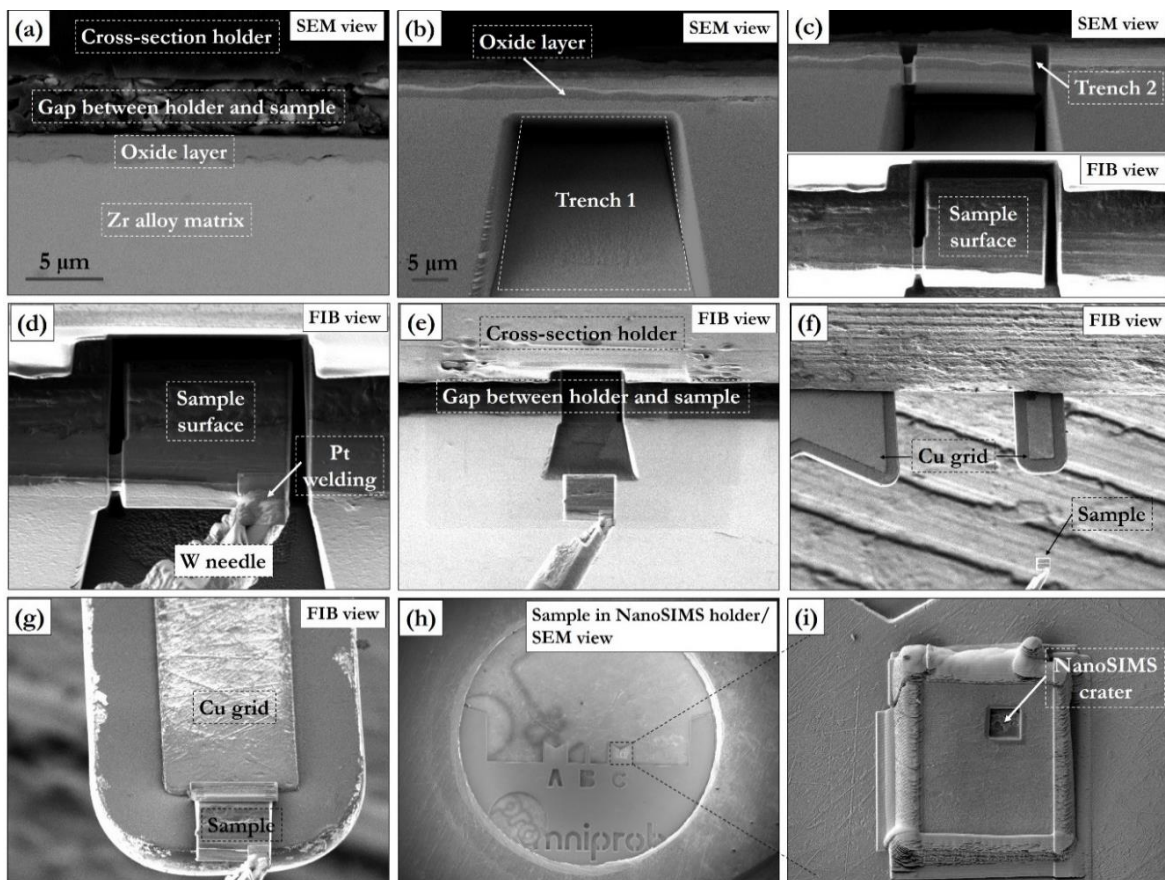


Figure 5.6 Preparation routes of site-specific radioactive samples for NanoSIMS analysis.

Chapter 6 Technique Development

This chapter describes contributions I have made during this work to the techniques I have used extensively. Two technical notes are summarized describing foreshattered electron imaging in an SEM and on defining the depth resolution of TKD.

I would like to thank Dr. Daniel Goran, Bruker Nano GmbH, Germany, for helpful discussions and providing useful geometry information on the OPTIMUS™ head.

6.1. Foreshattered Electron Imaging of Nanoparticles in an SEM

6.1.1. Introduction

The size and distribution of SPPs in Zr alloys play a critical role in determining mechanical properties and corrosion resistance. Normally, the characterisation of SPPs is carried out in a TEM. As part of this work on characterisation of the as-received alloys, I got the opportunity to work on an ARGUS™ imaging system (developed by Bruker). This is an SEM-based imaging system which can generate images by collecting the foreshattered electrons in a transmission geometry, and I was interested to find out what it could do and how it can be applied in the characterisation of materials at the nano scale.

Advances in high-resolution characterisation techniques such as scanning electron microscopy (SEM), Energy-dispersive X-ray (EDX), transmission electron microscopy (TEM) and atom probe tomography (APT) have enabled the study of materials at the nanoscale [54, 253, 254]. Microstructures such as embedded nano-particles, phase interfaces and grain boundaries can be imaged using backscattered electrons (BSE) [255, 256] and secondary electrons (SE) [257] in an SEM with adequate signal-to-noise ratios (SNR). However, the large electron interaction volume in a normal bulk SEM specimen will limit the spatial resolution, especially when using BSE for imaging. Although the use of SE

images would greatly reduce the interaction volume, SEs provide more surface topographical contrast than Z (atomic number) contrast, making it difficult to distinguish nanoparticles from surface features or contamination. TEMs are capable of achieving a spatial resolution below 1 nm from embedded particles in electron transparent foils, but when the TEM images contain other features like dislocations, surface oxides, and diffraction-related bend contours, it can be difficult to identify the precise shape of embedded nano-particles. The dominance of Z-contrast in high-angle annular dark-field (HAADF) imaging in a scanning transmission electron microscope (STEM) makes it ideal for the characterisation of embedded nano-particles with high spatial resolution, irrespective of the surface topography. However, the maintenance/operation of a STEM compared with a normal SEM is generally complex and more costly.

An alternative operating mode, the so-called STEM-in-SEM method, has been shown to have the interesting capability to generate STEM-like images in relatively inexpensive instruments and with much shorter downtime for sample exchange [258-260]. However, the commercially available STEM-in-SEM systems normally have very complex imaging components with a retractable STEM detector containing BF and DF segments as well as additional apertures to select angularly distributed transmitted electrons [259]. In this paper, we introduce a new STEM-in-SEM system consisting of only a few imaging components, but capable of generating STEM-like images without complex operating protocols. Some recommendations on an experimental strategy to achieve the optimum contrast inversions (atomic number or diffraction contrast) when using the foreshattered electrons in the new STEM-in-SEM system for imaging nanoparticles embedded in a thin foil will also be offered. This work is based on Monte Carlo simulations combined with experimental observations of electron interactions with embedded Nb-rich nanoparticles in a thin foil and the analysis of SEM, TEM and STEM images from a model Zr-Nb alloy.

It should be noted that, although I will retain the terminology “forescattered detector” to refer to the images acquired with this detector, I do not in fact collect forescattered electrons but transmitted electrons that have travelled through the electron transparent TEM samples.

6.1.2. Materials and experimental methodologies

A Westinghouse RXA Zr-1.0Nb alloy containing small SPPs was used in this study as described in section 4.3. These SPPs are homogeneously distributed inside the grains, and are mostly β -Nb particles with a few $\text{Zr}(\text{Nb},\text{Fe})_2$ Laves phase particles. Typical microstructures of the RXA Zr-1Nb alloy can be seen in Figure 6.1. Two $\text{Zr}(\text{Nb},\text{Fe})_2$ Laves particles of larger size are highlighted by dashed rectangles. The β -Nb particles are smaller with an average diameter of ~ 50 nm. A 3D representative model used for the modelling study was then built based on the average size of the β -Nb particles.

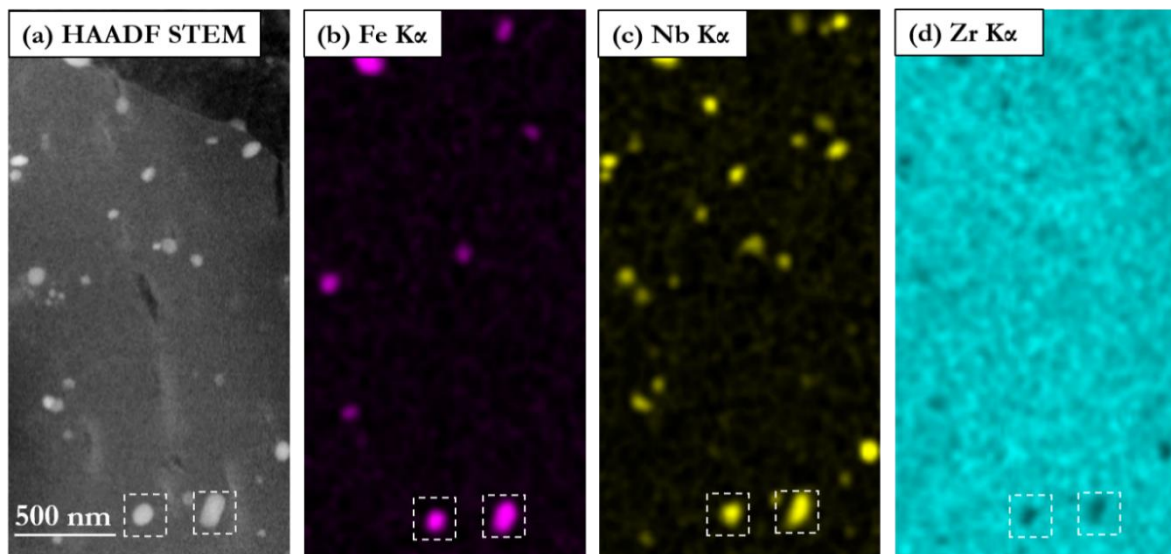


Figure 6.1 (a) A HAADF STEM image and (b, c and d) corresponding EDX maps showing the composition and distribution of SPPs in the Zr-Nb sample. Boxes indicate larger $\text{Zr}(\text{Nb},\text{Fe})_2$ Laves phase SPPs.

Electron transparent thin foil specimens were prepared using the in-situ FIB lift-out method on a Zeiss Crossbeam 540 FIB/SEM system following the steps described in section 5.2.

The sample thickness is estimated to be ~ 100 nm based on its transparency at 7 kV in secondary electron SEM images. Conventional TEM images were acquired on these specimens using a JEOL 2100 microscope operating at 200 kV, and STEM images using a JEOL ARM 200F microscope operating at 200 kV with a pixel size of ~ 1 nm. Using a camera length of 8 cm, the HAADF detector collected scattered electrons with an angular range between 72 and 235 mrad. The BF detector collected electrons with a scattering angle up to 16 mrad. Fore-scattered electron imaging was carried on a Zeiss Merlin FEG-SEM system equipped with a Bruker e-Flash high-resolution EBSD system with an OPTIMUSTM head, Figure 6.2. The OPTIMUSTM head consists of a phosphor screen and three fore-scattered electron detectors (FSD). When using the FSD imaging mode, Figure 6.2(a), the centre of the low-angle fore-scattered electron detector (labelled as ‘LAFSD’) is aligned normal to the optic axis for generating bright-field images, and the two high-angle detectors (labelled as ‘HAFSD’) for dark-field images. When working in TKD mode, the phosphor screen is aligned normal to the optic axis for collecting the on-axis transmission Kikuchi diffraction patterns, Figure 6.2(b).

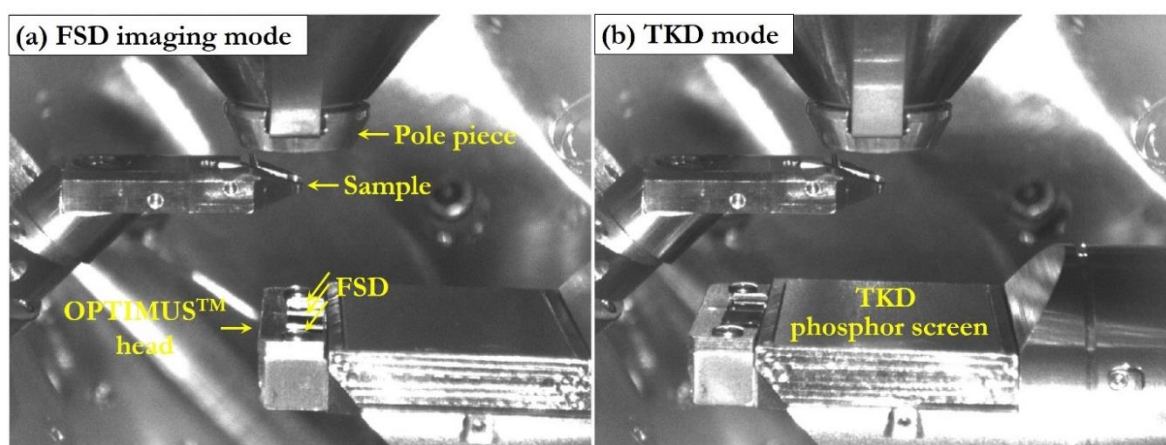


Figure 6.2 In-chamber camera images of typical experimental configurations for (a) FSD imaging mode, (b) transmission Kikuchi diffraction mode.

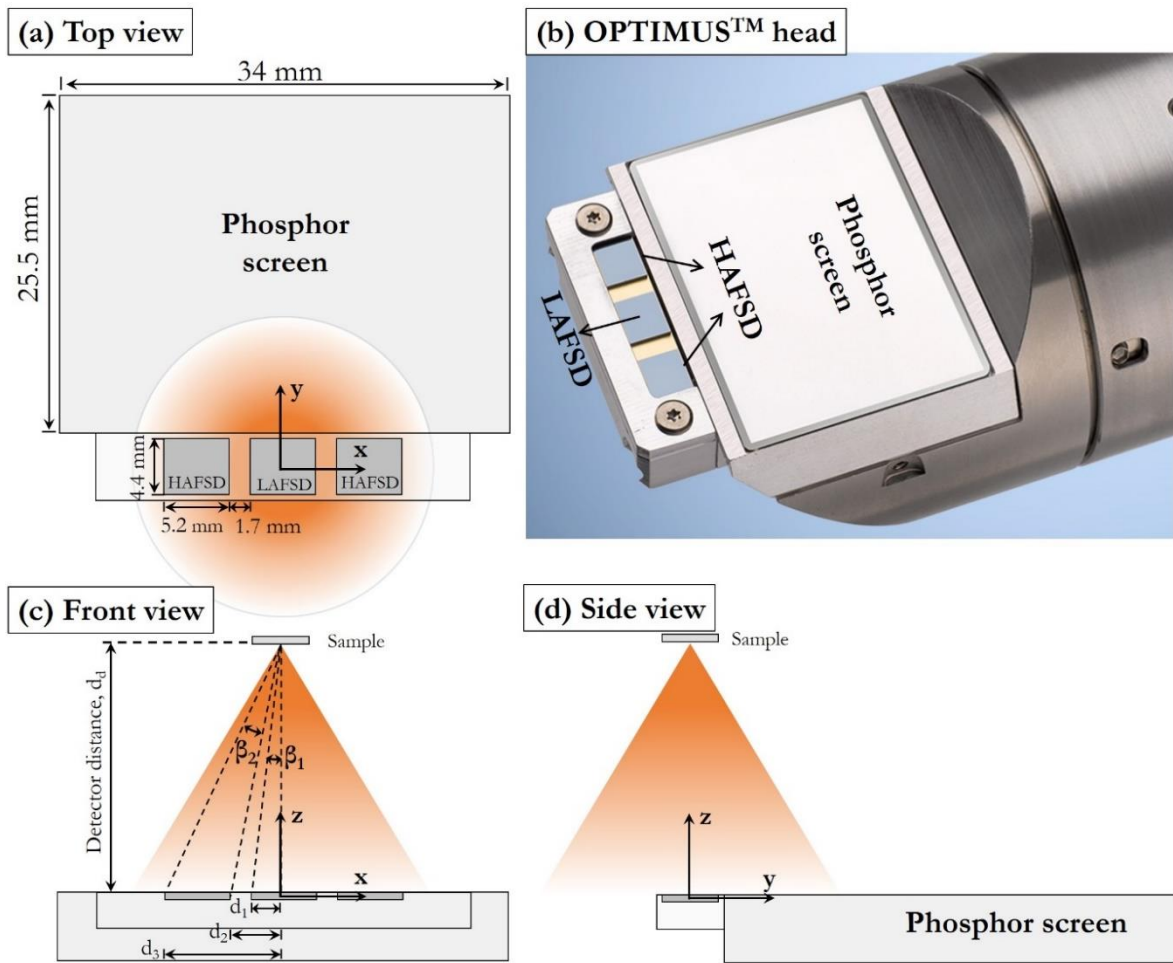


Figure 6.3 (a, c and d) Schematic views of the OPTIMUS™ head working in the FSD imaging mode identifying the key parameters; detector size, working distance (d_w), detector distance (d_d) and collection angles (β_1 and β_2). The intensity distribution of transmitted electrons shown in colour gradients is drawn schematically according to electron trajectories from Monte Carlo simulations. (b) an enlarged image showing the configurations of the OPTIMUS™ head [261].

Figure 6.3 shows schematic views of FSD detector geometries, and an enlarged image of the configurations of the OPTIMUS™ head. Distinct from the angular dark-field (ADF) detectors used in STEM, the three FSDs in the ARGUS™ system are rectangular. Even though slightly different collection semi-angles are associated with the x and y directions, this does not induce significant changes in the image contrast and thus the calculation of the corresponding collection semi-angles at different detector distances (d_d) was only carried along the x-direction, Figure 6.3(a and c), based on the following equations,

$$\beta_1 = \arctan\left(\frac{d_1}{d_d}\right)$$

$$\beta_2 = \arctan\left(\frac{d_3}{d_d}\right) - \arctan\left(\frac{d_2}{d_d}\right)$$

where β_1 and β_2 are the semi-angles of the LAFSD and HAFSD respectively, $d_1=2.6$ mm, $d_2= 4.3$ mm, $d_3= 9.5$ mm. The results are summarized in Table 6.1.

Table 6.1 FSD collection semi-angles (mrad) as a function of detector distances

d_d (mm)	5	10	15	20	25	30	35
LAFSD	0-480	0-250	0-170	0-130	0-100	0-90	0-70
HAFSD	710-1100	410-760	280-570	210-440	170-360	140-310	120-270

Monte Carlo simulations, using random numbers and probability distributions to represent the physical interactions between the electrons and the sample, are widely used to understand the capabilities of electron microscopes [262-264]. Casino Monte Carlo software v3.3 [264], which describes electron trajectories by discrete elastic scattering events and inelastic events approximated by a mean energy loss model between two elastic scattering events, was used to simulate foreshattered electron imaging. Using the electron transport three-dimensional feature of Casino v3.3, the beam and scanning parameters allow the simulation of realistic images [264]. A 3D model was built based on the size of the β -Nb nano-particles shown in Figure 6.1. A niobium sphere ($\rho = 8.56 \text{ g.cm}^{-3}$, plasmon energy = 9.12 eV and work-function = 4.3 eV) with a diameter d of 50 nm is introduced at mid-thickness of a Zr foil ($\rho = 6.49 \text{ g.cm}^{-3}$, plasmon energy = 16.6 eV and work-function = 4.05 eV) with a thickness of 100 nm, as shown in Figure 6.4. The work function and plasmon energies are important for simulating the generation of secondary electrons and the values for some elements are available in the Casino Monte Carlo software v3.3 [264]. The Nb particles vary only 1 in atomic number compared to the matrix (Nb $Z= 41$, Zr $Z= 40$), though they have significantly higher density. Pre-calculated values of the electron elastic and inelastic collision cross sections and the mean energy loss model in the software were used for the calculations. Each simulated image contains 30 x 30 pixels, with an effective pixel size of 4 nm. A beam

diameter of 3 nm was selected which is approximately equal to that reported in the literature [265], and on average for each point in the calculated images 2×10^5 electron interactions were simulated. Accelerating voltages of 10 kV, 20 kV and 30 kV were used. The shot noise of the electron gun was included by varying the nominal number of electrons per point based on the noise characteristics of a field emission gun [264].

6.1.3. Results and discussion

6.1.3.1. Contrast inversions revealed by Monte Carlo simulations

A cross-sectional view of electron trajectories, Figure 6.4, shows an example of interactions between the electron beam ($E_0 = 30$ kV) and a niobium nanoparticle embedded in a Zr matrix. As expected, the electron beam is clearly seen to broaden after interacting with the sample, and the degree of electron scattering depends mostly on material composition, accelerating voltage and sample thickness. By collecting the electrons forescattered over different angular ranges, the modelled image can exhibit different degrees of Z contrast.

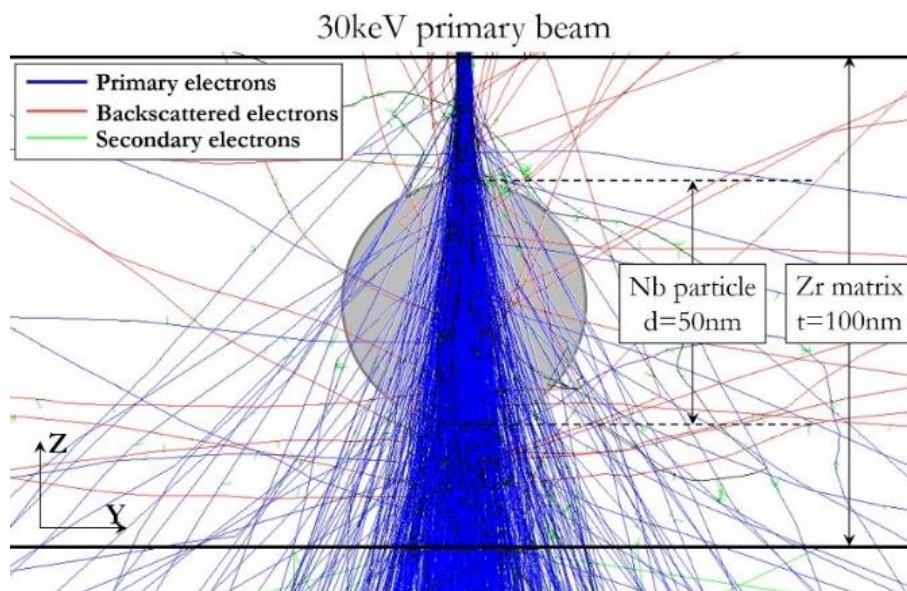


Figure 6.4 Cross-sectional view of the 3D sample model and typical electron trajectories (200 electrons are shown) simulated by the Monte Carlo method.

At high angles we expect the dominant signal to be from Rutherford scattering and the intensity of each pixel in the image will be proportional to tZ^2 , where t is the foil thickness and Z is the average atomic number [213]. The modelled angular distribution of foreshattered electrons as a function of the incident electron energy is plotted in Figure 6.5(a). As expected, more electrons are scattered to higher angles when the accelerating voltage is decreased from 30 kV to 10 kV, and as a result the beam broadening effects are more obvious for primary beams of lower energies. By using a detector distance/accelerating voltage combination that gives large collection angles (e.g. $\beta > 400$ mrad when $E_0 = 30$ kV) most of the collected electrons will be Rutherford scattered [213]. If the collection angles are large enough, signals from coherent elastic scattering (diffraction) can also be much reduced, or even eliminated, and thus we can generate images exclusively with Rutherford scattered electrons showing Z-contrast [213]. Figure 6.5(b) shows a series of images (30 kV accelerating voltage) simulated by collecting different signals; SE, BSE and electrons foreshattered over different angular ranges. In each case the image intensity is normalized by the number of incident electrons simulated. The contrast, C , was calculated according to $C = \frac{I_P - I_M}{I_M}$ [265], where I_M and I_P are the average intensities of pixels in the particle and matrix respectively. The SE image provides less compositional contrast [266] making it difficult to distinguish the nanoparticle, Figure 6.5(b-1). BSE imaging, Figure 6.5(b-2), allows structures with different compositions to be distinguished, thus a stronger contrast 0.145, but the intensity is relatively low, as more than 90% of the electron beam is transmitted. This decrease in signal intensity increases the effect of noise on the image resolution. When the electron beam passes through the heavier Nb ($Z=41$) particle, more electrons will be scattered to higher angles compared with in the Zr ($Z=40$) matrix. As a result, by collecting the high-angle scattered electrons (e.g. $\beta > 400$ mrad), the image shows stronger Z-contrast, Figure 6.5(b-4), compared with collecting the low-angle scattered

electrons (e.g. $\beta < 100$ mrad), Figure 6.5(b-3). Signals from coherent elastic scattering (i.e. diffraction contrast) are not taken into consideration in these simulations [264].

In the absence of diffraction, the absolute contrast value of the low-angle scattered electron image (Fig. 5(b-3)) is similar to that of the high-angle scattered (Fig. 5(b-4)) and backscattered (Fig. 5(b-2)) electron images, but with much higher intensities. In a realistic case, if diffraction effects do not strongly contribute to the signal (e.g. imaging amorphous particles in an amorphous matrix), the image contrast will mainly originate from the Rutherford scattering, which will be very close to the Monte Carlo simulations, and thus when the contrast in these images are similar, we would suggest using the low-angle scattered electrons for imaging as a higher intensity will contribute to a better signal-to-noise ratio (SNR).

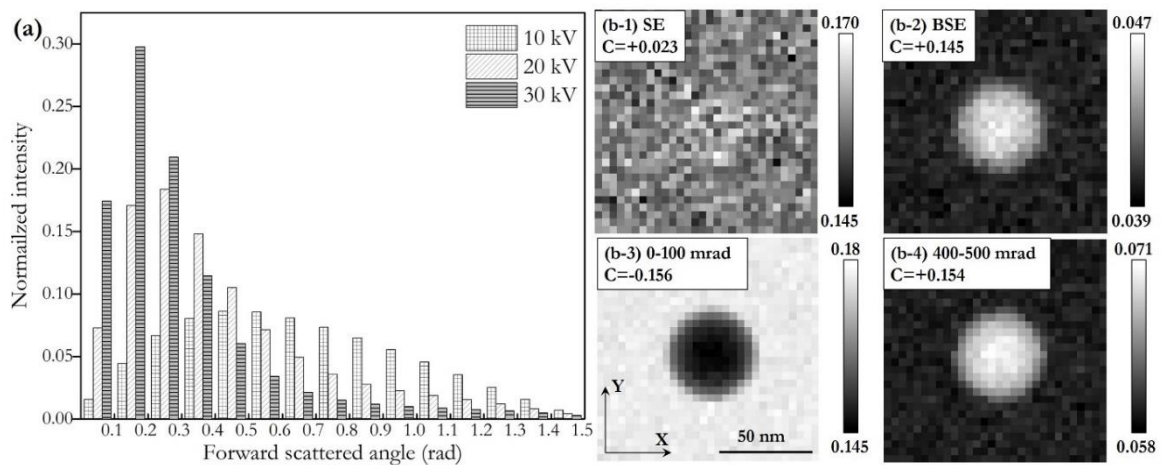


Figure 6.5 Monte Carlo simulations showing (a) angular distributions of foreshattered electrons and (b) images formed at 30 kV accelerating voltage and by collecting (b-1) secondary electrons (SE), (b-2) backscattered electrons (BSE) and (b-3) foreshattered electrons (FSE) within 0-100 mrad, and (b-4) FSE over 400-500 mrad respectively.

Figure 6.6 shows the contrast changes in images simulated by collecting foreshattered electrons over different scattering angles and using different accelerating voltages. Contrast reversals can occur depending on the collection angles Figure 6.6(a). The critical values for contrast reversal increases with decreasing accelerating voltage, and as a result images

acquired at different accelerating voltages can show different contrast (e.g. Z-contrast or diffraction contrast) even using the same detector distance (corresponding to specific collection angles). Examples of simulated images using the same collection angles (300-400 mrad) but different accelerating voltages are shown in Figure 6.6(b). For each image, the brightness range was equalized, and the intensity of each pixel normalized by the number of incident electrons simulated. The particle is visible in both Figure 6.6(b-1) and (b-3) but with inversed contrast. In comparison, for this specific range of collection angles, the particle is almost invisible at 20 kV, Figure 6.6(b-2).

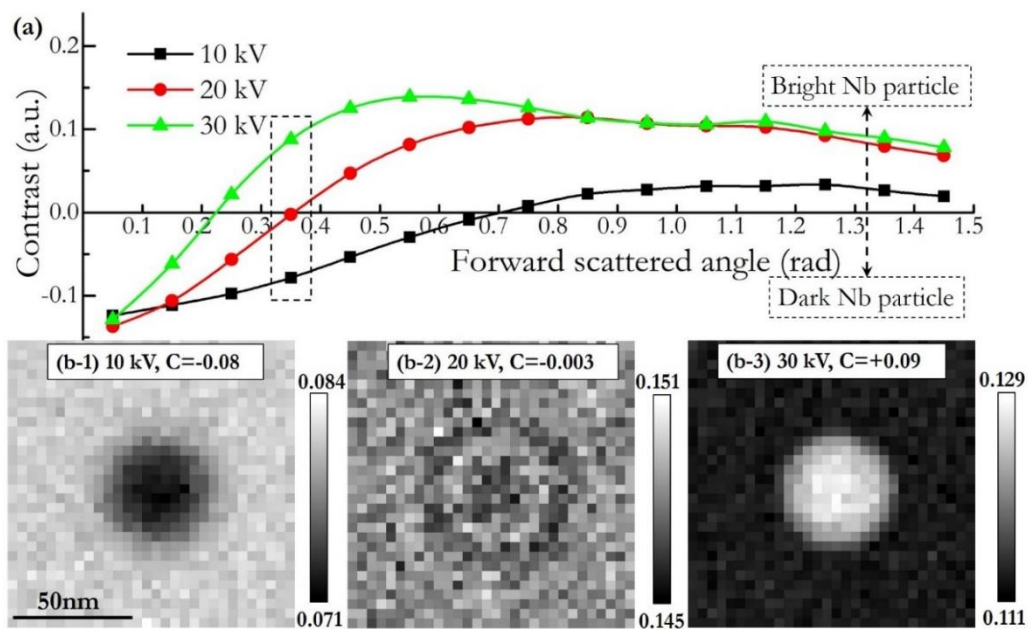


Figure 6.6 (a) Monte Carlo simulations showing contrast inversions as a function of collection angles and accelerating voltages. (b) examples of simulated images using electrons scattered in the range 300-400 mrad.

The diode detectors used in the experimental apparatus generally have a cut-off threshold energy, and linear scaling with electron energy above this value [267]. The energy distribution of the transmitted electrons simulated in this work is shown in Figure 6.7. The energy variance of foreshattered electrons is very small, especially for 20 and 30 keV electrons. For example more than 90% of the foreshattered electrons for 30 keV primary electrons have an energy ranging from 29.5 keV to 29.6 keV. I believe this small energy

variance will not induce significant changes in the image contrast, and this possibility was not pursued here.

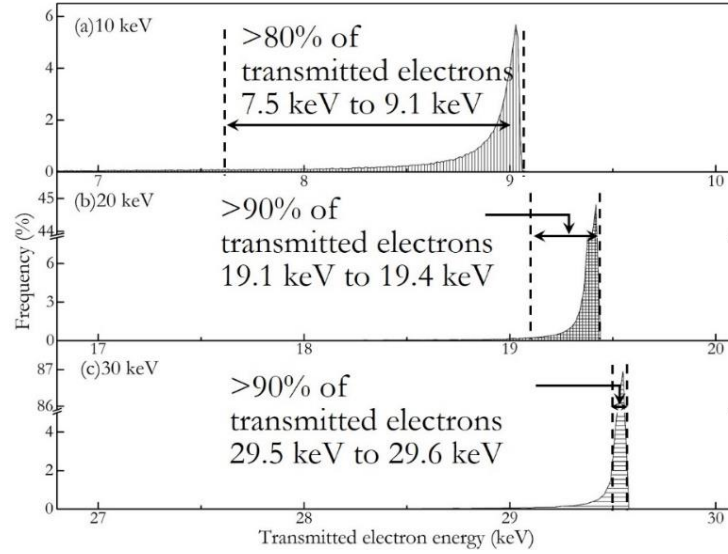


Figure 6.7 Calculated energy distributions of transmitted electrons as a function of incident electron beam energy.

I have calculated and summarized the collection angles of the detectors in Table 6.1. By modelling the collection of electrons over those angular ranges, the simulated images can be compared with the experimental results. The contrast from LAFSD and HAFSD imaging as a function of detector distance and accelerating voltages is plotted in Figure 6.8(a).

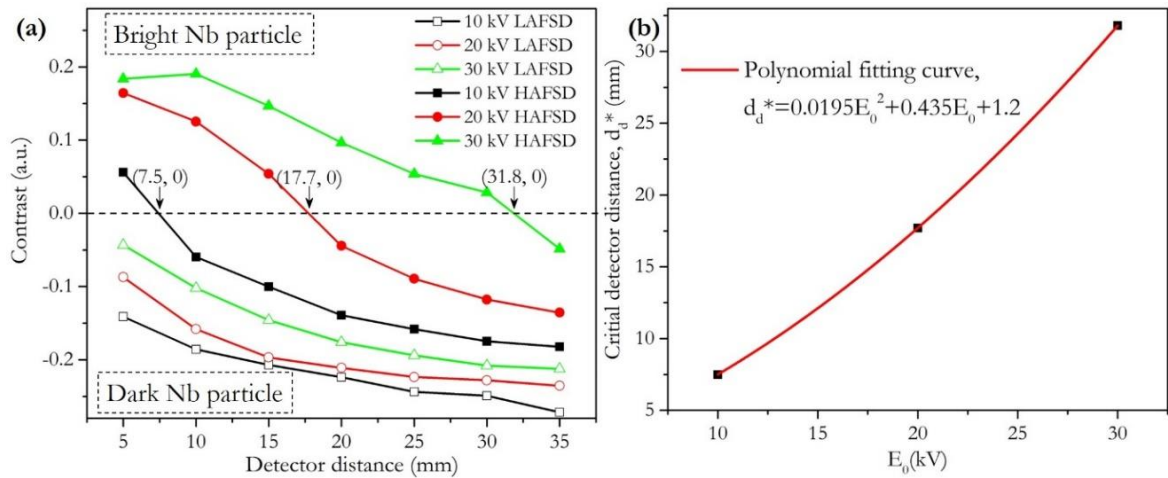


Figure 6.8 (a) Monte Carlo simulations showing the imaging contrast when using HAFSD to image the Nb-particle embedded in a Zr matrix as a function of FSD detector distances and accelerating voltages and (b) polynomial fitting curve of critical detector distance (d_d^*) as a function of accelerating voltages to show Z-contrast.

In the range of available detector distances, LAFSD imaging always shows inverse Z-contrast regardless of the accelerating voltages. If the sample is crystalline, LAFSD imaging could also show strong diffraction contrast [204], which has the potential to significantly alter the contrast from that simulated. In the case of HAFSD imaging, the degree of Z-contrast depends on the selected combination of accelerating voltage and detector distance. The critical detector distances (d_d^*) below which Z-contrast shows the Nb particle as bright increases with increasing accelerating voltage. In other words, when using low accelerating voltages (e.g. 10 kV), the smaller the detector distance the more Z-contrast we have in the images. Using the threshold values obtained from Figure 6.8(a), an expression for the critical detector distances to image Nb nanoparticles in a Zr matrix showing Z contrast (brighter particle in darker matrix) has been derived by polynomial regression, Figure 6.8(b). The mathematical form of the regression function has no physical meaning, but could offer guidelines for setting specific detector distances when use the FSD system to image nanoparticles at different acceleration voltages.

6.1.3.2. Experimental results

Figure 6.9 shows a series of experimental images acquired from the same region in a Zr-Nb sample by HAFSD and LAFSD imaging at different detector distances and acceleration voltages. The particles show higher contrast in the Z-contrast images acquired at a detector distance of 10 mm for both 20 kV and 30 kV accelerating voltages. At 20 mm, the Z-contrast becomes less visible in the HAFSD image generated with an accelerating voltage of 20 kV, and with increasing detector distances the images start to show diffraction contrast. In summary, when Z-contrast images are required, the smaller the detector distance used the higher the Z-contrast can be achieved. A similar tendency is also seen in the images generated with an accelerating voltage of 30 kV, although the contrast reversal occurs at a

larger detector distance, ~ 30 mm, in good agreement with the Monte Carlo simulations. The contrast of a particle imaged at different detector distances and accelerating voltages is measured and plotted in Figure 6.9(b), and the trend of contrast evolution with detector distance and accelerating voltage is in good agreement with that predicted by the simulations in Figure 6.9(a). The absolute values of contrast revealed by the simulations, Figure 6.8(a), are around a factor of 6 lower than those experimentally measured, Figure 6.9(b). This is perhaps not surprising since the simulation does not accurately reproduce the brightness and contrast settings used for the experimental acquisitions nor the detection efficiency.

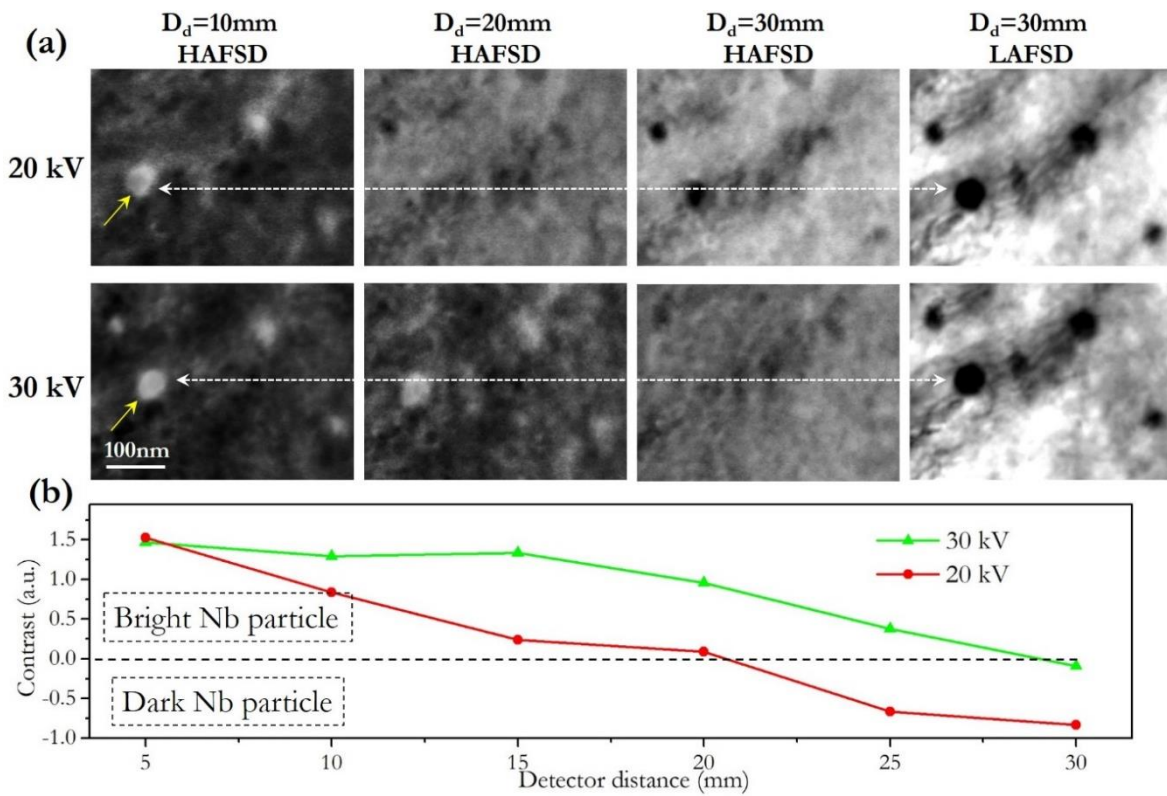


Figure 6.9 (a) HAFSD and LAFSD images of the same region in a Zr-Nb sample using different detector distances and acceleration voltages, (b) the measured contrast of the same particle highlighted by yellow arrows in (a) at different detector distances.

The contrast evolution can also be reflected by the distribution of foreshattered electrons which carry the diffracted information. A transmission Kikuchi pattern (TKP) was acquired from this same specimen at 30 keV, Figure 6.10. It can be seen that the majority of

diffraction signal in the TKP is within a radius of ~ 15 mm from the diffraction centre, Figure 6.10(a). Considering the detector distance used for acquiring this TKP, $d_d = 20$ mm), it can thus be estimated that foreshattered electrons carrying diffracted information (or contributing to the diffraction contrast in an image) are mainly distributed in a cone with a semi-angle ~ 540 mrad as shown in Figure 6.10(b). When FSD imaging is carried out at larger detector distances, HAFSD will collect more diffracted electrons and show weak Z contrast. When $d_d < 10$ mm, few diffracted electrons will be collected by HAFSD and the images will thus show strong Z contrast.

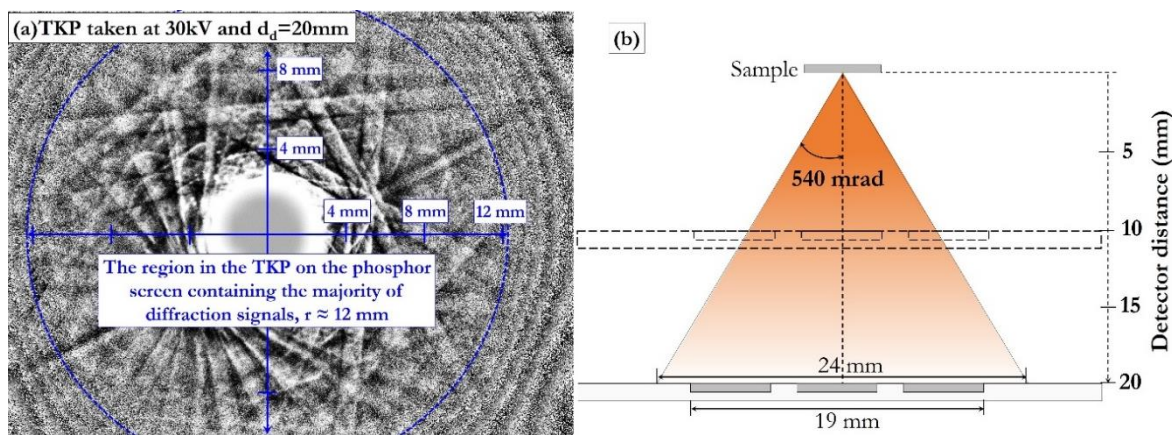


Figure 6.10 (a) a transmission Kikuchi pattern acquired at a detector distance of 20 mm and 30 keV and (b) a schematic showing the angular range of the foreshattered electrons.

Comparisons of the contrast shown by embedded Nb nanoparticles in the Zr-Nb alloy imaged by the FSD imaging system and the other techniques are shown in Figure 6.11. As a result of the large difference in the accelerating voltages, 30 kV vs 200 kV, more diffraction contrast can be seen in the LAFSD image compared with the bright field (BF) STEM image, Figure 6.11(a and b), but the particle morphology and interface structure in the LAFSD image, Figure 6.11(a), is comparable with that shown in the BF STEM image. The BF TEM image is known to be sensitive to strain fields [268] induced by features like dislocations [269], surface oxides [270] and bend contours, which can make it more difficult to distinguish nanoparticles from these features or contamination spots in BF TEM images

than in FSD or STEM images. In the dark field mode (DF), both the HAFSD and HAADF STEM images show obvious Z-contrast.

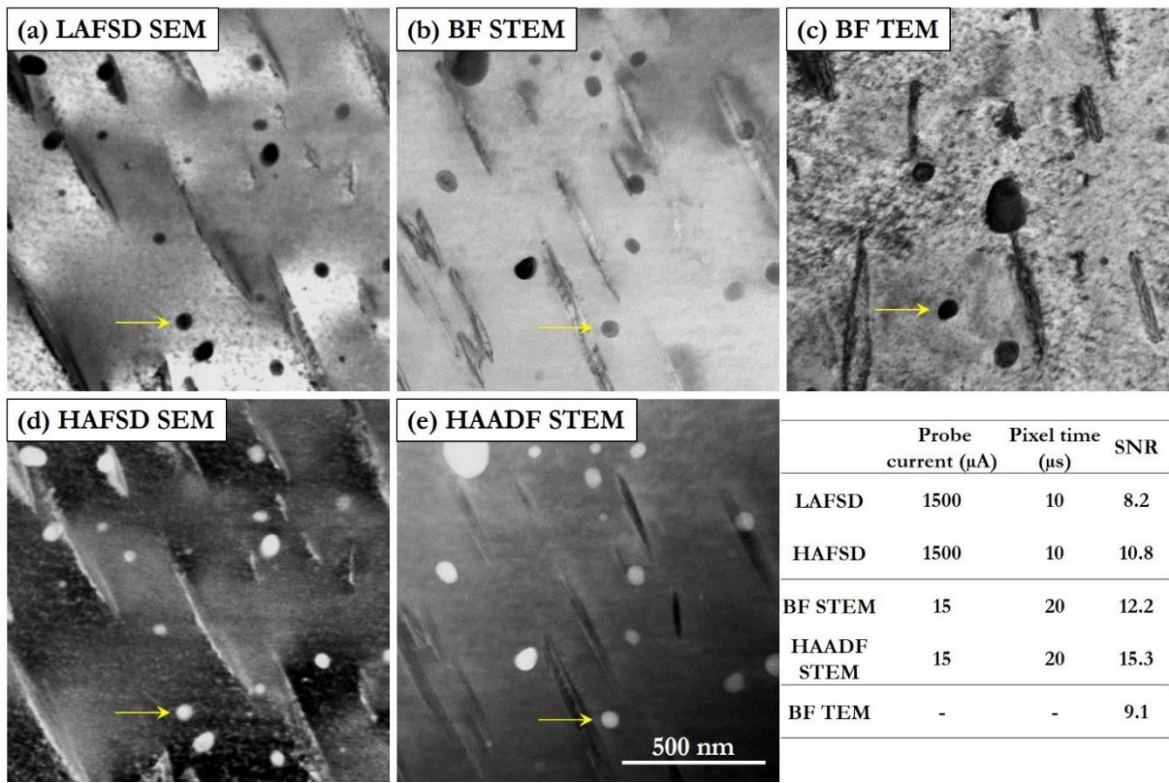


Figure 6.11 Comparisons of the contrast of embedded Nb particles in the Zr-Nb sample imaged by (a, d) FSD in an SEM at 30 kV, $d_d=20$ mm, (b, e) BF and HAADF STEM in a STEM at 200 kV and (c) BF TEM at 200 kV.

In comparison with the HAADF STEM image formed exclusively by Z contrast, some surface features can also be seen in the HAFSD image, probably because the collection angle for the HAFSD image is not high enough and some contribution from coherent elastic scattering (diffraction) is also collected by the detectors [204, 213]. Values of imaging parameters and SNR of these images are also summarized in Figure 6.11. The SNR is calculated according to $SNR=\frac{|\bar{I}_p-\bar{I}_M|}{\sigma_M}$, where $\bar{I}_p$ is the average signal intensity of the particle, $\bar{I}_M$ and σ_M are the average and standard deviations of signal intensity of the matrix. A threshold $SNR > 1$ has been suggested by Österreichere et al. [255] for a particle to be visible in an electron micrograph. Although the probe current and dwell time used in FSD and

STEM imaging are different, for particles of similar size, comparable values of SNR, ~ 10 , can be seen from these images, suggesting the FSD image quality is comparable with STEM and TEM images. Although the square-geometry detectors used for the HAFSD imaging here collect a smaller fraction of angularly distributed electrons than the annular type detectors used for HAADF STEM images, the HAADF and HAFSD images in Fig. 10 show comparable image qualities (in terms of SNR values of ~ 10 , measured for a particle of similar size). This is likely to be a result of the higher beam current of $1500\ \mu\text{A}$ used in the SEM compared to $15\ \mu\text{A}$ for the HAADF images.

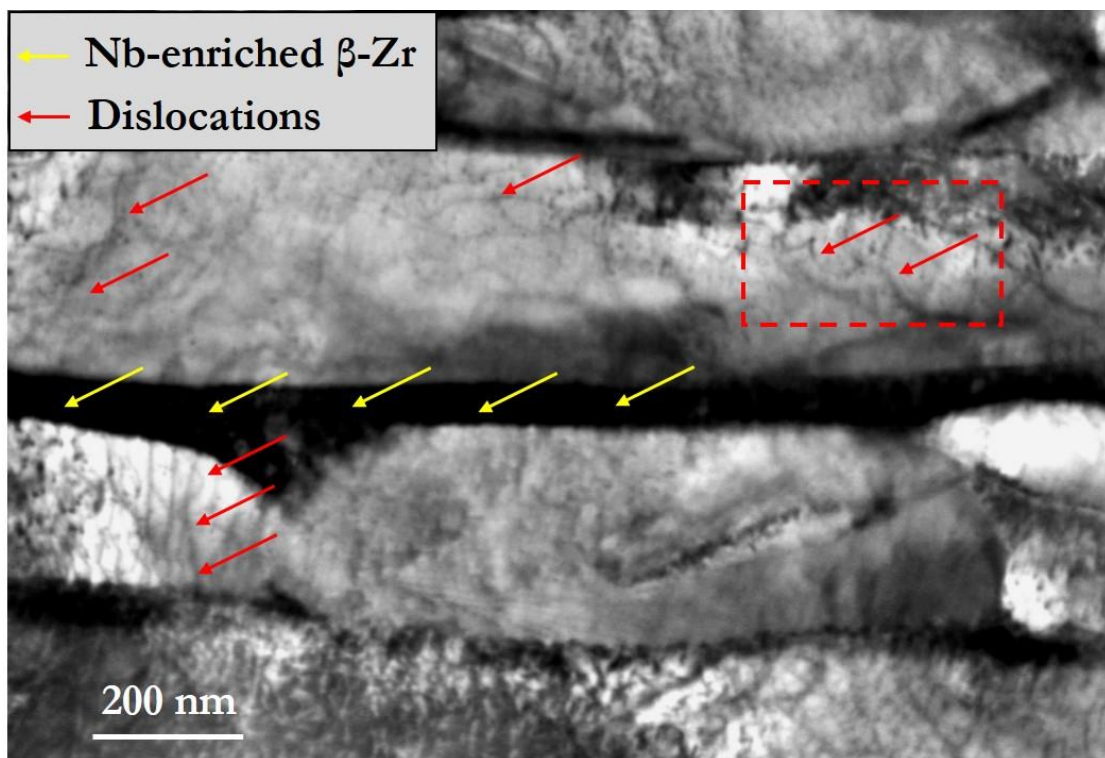


Figure 6.12 An example of LAFSD ($E_0=30\ \text{keV}$, $d_d=20\ \text{mm}$) image showing the microstructure of Zr-2.5Nb. Features such as dislocations (red arrows) and second phase (yellow arrows) are highlighted.

Apart from characterizing embedded nanoparticles, the FSD imaging (ARGUSTM) system in an SEM can also be applied to reveal other features at the nanoscale, like dislocations. The following example illustrates the application of FSD imaging to the characterisation of a similar Zr-2.5Nb alloy (B166, Table 4.3), Figure 6.12. Determination of grain morphology

and the size and distribution of second phase particles is possible by LAFSD imaging, but even smaller features such as individual dislocations can also be easily seen. As an illustration, in the region marked by the dashed rectangle in Figure 6.12, dislocation pinning by nanoscale obstacles is clearly observed. As described in section 6.1.2, the OPTIMUS™ head can also work in TKD mode, which means the dislocation imaging can be combined with orientation mapping in order to get some crystallographic information on the dislocations. This could be the focus of future work using the LAFSD and TKD technique to characterise dislocations.

6.1.4. Conclusions

These results indicate that imaging a thin foil in a transmission geometry with foreshattered electrons in an SEM is an effective method to investigate the microstructure of engineering materials, including the size and distribution of embedded nanoparticles that we would normally only expect to be able to study in a (S)TEM. A few recommendations are listed in order to assist future users in designing experimental conditions to apply this imaging method on other materials systems:

- The new FSD imaging system in an SEM is capable of imaging features at the nanoscale by selecting suitable imaging parameters in either Z-contrast or diffraction contrast imaging modes to give FSD image quality comparable with STEM images.
- When imaging heavier particles (Nb particles in a Zr matrix for example), the particles show brighter contrast at shorter detector distances. We suggest using these Z-contrast images to identify the shape and number density of nanoparticles as the diffraction contrast generated from dislocations, surface oxides, and diffraction-related bend contours will be minimized.

- For a selected accelerating voltage, there will be a critical detector distance at which the Z-contrast for HAFSD images is close to 0. Under these conditions, diffraction contrast would be the dominant contrast mechanism, which can be used to characterise features like dislocations. The critical detector distance can be found using CASINO Monte Carlo simulation as we have shown in Figure 6.8.
- The contrast/quality of images acquired at the same imaging conditions (HV and detector distance) will also depend strongly on the choice of sample material. A quick Monte Carlo simulation using the CASINO software can help users to select suitable imaging parameters for optimizing Z-contrast or diffraction-contrast conditions as we have shown in Figure 6.8.
- Compared with TEM and STEM instruments normally working at higher accelerating voltages, FSD imaging in an SEM can use much lower voltages (<10 kV) which means it is also potentially useful to study some electron beam-sensitive materials (e.g. carbon-based).

6.2. Depth Resolution of Transmission Kikuchi Diffraction (TKD) Analysis

6.2.1. Introduction

As described in section 3.2, compared to conventional EBSD and 'off-axis' TKD configurations, the new 'on-axis' detector geometry, where the optic axis of the SEM intersects the centre of the phosphor screen, allows acquisition of Kikuchi patterns directly below the sample where the signal yield is strongest and gnomonic distortions are minimised. This improves the acquisition speed, lateral spatial resolution and indexing rates without sacrificing angular resolution [186, 196, 269]. Automated crystal orientation mapping in the transmission electron microscope (ASTAR) is capable of achieving a lateral resolution of 1 nm, similar to 'on-axis' TKD, but overlapping of fine grains in the sample thickness will result in the formation of composite diffraction patterns which can lead to deconvolution problems during the template matching process. In addition, dynamical errors are always present in ASTAR analysis, and can be a major factor limiting angular resolution [195]. I have explored if these problems can be addressed by the application of 'on-axis' TKD.

A better understanding of the spatial resolution, angular resolution and Kikuchi pattern formation mechanisms in TKD are still required to understand the potential and the limitations of the technique and so define how it can best be applied to addressing real materials questions at the nano-scale. A number of authors [186, 187, 271-273] have studied the spatial resolution of TKD analysis; especially lateral resolution where it has been shown that combining high accelerating voltages and low sample thicknesses give the best results [271]. However, to obtain more quantitative information on the microstructure, e.g. phase fraction and particle number density, one has to know the sample volume from which the TKD signal originates. Though it has been clearly shown that TKD signals are generated close to the bottom surface of the specimen [190, 274, 275], little quantitative data on either the information depth or depth resolution (d_d) is presently available. More practically, a

better understanding of the depth resolution can also provide a guide for preparing samples of ideal thickness for TKD analysis.

In the same way as two definitions exist for lateral resolution, the physical and effective lateral resolution [187, 245], depth resolution in TKD can also have two definitions. The physical depth resolution (d_{phy}) is the maximum depth from which diffraction information is collected and the effective depth resolution (d_{eff}) is a measure of how accurately the predominant orientation can be extracted from overlapping patterns from through thickness variations in phase or orientation. By using bi-crystal samples, Brodu et al. [276] and Sneddon et al. [277] have experimentally measured the physical depth resolution of Al, Si, Cu and Pt layers exposed to 30 keV electrons based on the visibility of Kikuchi bands originated from the materials closest to the incident electron beam. The physical depth resolution is seen to be both highly materials- and energy-dependent, but rather independent of sample thickness. Based on their results, Brodu et al. [276] proposed the function describing the physical depth resolution to be $d_{\text{phy}}=0.026E/\mu_0$, where E is the primary beam energy and μ_0 (nm^{-1}) is the absorption coefficient for the thermally diffuse scattered electrons for samples exposed to 100 keV electrons. The practical application of this relationship may be limited due to the availability of data on μ_0 values in a wider range of engineering materials. The experimental determination of the effective depth resolution in 'on-axis' TKD has not yet been reported. Clearly, this effective depth resolution depends both on the physical resolution and the capacity of the software to extract the predominant orientation from overlapping patterns [175, 176]. In conventional EBSD, the values of effective resolution are found to be approximately 3 times smaller than the physical resolution [278], but it is not clear whether this is also true for TKD. In terms of practical applications, a better understanding of both the physical and the effective depth resolutions can provide a guide for preparing samples of ideal thickness for TKD analysis.

During this project, I have experimentally measured the physical and effective depth resolutions from an SEM with an 'on-axis' TKD system, showing that TKD analysis to be extremely surface sensitive. This needs to be carefully considered when conducting orientation mapping on nano-crystalline materials because different grain structures are analysed when opposite sides of a nano-crystalline foil are scanned.

6.2.2. Experimental methods

Electron transparent thin foils were prepared from the Zr-1.0Nb alloy (N1-3, Table 4.3) following the procedures described in section 5.2. The TKD study was carried out on a Zeiss Merlin FEG-SEM system equipped with a Bruker e-flash high-resolution EBSD detector and an OPTIMUS™ TKD head, Figure 6.2. The detailed mapping parameters used are summarized in Table 3.1. The pattern background correction and indexing was performed by ESPRIT 2.0 software from Bruker. The crystallographic information for each phase used in identifying the phase distribution in the sample is summarized in Table 3.2. The thicknesses of the regions of interest in the samples studied were determined using Electron Energy Loss Spectroscopy (EELS) in a JEOL ARM 200F microscope operating at 200 kV with a step size of 2 nm, a convergence angle of 30 mrad and a collection angle of 40 mrad using the t/λ method suggested by Malis et. al. [250], which after experimental calibration [279] can determine the absolute thickness to an accuracy better than 5%. As this calibration for λ was not conducted on exactly this sample, we suggest using a more conservative error estimate of 10% is appropriate. To reduce the surface carbon contamination which can be induced during EELS mapping, we have used a short pixel time, 10 μ s, and the sample was further plasma cleaned before TKD scanning.

These particular Zr alloy samples were selected for study because they have very well defined microstructure containing second phase particles (diameter $\sim$ 50 nm) of a convenient

size for these experiments, Figure 6.1. With a typical sample thickness of ~ 80 nm, some particles will be fully embedded inside the foil while the others may lie closer to one surface than the other, and indeed may be truncated by the foil surface. TKD orientation mapping was carried out for the same region but from both sides of the TEM foil using the same mapping parameters. The physical depth resolution can thus be estimated by the visibility of Kikuchi bands in carefully selected regions with overlapping phases, and the effective resolution estimated depending on the capability of the software to deconvolute the predominant orientation from the overlapping Kikuchi patterns. The accuracy of depth resolution experimentally determined thus depends strongly on the quality of the overlapping patterns, which is further determined by the hardware and software (e.g. indexing and background correction methods) used and the imaging parameters (e.g. accelerating voltage, beam current, detector distance and counting time per pixel). It will be important to carry out more studies to investigate the variation of depth resolutions achieved using different software and imaging parameters, but in this initial study to demonstrate a technique to measure depth resolution we have kept the indexing method and imaging parameters constant and focussed on interpreting the Kikuchi patterns generated from various thicknesses of overlapping phases.

6.2.3. Results

Figure 6.13 shows bright field (BF) and dark field (DF) foreshattered electron (FSD) images and the corresponding TKD maps acquired from the same region on the sample but scanned from opposite sides (the sample was flipped on the holder in between acquisitions).

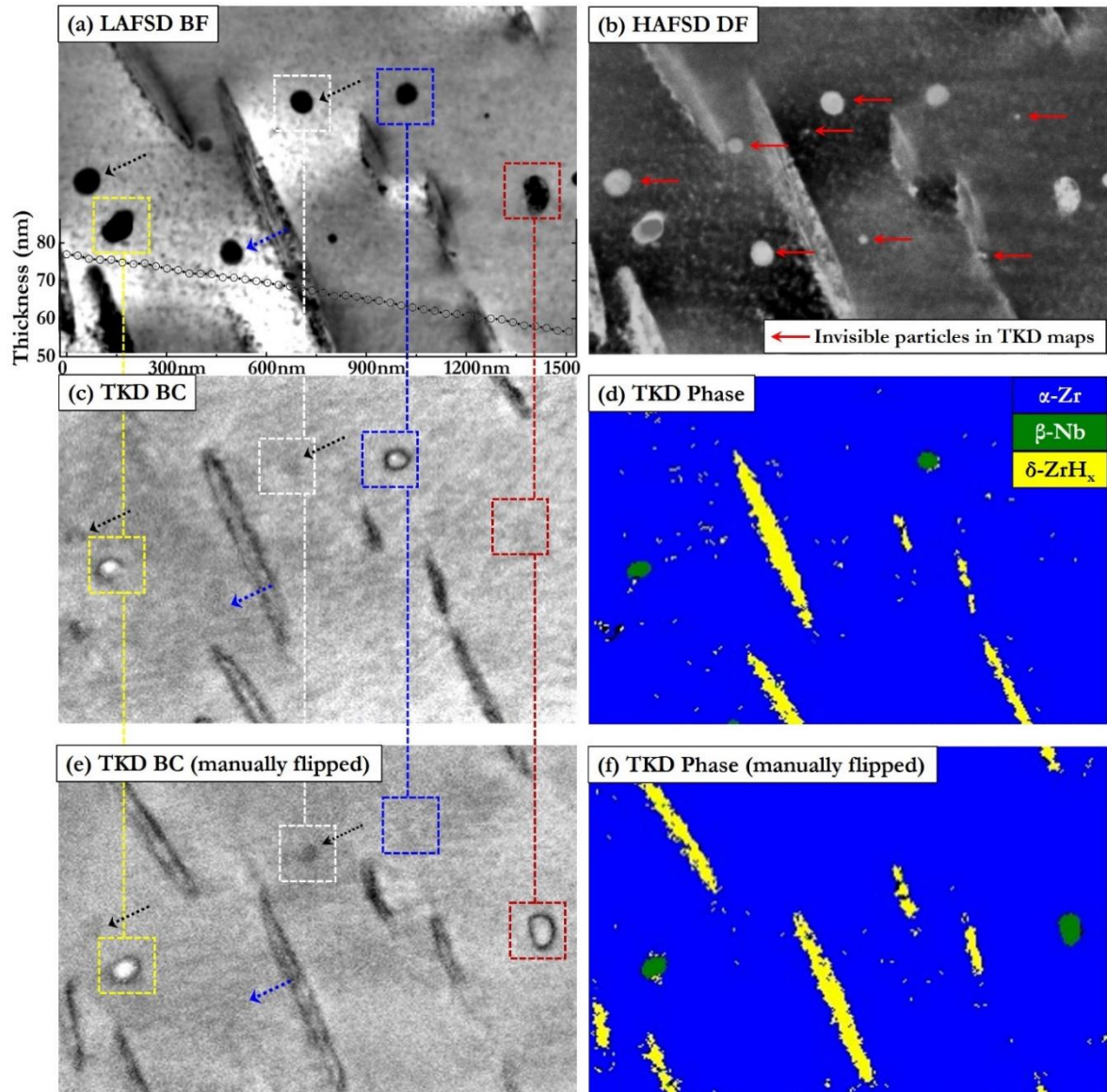


Figure 6.13 (a, b) BF and DF images using foreshattered electrons and showing the size and distribution of Nb particles. (c, d, e and f) TKD band contrast (BC) and phase maps from scanning the same region of the Zr-Nb sample in both directions. The corresponding thickness profile of the mapped region is plotted in (a).

The FSD images in Figure 6.13 are generated by collecting the foreshattered electrons distributed within different angular ranges. As discussed above, the low-angle foreshattered (LAFSD) image shows more diffraction contrast, Figure 6.13(a), while the high-angle foreshattered (HAFSD) image shows more Z (atomic number) contrast, Figure 6.13(b). As the signal contributing to the formation of both LAFSD and HAFSD images is integrated from the whole thickness of the specimen, all the particles whether embedded fully or

partially in the thin foil can be detected in these FSD images. In comparison with these FSD images, both the number density and the size of particles detected by the TKD band contrast (BC) images and the phase maps are smaller, Figure 6.13(c-f). Of the ten particles observed in the FSD images, only one can be seen in both of the TKD maps scanned in opposite-directions, highlighted by the yellow rectangles in Figure 6.13(a, c and e). We can also see that the apparent size of this particle in both of the TKD BC maps is smaller than in the FSD images. Two other particles are visible in only one of the TKD maps, highlighted by blue and red rectangles in Figure 6.13(a, c and e), indicating these particles lie near one surface of the thin foil. All the other particles, highlighted by the red arrows in Figure 6.13(b), are invisible in both of the TKD BC maps regardless of the particle size. The hydrides, which are artefacts of the FIB sample preparation [280], also show different morphologies through the thin foil thickness, Figure 6.13(d and f).

However if we look at the FSD images and TKD BC maps carefully, in the regions with particles fully embedded, although they are not resolved in the phase maps we still can see a contrast/brightness difference from those regions compared with the surrounding matrix, e.g. the regions highlighted by black dashed arrows in Figure 6.13(c and e). The contrast of a TKD BC map is generally related to the image quality of the captured patterns, essentially based on the contrast (or sharpness) of the Kikuchi bands compared to the background, and this contrast is useful in giving a visual rendering of features that cause poor band contrast [281], e.g. grain boundaries, phase interfaces and surface imperfections. In this case, the poor band contrast will probably be a result of the complex overlapping patterns caused by the buried SPPs in a matrix. Depending on the size of the particle, and the local thickness of the matrix above and below it, the contrast changes caused by the overlapping phases differ from region to region. In Figure 6.13, particles of diameter smaller than 20 nm that are either fully or partially embedded in the foil show little influence on the band contrast if the

mapped region has a thickness between 55 nm and 75 nm. The critical value of particle diameter that appears to induce detectable changes in the band contrast is observed to be ~ 50 nm in a foil of total thickness of ~ 70 nm; an example is highlighted by blue dashed arrows in Figure 6.13(c and e).

Apart from a poorer band contrast, an embedded particle can also affect the pattern indexing reliability/accuracy of TKD data from the underlying matrix. This can be reflected in the mean angular deviation (MAD) distribution shown in Figure 6.14. The MAD indicates the misfit between the measured and the calculated angles between bands, so the larger the MAD value the higher the misfit and the lower the indexing confidence. Data from the region covering the particle shows a larger mean value of MAD when compared with that from the surrounding region, as a result of both low pattern quality caused by overlapping patterns and maybe also by lattice strain around the buried particle.

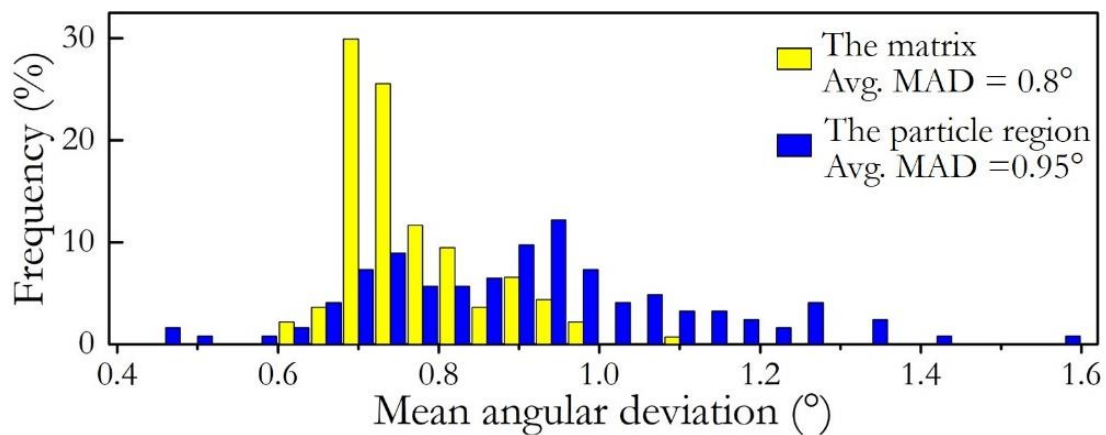


Figure 6.14 Frequency distribution of mean angular deviation (MAD) from the region highlighted by the white rectangle in Figure 6.13(e) (blue bars), and from the surrounding matrix (yellow bars) of a region of the same size.

Figure 6.15 shows the HAFSD image and TKD phase map from one α -Zr grain containing several β -Nb particles. All the particles are seen in the HAFSD image, but only those near the bottom surface of the foil in the TKD map. From these images, we can identify 3 particles with different sizes and different locations through the foil thickness, labelled P1, P2 and P3,

as shown in the schematic diagram in Figure 6.15(c) which also captures the measured foil thickness variations in this region of the sample. Kikuchi patterns acquired from the regions containing each of these particles and the matrix are also shown in Figure 6.15, with the Kikuchi bands originating from the α -Zr matrix highlighted by yellow dashed lines and from β -Nb by red dashed lines. When particles are only partially embedded in the TEM foil, I have assumed that they are spherical and that roughly half of the particle remains inside the foil, P3 in Figure 6.15(c), such that the maximum depth that they penetrate into the foil surface is the observed radius. In the region of P3, the dominant bands are diffracted from the β -Nb phase, Figure 6.15(g), while bands from the α -Zr matrix show only very weak contrast. This indicates that the depth of penetration of particle P3 up into the foil, ~ 20 nm, is close to the physical depth resolution of TKD information under these specific imaging and sample conditions. From the HAFSD and TKD images, and Figure 6.13, it can be concluded that particles P1 (diameter ~ 60 nm) and P2 (diameter ~ 50 nm) are both fully embedded in the TEM foil. In the pattern acquired from the region of P2, Figure 6.15(f), the α -Zr bands are very well defined but there is little sign of diffraction from the relatively large Nb-rich precipitate, similar to the pattern acquired from the matrix, Figure 6.15(e). In comparison, in the pattern acquired from the region of P1, Figure 6.15(d), even though the dominant Kikuchi bands are still indexed as α -Zr, Figure 6.15(b and d), some well-defined bands from the β -Nb phase can be seen, Figure 6.15(d). If, as defined above, we assume that signals contributing to detectable Kikuchi bands originate from a depth of ~ 20 nm (physical depth resolution) from the bottom surface, and if we further assume that particle P1 lies in the middle of the thin foil, the thickness of the two phases that contribute to the formation of Kikuchi bands in the region of P1 can be estimated to be ~ 10 nm α -Zr and 10 nm β -Nb. We thus can estimate that the effective depth resolution for α -Zr to be ~ 10 nm under these imaging conditions, corresponding to approximately half the physical depth resolution.

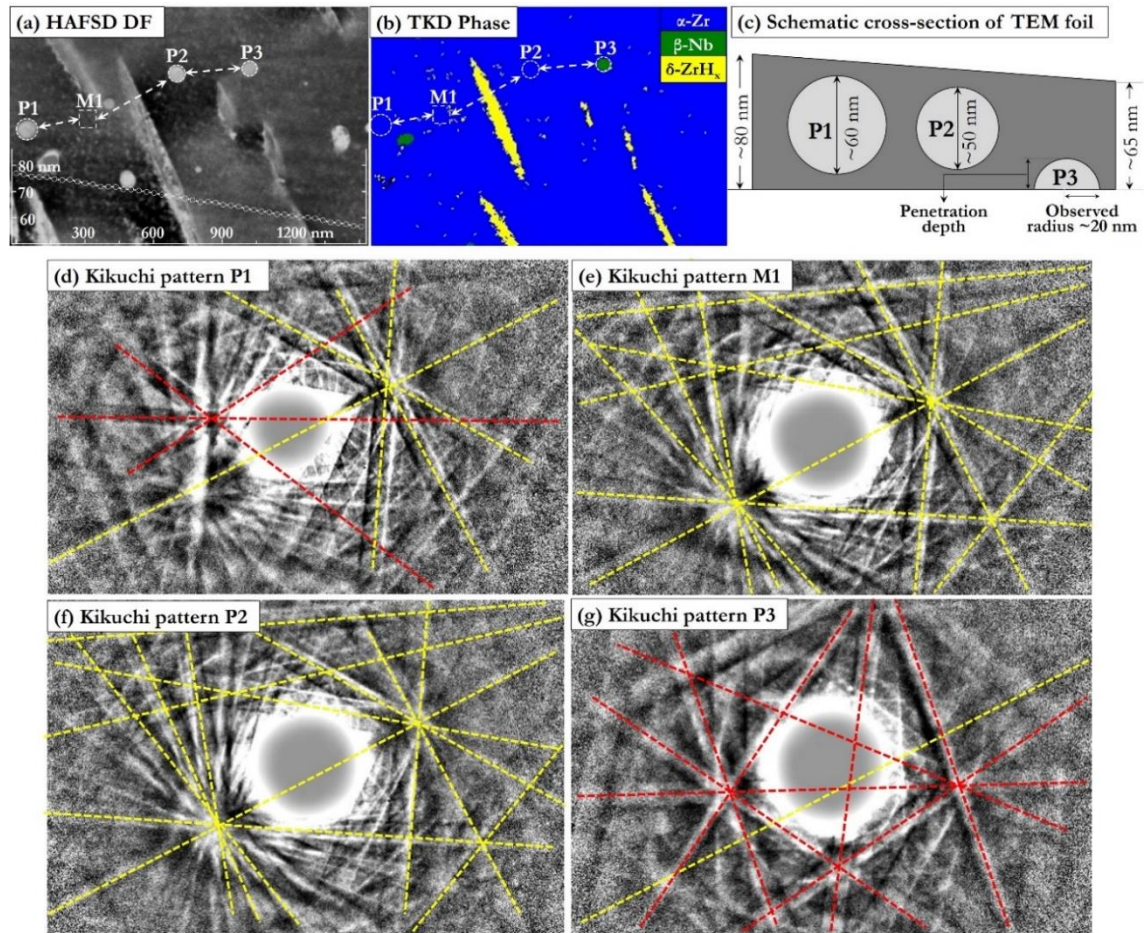


Figure 6.15 The influence of overlapping phases on Kikuchi patterns. (a) and (b) are the HAFSD image and TKD phase map showing the locations from which Kikuchi patterns were acquired. (c) is a schematic cross-sectional view of the TEM foil showing possible locations of 3 selected particles. (d, e, f and g) show the details of Kikuchi patterns obtained from the locations of these 3 particles and from the surrounding matrix. Kikuchi bands from the β -Nb phase are highlighted by the red dashed lines and α -Zr by yellow dashed lines.

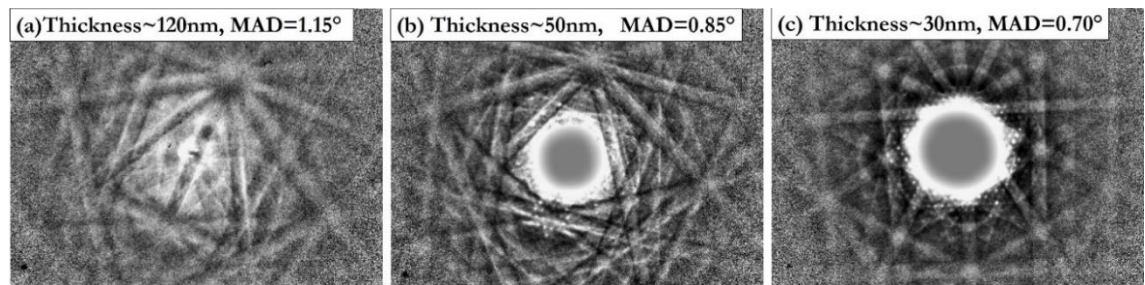


Figure 6.16 Kikuchi patterns from a Zr-Nb sample from regions of different thickness.

Figure 6.16 shows a series of Kikuchi patterns acquired from a similar Zr-Nb sample, but from regions of different thickness. Clear and indexable Kikuchi patterns can be seen from the region of thickness $\sim 120\text{nm}$, but the intensity of the background is clearly stronger

compared with the patterns generated from thinner regions above as a result of thermal diffuse scattering (TDS). Discrete diffraction spots start to be seen at a thickness of 50 nm, and become more obvious at 30 nm as expected. The average values of MAD are also shown in Figure 6.16. Under the same imaging conditions, these MAD values increase gradually with the sample thickness from 30 nm to 120 nm, indicating a gradually decreasing indexing confidence, which is mainly caused by the variation in sample thickness and diffuse scattering, but also could be a result of local strain [175, 282].

6.2.4. Discussion

When a thin foil with embedded particles is scanned in TKD, depending on the combination of microscope parameters such as accelerating voltage, and materials properties like density and atomic mass, different volume of material above the bottom surface will contribute strongly to the formation of the detected Kikuchi patterns. Depending on the capabilities of the indexing software, mounting the sample the other way up may give different apparent microstructures; especially the particle size and number density. Based on the experimental results presented above, Figure 6.17 shows a schematic illustrating our suggested correlation between the buried depth of β -Nb particles in a thin foil and their visibility in TKD. It is also clear that different microstructures will be seen by different techniques even from the same sample. For example, by collecting signals integrated from the whole foil thickness, e.g. TEM or FSD imaging, we can detect all the particles shown in Figure 6.17. However, the particles that are close to the top surface, e.g. the ones labelled 3, 4 and 5 in Figure 6.17, are the only ones shown by secondary electron imaging, with an information depth of a few nanometers [266]. By comparison, in a TKD map only the particles that are distributed close to the bottom surface and have a size larger than the effective depth resolution can be detected. As mentioned in the introduction knowledge of the depth resolution is critical in

moving from quantification of the map or image to the quantification of microstructural features. Figure 6.17 illustrates how the size and number of Nb particles observed, even from the same part of the foil depends strongly on whether the signal originates from the top (SE), bottom (TKD) or entire thickness (FSD) of the sample. For example, correctly converting the number of particles per unit area seen in the TKD maps to a number density (i.e. number per unit volume of material) can only be done with knowledge of the information depth. Figure 6.17 makes it clear that actual particle diameters are likely significantly larger than that observed in the TKD maps, and that the stereological conversion from particle image size distributions to actual particle size distributions depends on the depth resolution.

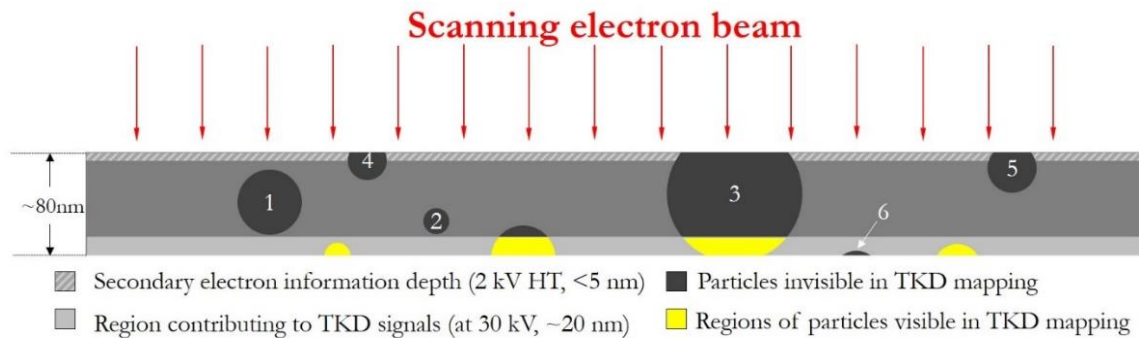


Figure 6.17 Schematic of the correlation between the depth of Nb particles in an electron transparent Zr thin foil and their visibility in TKD mapping at 30 kV

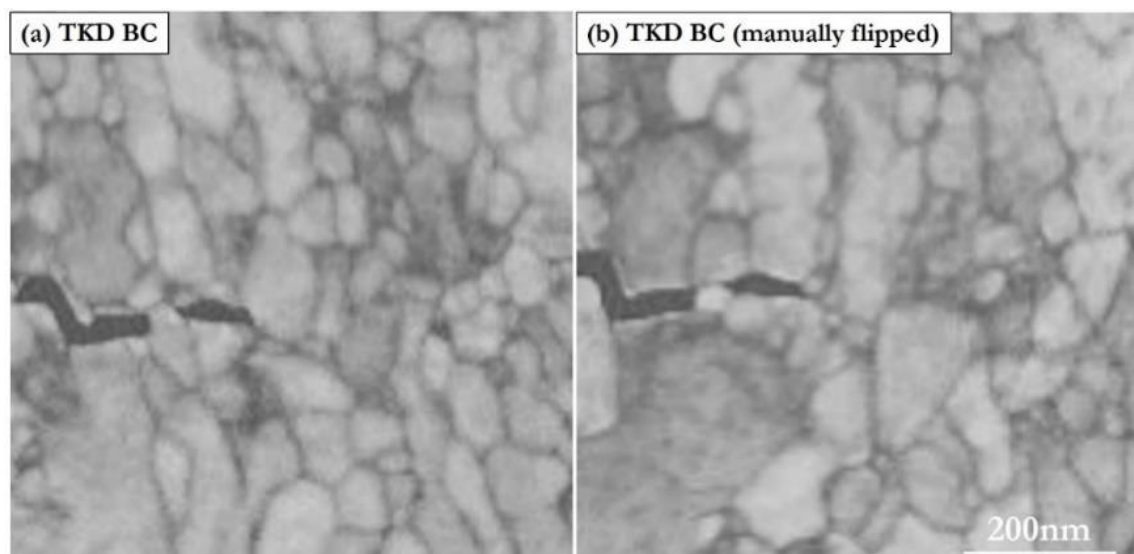


Figure 6.18 TKD band contrast maps scanned from opposite sides of the same region in a nano-crystalline zirconium oxide showing different grain structures

The existing surface-sensitive nature of TKD [190, 276] thus needs to be taken into consideration, especially when analysing nano-crystalline materials with grain size of the order of the sample thickness. An example, a nanocrystalline sample of zirconium oxide scanned by TKD over the same region but from opposite directions is shown in Figure 6.18. It can be seen that from a sample ~ 100 nm thick of a material with a grain size that ranges from tens to hundreds of nanometres, mounting the sample the other way up results in images with significantly different apparent grain structures.

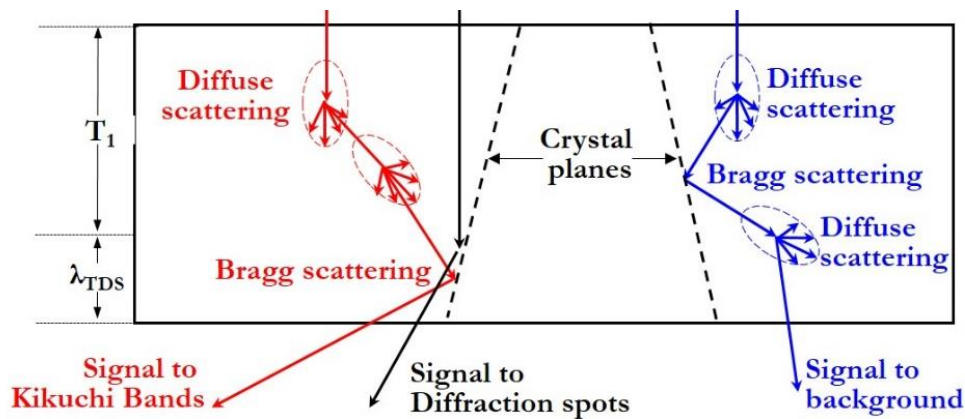


Figure 6.19 Schematic diagrams showing multiple scattering processes in a crystal contributing to the formation of Kikuchi bands (red), diffraction spots (black) and the background (blue). The fan-shaped diffuse scattering represents the intensity angular distribution of the TDS electrons.

Before I can propose a model for the depth resolution, an understanding of the formation mechanisms of Kikuchi patterns in TKD is required. Discrete diffraction spots, diffraction lines/bands or a combination of both can be observed under different diffraction conditions. In TEM, discrete diffraction spots arise from coherent scattering of the incident beam, while the formation of Kikuchi bands is a two-step process consisting of incoherent scattering of the primary beam followed by coherent scattering of these forward biased electrons [245, 283-285], Figure 6.19. Several papers [286-289] discuss the thermal diffuse scattering (TDS) caused by thermal vibrations of the atoms as a major mechanism for incoherent scattering, and every such incoherent scattering event then acts as a point source of electrons that can

contribute either to the formation of Kikuchi bands or background intensity [286, 289, 290], Figure 6.19. As electrons generated by TDS contain no crystallographic information, they can lead to a diffuse background intensity that suppresses the contrast and sharpness of Kikuchi bands, especially when TDS arises close to the bottom surface of the foil [289, 291], as highlighted in blue in Figure 6.19.

If we define the physical depth resolution as the depth from which Kikuchi patterns originate, and based on the formation mechanisms of Kikuchi bands described above, it is reasonable to infer that the physical depth resolution (d_{phy}) of Kikuchi patterns formed in TKD is related to the position of the deepest thermal diffuse scattering event contributing to the pattern, or the TDS mean free path (λ_{TDS}), $d_{\text{phy}} \approx \lambda_{\text{TDS}}$. However, only a few experimental data on physical depth resolution can be found in the literature, and even less data on values of λ_{TDS} , especially for the low energy range of 10 to 30 keV. In Table 6.2, we summarize all the values of TKD physical depth resolution we could find, and the mean free paths of the corresponding scattering events. Since the same formation mechanisms for Kikuchi patterns should apply in both off-axis and on-axis TKD geometries, we do not expect significant differences in the depth resolution achieved, so the depth resolution data in Table 6.2 also includes those measured for the off-axis geometry, e.g. for Al, Cu and Pt.

Inelastic scattering is a very general term which refers to any process which causes the primary electron to lose a detectable amount of energy, including plasmon scattering, single valence electron excitation and inner shell excitation. The inelastic mean free paths (λ_{IMFP}) for 41 elemental solids for electron energies from 50 eV to 30 keV can be found in [292]. TDS is not fully incoherent but also includes an inelastic component with an average energy loss per event less than 0.1 eV [293]. However, values of λ_{TDS} for 30 keV primary beam are not currently available, and those shown in Table 6.2 are calculated based on a 100 keV primary beam. It can be seen that values of physical depth resolution correlate better with

λ_{TDS} than λ_{IMFP} , and these slight differences might be further reduced if more accurate low voltage data on λ_{TDS} were available. The predicted correlation between λ_{TDS} and physical depth resolution is also in agreement with Monte-Carlo simulations carried by van Bremen et al. [271] in which they calculated the depth at which the final incoherent electron scattering events occurred, and reported a physical depth resolution of ~ 12 nm in Au samples exposed to 30 keV electrons ($Z=79$, $\rho=19.3$ g.cm $^{-3}$, $\lambda_{\text{IMFP}}= 21.3$ nm and $\lambda_{\text{MFP}}= 3.5$ nm), a material in which we would expect there to be a similar depth resolution as experimentally determined in Pt, 13 nm [277]. A similar relationship has been reported by Brodu et al. [276] for Si samples exposed to 30 keV electrons, $d_{\text{phy}} \approx 0.026E/\mu_0$ (where E is the beam energy and μ_0 is the absorption coefficient for 100 keV electrons in Si). If we consider the relationship between λ_{TDS} and absorption coefficient to be $\lambda_{\text{TDS}} \approx 1/\mu_0$ [293], the Brodu relationship is then similar to the value of d_{phy} proposed above.

Table 6.2 Experimentally determined values of TKD physical depth resolution at 30 keV and mean free paths of scattering events in the corresponding materials

	Al	Si	Cu	Nb	Pt
Physical depth resolution, d_{phy} , (nm)	80 [277]	60 [276]	33 [277]	20	13 [277]
Inelastic scattering mean free path, λ_{IMFP} , (nm) [292]	37.6	43	27	30.8	20.5
Elastic scattering mean free path, λ_{MFP} , (nm) [294]	23.7	24.8	8.0	5.7	3.5
TDS mean free path ¹ , λ_{TDS} , (nm)	90	87	40	-	-
Ratios ($d_{\text{p}}/\lambda_{\text{TDS}}$)	0.9	0.7	0.8	-	-
Ratios ($d_{\text{p}}/\lambda_{\text{MFP}}$)	3.4	2.4	4.1	3.5	3.7
Ratios ($d_{\text{p}}/\lambda_{\text{IMFP}}$)	2.1	1.4	1.2	0.6	0.6
Ratios (d_{p}/ρ)	29.6	25.9	3.7	2.3	0.6
Ratios (d_{p}/Z)	6.2	4.3	1.1	0.5	0.2
TDS absorption coefficient ² , (nm^{-1}) [210]	0.6	0.6	1.4	-	-
Atomic Number, Z	13	14	29	41	78
Density, ρ , (g.cm $^{-3}$)	2.7	2.3	9.0	8.6	21.5

¹The values of λ_{TDS} are estimated using equation, $\lambda_{\text{TDS}} \approx 1/\mu_0$ [293]

² The values of absorption coefficient μ_0 are calculated for 100 keV primary electrons

In addition, the ratio between the physical depth resolution and the elastic scattering mean free path (λ_{MFP}) is nearly constant, Table 6.2, indicating that the diffracted intensity contributing to the Kikuchi bands generated inside the sample has a high probability to escape the sample surface if the TDS position is within a distance $< 3.5\lambda_{\text{MFP}}$ or $< \lambda_{\text{TDS}}$ from the bottom surface. The implicit relationship that $\lambda_{\text{TDS}} \approx 3.5\lambda_{\text{MFP}}$ will need more calculations to confirm, and this lies beyond the scope of the current study. The outlier to this relationship is the data for Si, Table 6.2, where the determination of the physical depth resolution is based on the visibility of Kikuchi bands originated from the top crystal closest to the incident electron beam in a bi-crystal Si sample [276]. However, the authors did not take the influence of the thickness of the upper grain in their bi-crystal sample into consideration, which can affect the intensity of Kikuchi bands associated with this crystal. At the critical thickness of the bottom crystal, ~ 60 nm [276], which they regard as the physical resolution, the thickness of the top crystal is only ~ 40 nm, smaller than λ_{TDS} , and could limit the intensity of Kikuchi bands generated. It is thus reasonable to infer the physical depth resolution for Si exposed to 30 keV electrons could be larger than 60 nm. If we assume a value of 80 nm to be more realistic, then the ratio between physical depth resolution and λ_{MFP} in all the materials reported is close to 3.5.

Many papers have shown that sample thickness is very important in TKD analysis [273, 295]. Considering the role of TDS on the formation of Kikuchi bands, and so on the physical resolution and the intensity of the background as discussed above, I may thus suggest a suitable sample thickness to achieve clear and indexable Kikuchi patterns for TKD analysis to be $\leq 6\lambda_{\text{TDS}}$, or $21\lambda_{\text{MFP}}$ for samples of high crystalline symmetry. As the observed band intensity is proportional to the square of the structure factor amplitude [245, 296], I can expect the contrast and sharpness of Kikuchi bands in samples of lower crystalline symmetry will be more sensitive to the sample thickness, and samples $\leq 3\lambda_{\text{TDS}}$, or $10\lambda_{\text{MFP}}$ are suggested.

6.2.5. Conclusions

The formation mechanisms of Kikuchi bands in TKD follow a two-step process similar to that in TEM; incident electrons first undergoing incoherent thermal diffuse scattering followed by Bragg scattering from crystal planes. The physical depth resolution of TKD is then logically related to the depth where the deepest TDS event occurs. A function describing the physical depth resolution is thus suggested to be $d_{\text{phy}} \approx \lambda_{\text{TDS}}$, the mean free path of TDS in materials exposed to electrons of specific primary energies. The measured value of effective depth resolution was found to be approximately half the physical depth resolution. Based on the observed ratios between the physical depth resolution and the mean free path of elastic scattering, I propose that d_{phy} can be estimated as $3.5\lambda_{\text{MFP}}$. Compared with the limited data available for λ_{TDS} , especially in the lower energy range from 10 keV to 30 keV used in TKD analysis, λ_{MFP} for electrons with kinetic energies from 10 keV to 30 keV and materials with atomic number $Z=1$ to 92 can be easily calculated using the elastic scattering cross sections data in [294]. I suggest a guideline for the sample thickness in order to achieve clear and indexable Kikuchi patterns for TKD analysis $\leq 6\lambda_{\text{TDS}}$, or $21\lambda_{\text{MFP}}$ for samples of high crystalline symmetry, and lower values for samples of lower symmetry.

Chapter 7 Formation Mechanisms of Suboxide and Oxides by Aqueous Corrosion

7.1. Introduction

In this chapter, oxide films formed by the aqueous corrosion of Zr alloys have been analysed, and detailed information generated on phase distributions, grain size and crystallographic orientations. Displacive transformations have been widely reported in metals, alloys and ceramics, but rarely reported to be important in the aqueous corrosion of alloys. I report here my analysis of the formation of the hexagonal-ZrO suboxide during the aqueous corrosion of α -Zr alloys and propose this to be a paraequilibrium displacive transformation with the rate controlled by oxygen diffusion. These results provide a guideline for understanding the mechanisms of crystallographic evolution during oxide growth on commercial zirconium alloys, and also demonstrate the capability of transmission Kikuchi diffraction to investigate orientation relationships in nano-scale materials.

I would like to thanks my colleagues Dr. Hongbing Yu, Dr Phani Karamched and Guanze He for their assistance on the TKD and EELS data analysis. Without their patience and expertise, I would not have completed this part of the work.

7.2. Materials and Experimental Methods

Three types of zirconium alloys in the recrystallized conditions were selected to compare the structure of the oxide formed on a commercial Zircaloy-4 and a model Zr-0.5Nb alloy at an earlier corrosion stage, and a similar model Zr-1Nb alloy at a much later stage. Detailed sample information and corrosion data have been described in section 4.3.

Cross-sectional transmission electron microscopy foils containing both the oxide layer and the metal matrix were prepared using FIB lift-out method described in section 5.2. The on-

axis TKD study was carried out on a Zeiss Merlin FEG-SEM system equipped with an OPTIMUS™ TKD head. The off-axis TKD maps were acquired using the conventional configuration, where an EBSD camera with a vertical scintillator is used and more information about the TKD setup has been given in section 3.2.

The detailed map setting parameters used are summarized in Table 3.1, and the crystallographic information used in identifying the phase distributions in these samples is in Table 3.2. All the maps presented below have been further cleaned using the Channel 5 software to remove isolated pixels that have been incorrectly indexed or have no reliable solutions. Based on the crystal information acquired from TKD analysis, Crystal Maker® was used to reconstruct the interfacial atomic arrangements.

7.3. Results

7.3.1. Bulk oxide phases and texture analysis

A typical set of TKD band contrast and phase maps on zirconium oxides are shown in Figure 7.1. Thanks to the improved on-axis TKD acquisition efficiency, every region in the pre-transition oxide layers on the Zr-0.5Nb and Zircaloy-4 alloys were analysed, while when using off-axis TKD in the oxide layers of the Zr-1Nb alloy, only part of the oxide layers (the post-transition oxide + part of the pre-transition oxide) were mapped, Figure 7.1(b).

As expected, most of the small grains in the oxide layer on these three alloys are found to be m-ZrO₂, Figure 7.1(d, e and f). However, the grain morphology clearly differs from sample to sample. The oxide layers on Zr-0.5Nb contain more aligned columnar grains, while they tend to be more equiaxed on Zircaloy-4. It is well known that Zr alloys exhibit cyclic corrosion kinetics, and at the transition point the protectiveness of the oxide breaks down, the corrosion rate increases dramatically and a new corrosion cycle restarts [11]. Evidence for the second cycle of corrosion can be seen in the thicker oxide on the Zr-1Nb

sample, Figure 7.1(b). The pre-transition oxide on Zr-1Nb has a similar grain shape as that formed on Zr-0.5Nb, but the columnar structure of the post-transition oxide seems to be less well developed and more equiaxed. A few examples of the equiaxed grains formed post-transition are highlighted by arrows, Figure 7.1(b). If we define 2° misorientation as the threshold for low angle grain boundaries (LAGB) and the minimum grain area as 20 nm x 20 nm (25 pixels in the Zr-0.5Nb map, 16 pixels in the Zircaloy-4 map and 2 pixels in the Zr-1Nb map), then an average grain size of 49 nm, 41 nm and 50 nm is measured for m-ZrO₂ on the Zr-0.5Nb, Zircaloy-4 and Zr-1Nb samples, respectively. On all three alloys, both the width and the aspect ratio of these m-ZrO₂ grains increases gradually towards the oxide/metal interface, Figure 7.1. Similar results have been reported previously, in which Zr-Nb alloys generally tend to form oxide grains with aligned columnar shapes [59, 81] and the oxide grains on Zr-Sn alloys tend to be more equiaxed [71, 193].

A small volume fraction of equiaxed t-ZrO₂ grains are found scattered throughout the oxide. The average grain size and tetragonal fraction values are ~16 nm and ~1.6% for Zr-0.5Nb (on-axis TKD, 4 nm step size), ~15 nm and ~2.8% for Zircaloy-4 (on-axis TKD, 5 nm step size) and ~18 nm and ~2.8% for the Zr-1Nb (off-axis TKD, 11 nm step size). Similar t-ZrO₂ volume fractions of ~3% [103] were reported in thin TEM samples from 55 day-corroded samples analysed by the ASTAR technique which has a similar spatial resolution to on-axis TKD. The grain size of the tetragonal phase is similar in these three materials, around 20 nm. The values of tetragonal phase fraction are significantly lower than reported by bulk measurement techniques, laboratory and synchrotron XRD for example, where analysis of oxide layers formed on similar alloys reported the tetragonal phase fraction to lie in the range 3–15% [16, 22, 60, 65]. However, the non-destructive nature of these measurements should preserve the stress state in the oxide, while stress relaxation is expected to occur during the preparation of the thin TEM samples which may lead to transformation of stress-stabilized

tetragonal grains into the equilibrium monoclinic phase [297]. Other factors which can affect the phase fraction measured through TKD include FIB-induced phase transformations [145, 249] and the possibility of mis-indexing those very small grains.

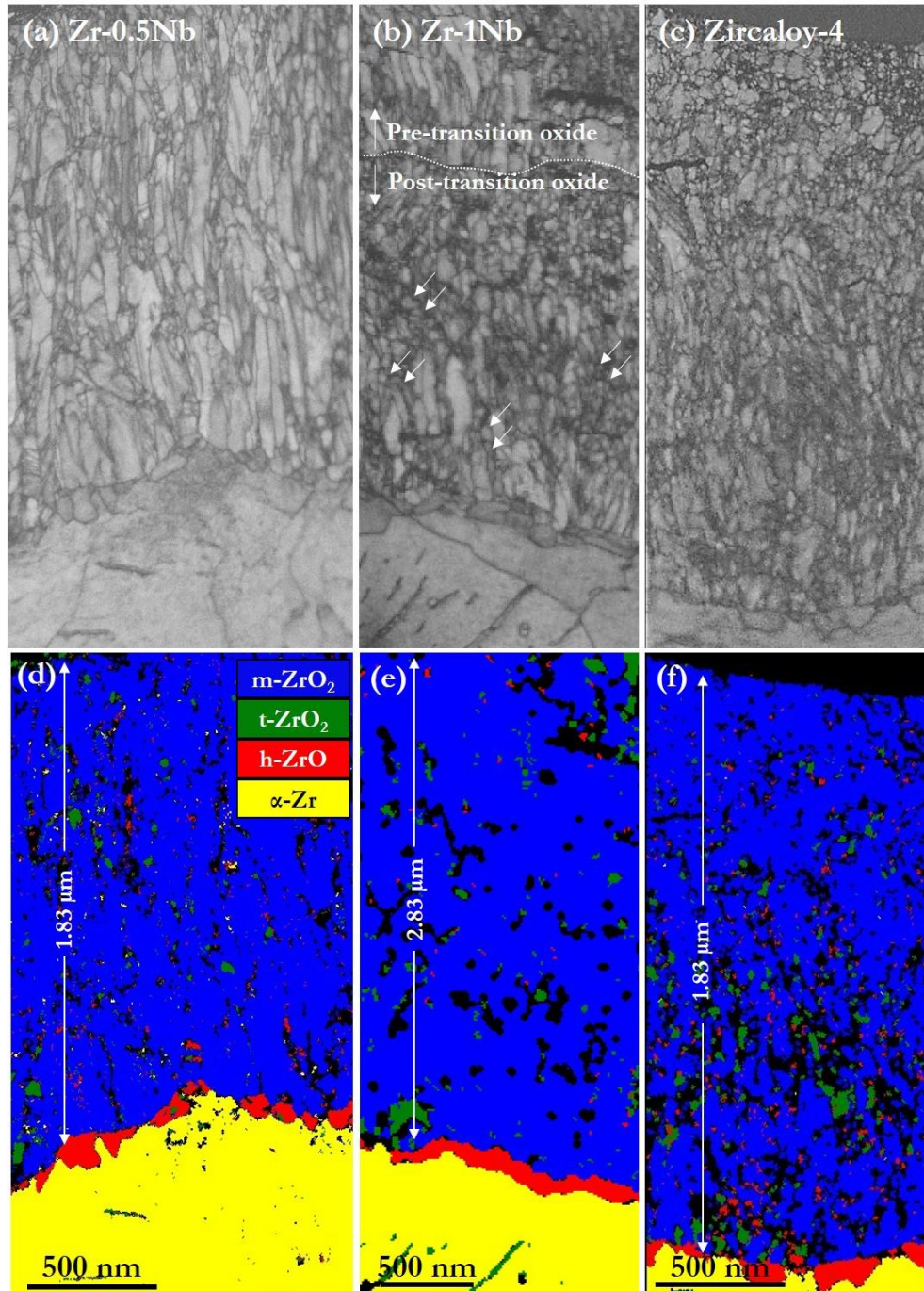


Figure 7.1 (a, d) On-axis TKD band contrast and phase maps from the whole oxide layer on the Zr-0.5Nb tube sample, (b, e) off-axis TKD band contrast and phase maps from inner part of oxide layer on the Zr-1Nb tube sample and (c, f) on-axis TKD band contrast and phase maps from the whole oxide layer on the Zircaloy-4 sheet sample.

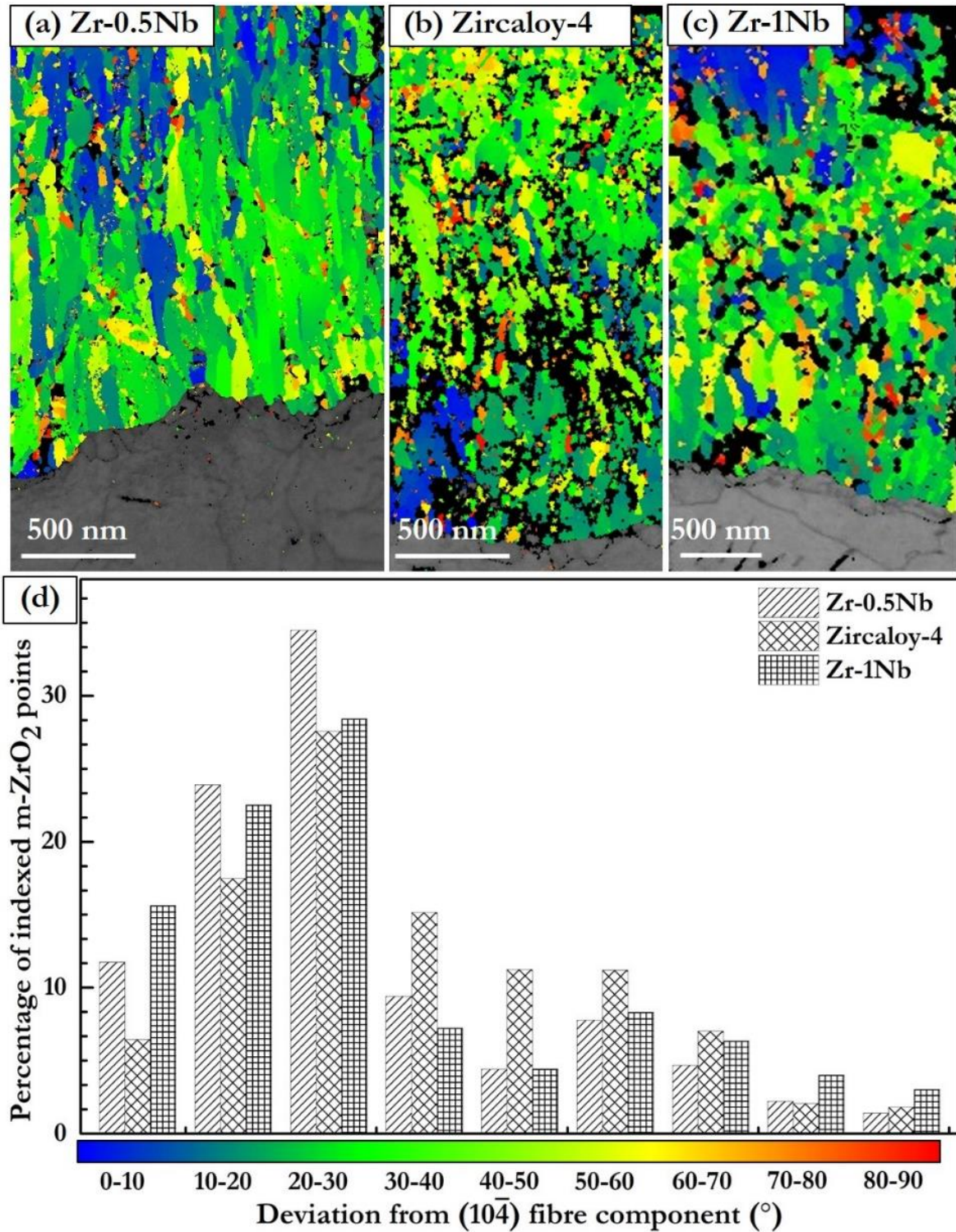


Figure 7.2 Combined TKD m-ZrO₂ texture component and band contrast map for (a) Zr-0.5Nb, (b) Zircaloy-4 and (c) Zr-1Nb alloy samples. The grains are coloured according to the angular deviation of their (104) poles from the RD. (d) Statistical angular of the frequencies of grains with the (104) poles deviating away from the RD.

The texture component maps for the three materials are shown in Figure 7.2. The oxide has been widely reported to have a strong fibre texture with the majority of the m-ZrO₂ grains

with directions between $(10\bar{2})_{\text{m-ZrO}_2}$ and $(10\bar{6})_{\text{m-ZrO}_2}$ lying parallel to the surface normal [62, 65]. The mechanisms leading to the varying texture orientations are still not clear. In this thesis, I have consistently used the $(10\bar{4})_{\text{m-ZrO}_2}$ ||RD fibre component to compare the texture strength on different samples. The maps in Figure 7.2 are coloured according to the orientation deviation of grains away from the $(10\bar{4})_{\text{m-ZrO}_2}$ ||RD fibre component. The statistical distributions of the frequency of textured oxide grains as a function of angular deviation away from the fibre component are plotted in Figure 7.2(d) for these three materials. More than 50% of the indexed m-ZrO₂ grains are observed to have $(10\bar{4})_{\text{m-ZrO}_2}$ lying within 30° of the surface normal, in good agreement with previous normal EBSD [58] and ASTAR [103] results. The colour in the orientation maps changes gradually with depth in the oxide, with the texture component closer to $(10\bar{4})_{\text{m-ZrO}_2}$ ||RD in the outer few microns that increases in the angular deviation towards the oxide/metal interface. This can be a result of stress accumulation near the oxide/metal interface [22, 60, 88], while another possibility exists that the interface roughness may change the oxide growth direction and further affect the texture orientations.

It should be noted that any given oxide examined represents a “snapshot” of the corrosion process, which means that oxide grains far away from the oxide/metal interface are a product of oxidation of metal grains which might have a different orientation to the underlying surviving metal grains. Understanding the texture relationship between metal and oxide thus necessitates micro-texture and crystalline orientation analysis near the interface regions.

The formation of oxide texture has been proposed to be linked to preferred orientation relationships between the oxide and the α -Zr substrate [62, 87, 298]. Contoured $(10\bar{4})_{\text{m-ZrO}_2}$ pole figures (PF) and the (0002) poles of the underlying α -Zr grains from the regions shown in Figure 7.1 are plotted in Figure 7.3. Again, the m-ZrO₂ fibre texture is close to the $(10\bar{4})_{\text{m-ZrO}_2}$ normal and the grains are free to rotate around this fibre axis. Only one or two

α -Zr grains are included in a typical TKD map, and for the Zr-0.5Nb and Zircaloy-4 samples the orientation of these are in good agreement with texture analysis from the bulk samples, with (0002) normal close to the RD in the tube sample or ND for the sheet sample. The (0002) poles of the α -Zr grains in the Zr-1Nb sample deviate more than 60° from the surface normal, and two grains with slightly different orientations can be seen in Figure 7.3(c). No specific orientation relationships between the fine grained m-ZrO₂ and underlying α -Zr grains can be identified from these results, hence other factors must be considered to control the oxide texture.

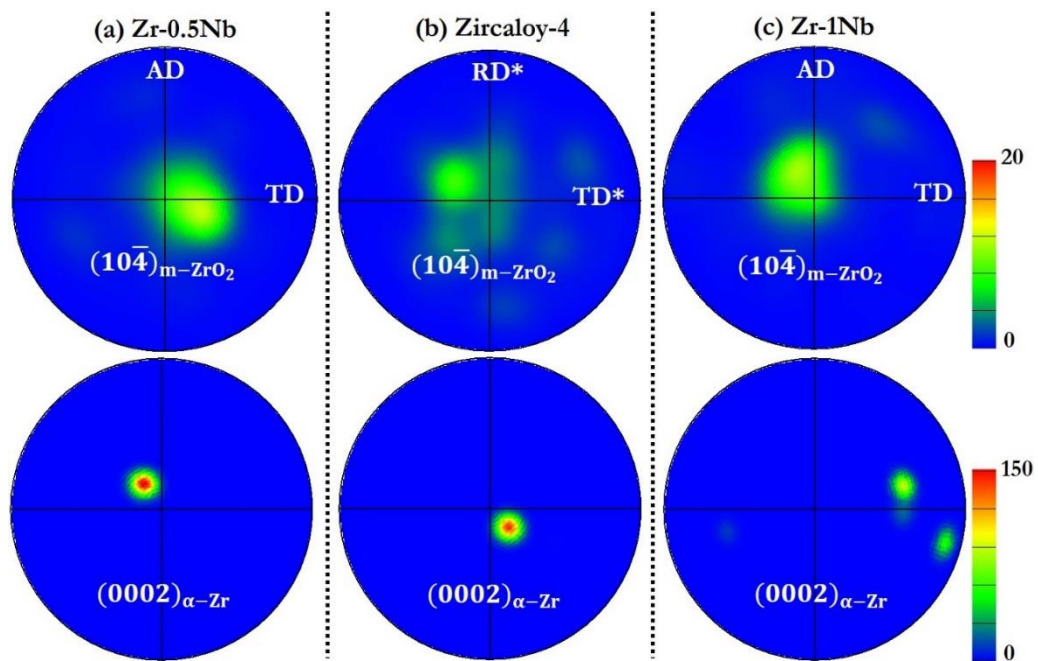


Figure 7.3 Contoured $(10\bar{4})$ poles (half width 20°) of all the m-ZrO₂ grains and (0002) poles (half width 10°) of the underlying α -Zr substrates viewed along the oxide growth direction for (a) Zr-0.5Nb tube, (b) Zircaloy-4 sheet and (c) Zr-1Nb tube samples.

7.3.2. Oxide/metal interface microstructure

Enlarged TKD maps showing the grain morphologies, phase distributions and the crystal orientations near the oxide/metal interface in the Zr-0.5Nb and Zr-1Nb samples are shown in Figure 7.4 and 7.6 respectively. Pole figures of the low index planes for the α -Zr substrate, h-ZrO and m-ZrO₂ from the corresponding O/M interface regions can be found in Figure

7.5 and 7.7. The contoured pole figures of the α -Zr phase in Figure 7.5(a) show the expected texture, with the (0002) basal pole of the grain in the zirconium substrate in the TEM foil aligned in the radial direction, and the $(11\bar{2}0)_{\alpha\text{-Zr}}$ prismatic pole parallel to the tangential direction of the tube sample. Two slightly misorientated α -Zr grains can be seen in Figure 7.6. The pole figures of the intermediate h-ZrO suboxide layer are relatively complex, as shown in Figure 7.5(b) and 7.7(b), even though all of these suboxide grains are in contact with the same underlying zirconium grain. As before, the monoclinic oxide texture lies between $(10\bar{2})_{\text{m-ZrO}_2}$ and $(10\bar{6})_{\text{m-ZrO}_2}$, Figure 7.5(c) and 7.7(c).

The distributions of texture components in the m-ZrO₂ and the α -Zr substrate for these two materials are plotted in Figure 7.4(d) and 7.6(e) respectively as a function of deviation angles between texture component and RD. In the Zr-1Nb tube sample, the (0002) main texture component of the underlying α -Zr substrate near the oxide/metal interface lies 80° away from the centre, so the (0002) basal pole is close to the tangential direction, while one of the $(10\bar{1}0)_{\alpha\text{-Zr}}$ poles lies close to the radial direction. The $(10\bar{4})_{\text{m-ZrO}_2}$ texture component of the oxide formed above this α -Zr grain is preferentially distributed 20°-25° away from the radial direction. In the Zr-0.5Nb sample, Figure 7.4, the $(10\bar{4})_{\text{m-ZrO}_2}$ texture component of the oxide is preferentially distributed 25°-30° away from the radial direction, while the (0002) texture component of the underlying substrate mainly lies between 15° and 20° away from the radial direction. Compared with the large misorientations, >60°, between the two underlying α -Zr grains, the difference between the texture distributions of the monoclinic oxide grains that lie above them is relative small, ~5°. These observations show that similar oxide micro-textures are formed near the oxide/metal interface in all these three alloys even though the underlying α -Zr grains can have very different orientations. This reinforces the point that factors other rather than specific macroscopic orientation relationships between α -Zr and m-ZrO₂ must be responsible for the formation of texture in the oxide.

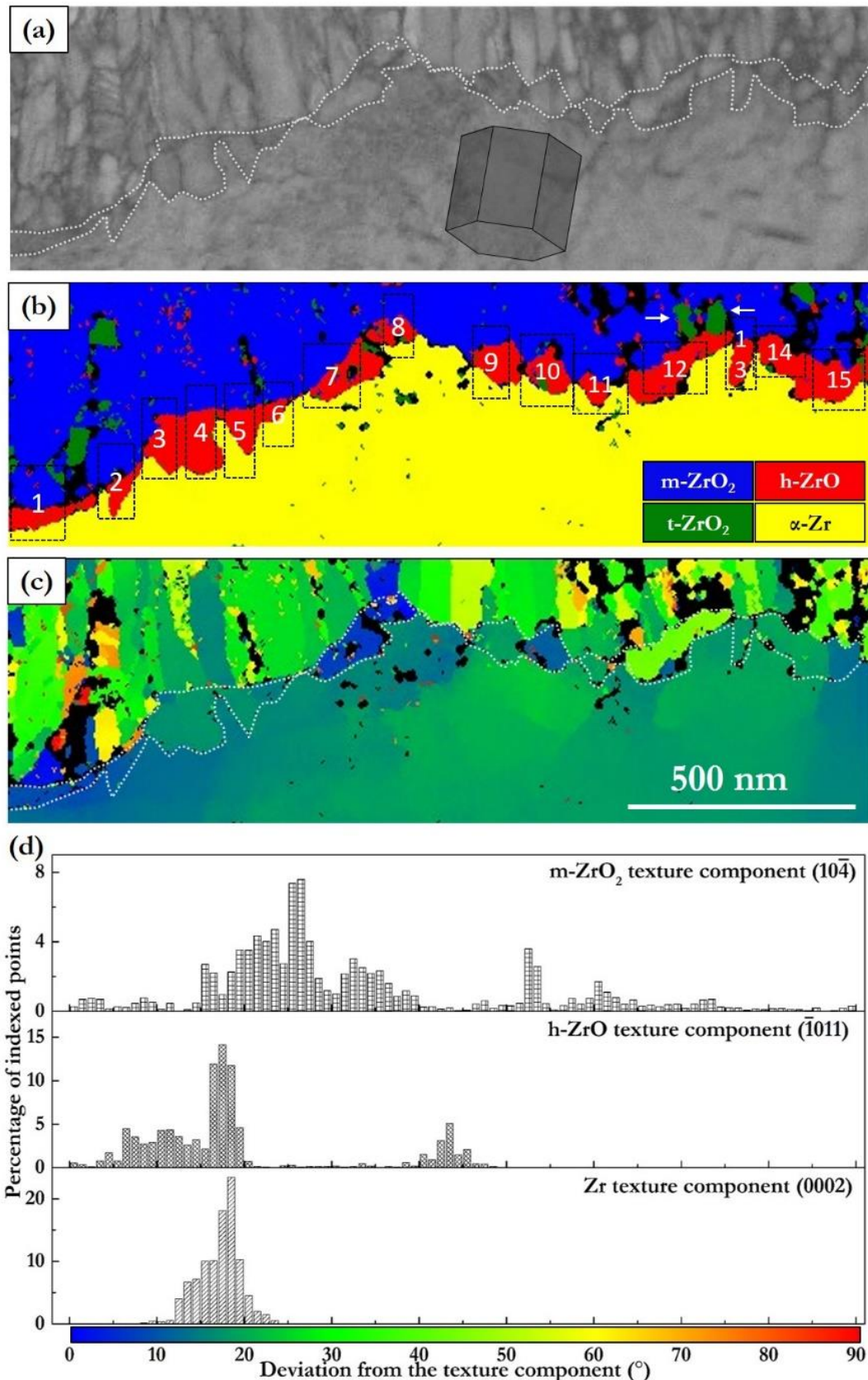


Figure 7.4 Enlarged TKD maps of the oxide/metal interface region in the Zr-0.5Nb tube sample, (a) band contrast map with schematic crystalline orientation of the substrate, (b) phase map and (c) texture component maps for m-ZrO₂, h-ZrO and α-Zr. The grains are coloured according to their angular deviation from the RD. (d) statistics and legend showing the frequencies of angular deviations away from the RD.

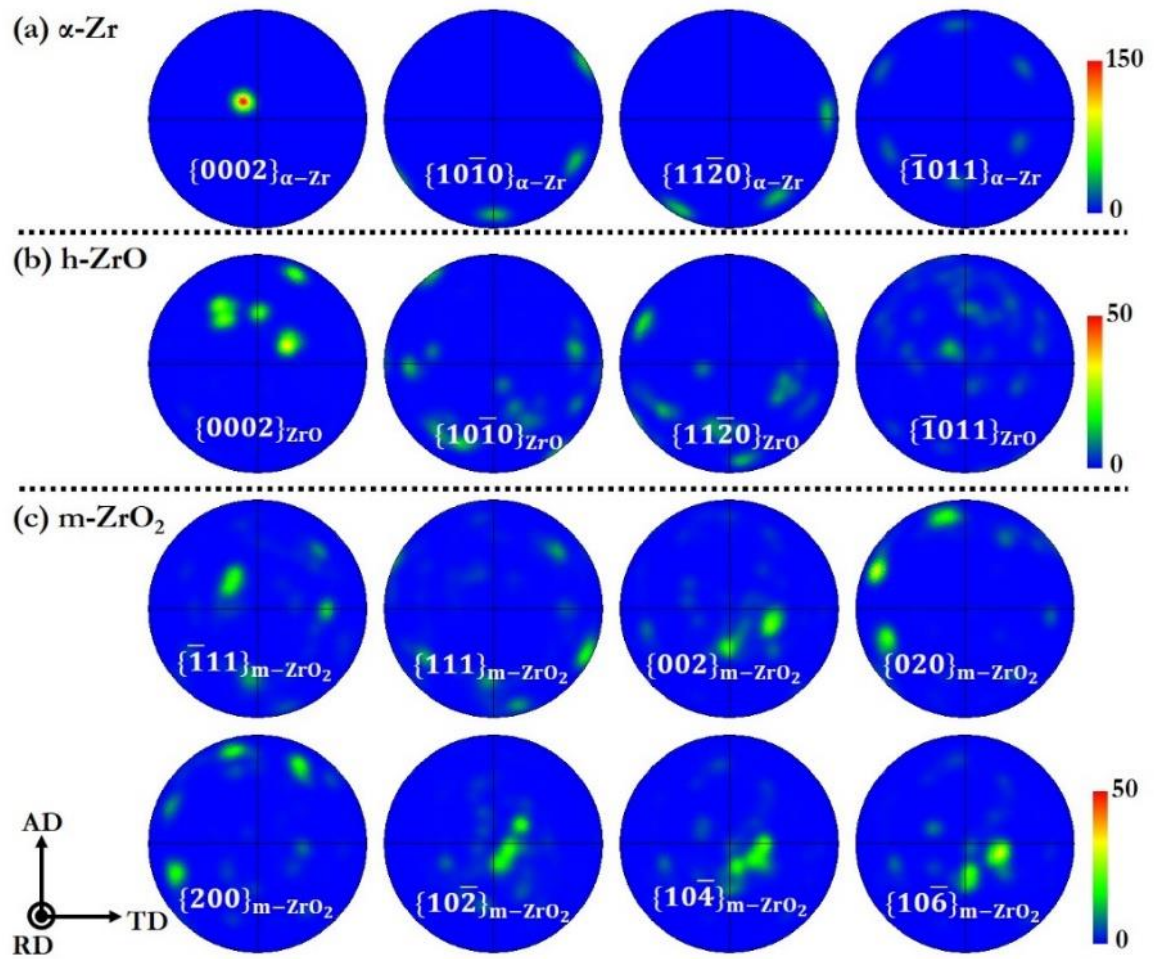


Figure 7.5 Contoured distributions of low index poles (half width 10°) from the α -Zr substrate, h-ZrO and adjacent m-ZrO₂ near the oxide/metal interface in Zr-0.5Nb tube.

The texture of oxide layers formed on different materials is also reported elsewhere to be very similar regardless of the substrate texture [240]. Based on the observations above, the nature of the formation of oxide texture may be related to the stress generated by the oxidation reaction at the oxide/metal interface [11, 20] since both experimental and simulation results show that a high level stress exists during oxidation, especially near the oxide/metal interface [22, 60]. Modelling results also indicate that bulk oxide orientations (the preferred $(10\bar{2})_{\text{m-ZrO}_2}$ to $(10\bar{6})_{\text{m-ZrO}_2}$ planes for example) occupying a smaller area at the metal/oxide interface are favoured in order to reduce the local compressive stress [88]. As the grains grow, they also become columnar so as to favour the growth of properly oriented grains to minimize stress accumulation.

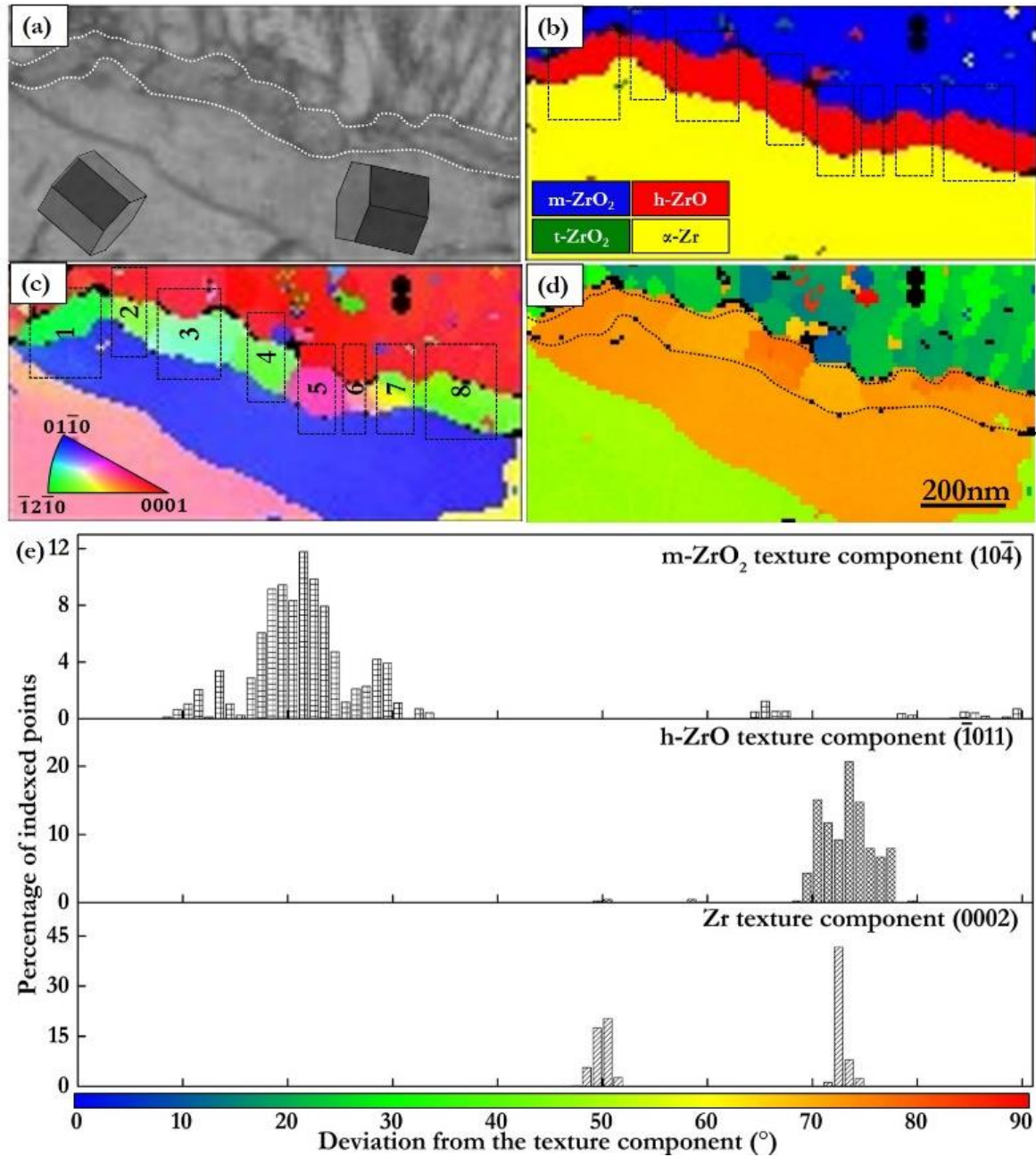


Figure 7.6 TKD maps of the O/M interface region in the Zr-1Nb sample (a) band contrast map with schematic crystalline orientation of the substrate, (b) phase map and (c) IPF Y map with the corresponding legend for h-ZrO and α-Zr, (d) texture component map where the grains are coloured according to their angular deviation from the radial direction shown in (e). (e) the frequencies of angular deviations away from the RD.

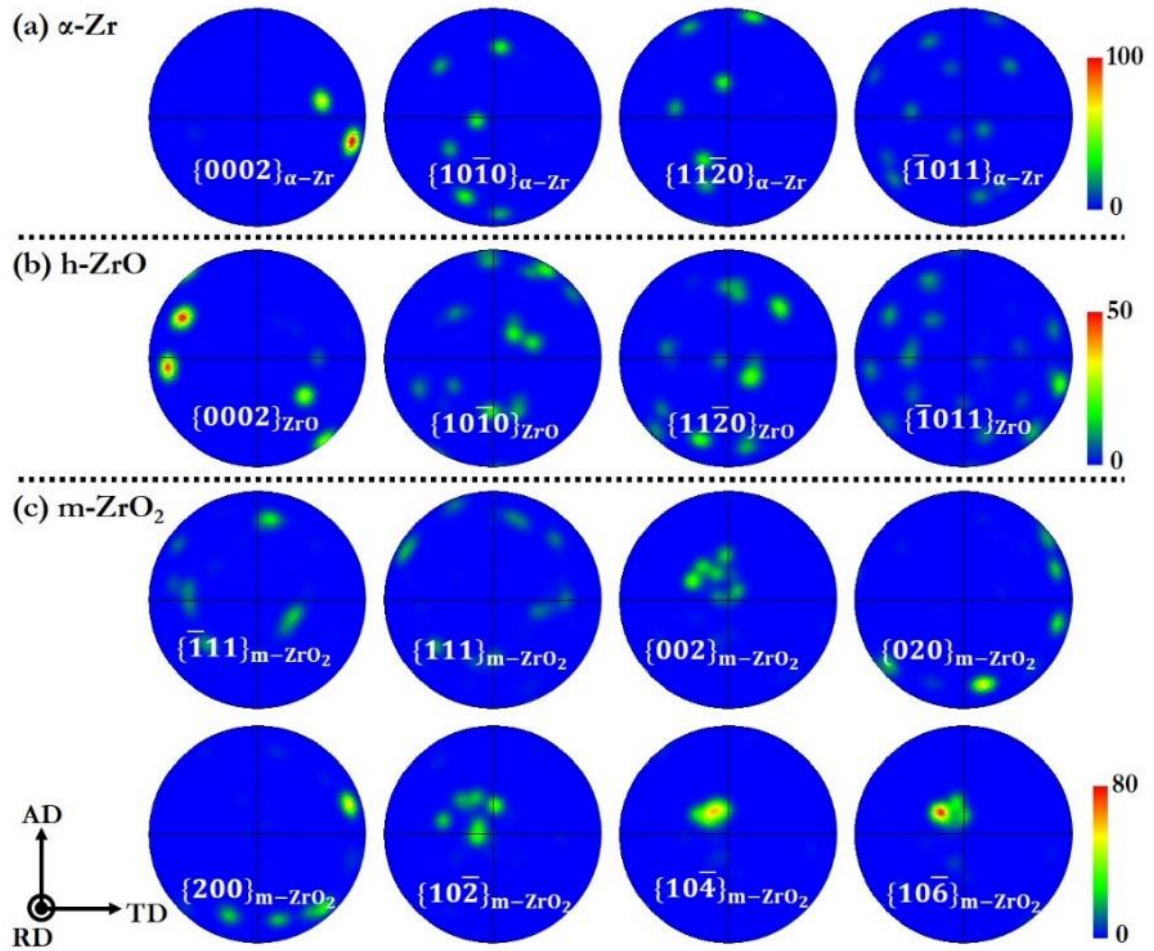


Figure 7.7 Contoured distributions of low index poles (half width 10°) from the α -Zr substrate, h-ZrO and adjacent m-ZrO₂ near the oxide/metal interface in Zr-1Nb tube.

A thin discontinuous layer of h-ZrO suboxide exists between the ZrO₂ and the α -Zr substrate in all three samples studied here. There are 19 h-ZrO grains in the areas studied on Zr-0.5Nb, 11 h-ZrO grains on Zircaloy-4 and 31 on Zr-1Nb, with average sizes ranging from 60-75 nm. The h-ZrO grains formed on Zr-0.5Nb and Zircaloy-4, Figure 7.1(a and b) and Figure 7.4, show Widmanstätten-type acicular shapes, suggesting a strong crystallographic correlation between the suboxide and underlying zirconium grains. The suboxide on the Zr-1Nb alloy, Figure 7.1(c) and Figure 7.6(c), shows a smoother or plate-shaped morphology. Most of the previous APT/TEM/EELS results report Widmanstätten-type suboxides [53, 58, 81, 299-302], but plate-like morphologies have been found in a few cases, Figure 4.51 in [303] for example. The obvious questions are what controls these differences in suboxide

grain morphology, what possible transformation mechanisms are involved in the transformation sequence $\alpha\text{-Zr} \rightarrow \text{h-ZrO} \rightarrow \text{ZrO}_2$, and what is the possible impact of these different morphologies on the overall corrosion behaviour? Two main orientation relationships have been reported between the Zr metal substrate and the h-ZrO suboxide (or $\omega\text{-Zr}$) [218, 304, 305], $(0002)_{\alpha\text{-Zr}} \parallel (\bar{1}011)_{\text{h-ZrO}}$ or $(0002)_{\alpha\text{-Zr}} \parallel (11\bar{2}0)_{\text{h-ZrO}}$. From the pole figures shown in Figure 7.5 and 7.7 it is difficult to determine the h-ZrO/ $\alpha\text{-Zr}$ orientation relationships, and so grain-by-grain analysis has been conducted in the regions highlighted in Figure 7.4 and 7.6.

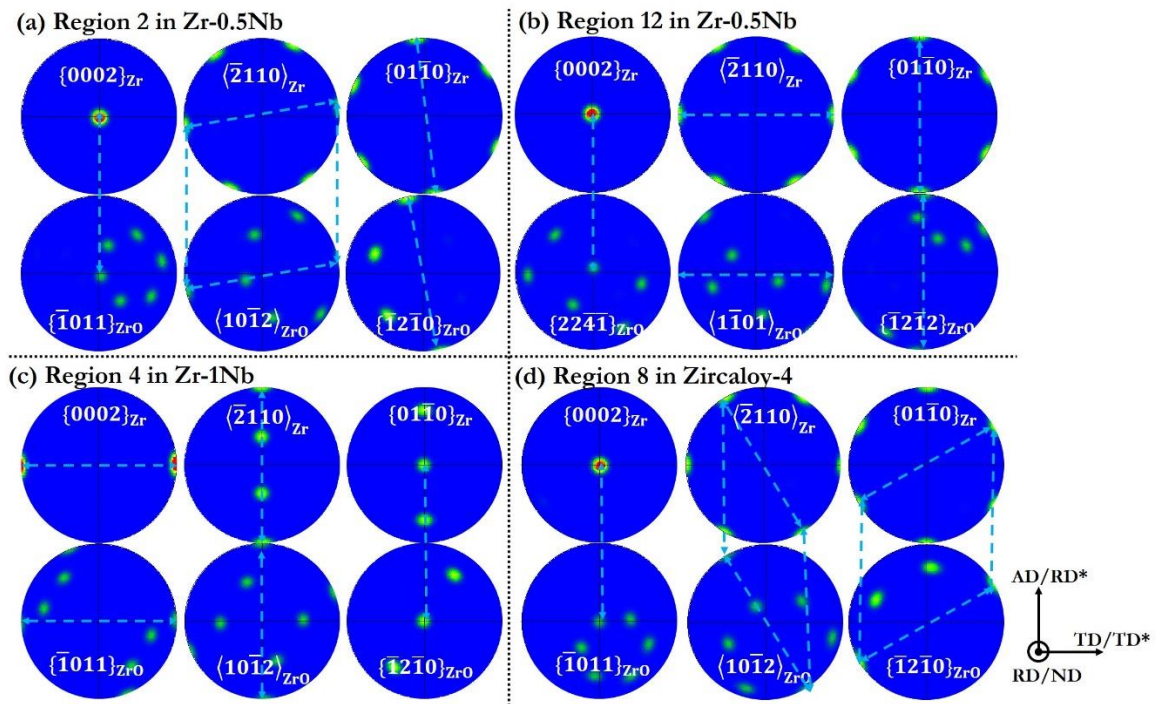


Figure 7.8 Selected pole figures from grain-by-grain analysis showing the orientation relationships between individual h-ZrO suboxide grains and the underlying $\alpha\text{-Zr}$ substrate in the (a, b) Zr-0.5Nb, (c) Zr-1Nb and (d) Zircaloy-4 samples.

The orientation of each identified h-ZrO grain has been plotted in an individual pole figure, which is then compared with the orientation of the underlying $\alpha\text{-Zr}$ matrix. Figure 7.8 shows some grain-by-grain orientation relationships between the $\alpha\text{-Zr}$ matrix and adjacent h-ZrO grains for the Zr-0.5Nb and Zr-1Nb samples. To compare these relationships clearly, I have

slightly adjusted the Euler angles in the TKD maps so that the $(0002)_{\alpha\text{-Zr}}$ poles are distributed along the radial direction for the Zr-0.5Nb sample and the tangential direction for the Zr-1Nb sample respectively.

In Figure 7.8(a, c and d) it can be seen that for all three alloys the $(0002)_{\alpha\text{-Zr}}$ and one of the 6 $(\bar{1}011)_{\text{h-ZrO}}$ planes are coincident, indicating a $(0002)_{\alpha\text{-Zr}} \parallel (\bar{1}011)_{\text{h-ZrO}}$ relationship, regardless of the orientation of the underlying $\alpha\text{-Zr}$ grains. From the $\langle \bar{2}110 \rangle_{\alpha\text{-Zr}}$ and $\langle 10\bar{1}2 \rangle_{\text{h-ZrO}}$ pole figures, it can also be seen that one of the $\langle 10\bar{1}2 \rangle_{\text{h-ZrO}}$ directions is parallel to one of the $\langle \bar{2}110 \rangle_{\alpha\text{-Zr}}$ directions. With this specific orientation relationship, a match between the $(01\bar{1}0)_{\alpha\text{-Zr}} \parallel (12\bar{1}0)_{\text{h-ZrO}}$ poles can be expected, and again this can be seen in the $(01\bar{1}0)_{\alpha\text{-Zr}}$ and $(12\bar{1}0)_{\text{h-ZrO}}$ pole figures, Figure 7.8(a, c and d). The only exception is the orientation relationship in region 12 in the Zr-0.5Nb sample, where from the $(0002)_{\alpha\text{-Zr}}$ and $(22\bar{4}\bar{1})_{\text{h-ZrO}}$ pole figures in Figure 7.8(b) it can be seen that one of the $(22\bar{4}\bar{1})_{\text{h-ZrO}}$ planes is nearly parallel to the basal plane of the $\alpha\text{-Zr}$, one of the $\langle \bar{2}110 \rangle_{\alpha\text{-Zr}}$ directions is parallel to one of the $\langle 1\bar{1}01 \rangle_{\text{h-ZrO}}$ directions, and there is a match between the $(01\bar{1}0)_{\alpha\text{-Zr}}$ and $(\bar{1}2\bar{1}2)_{\text{h-ZrO}}$ poles.

With the observation of only these two orientation relationships, it is reasonable to infer that a strong texture is developed in the suboxide layer. TKD texture component maps for $(10\bar{4})_{\text{m-ZrO}_2}$, $(\bar{1}011)_{\text{h-ZrO}}$, and $(0002)_{\alpha\text{-Zr}}$ are plotted in Figure 7.4(c) and 7.6(d), and the grains coloured according to their angular deviation from the radial direction. These maps together with the statistical distributions in Figure 7.4(d) and 7.6(e), reveal two preferred orientation relationships, $(0002)_{\alpha\text{-Zr}} \parallel (\bar{1}011)_{\text{h-ZrO}}$ and $[\bar{2}110]_{\alpha\text{-Zr}} \parallel [10\bar{1}2]_{\text{h-ZrO}}$ or $(0002)_{\alpha\text{-Zr}} \parallel (22\bar{4}\bar{1})_{\text{h-ZrO}}$ and $[\bar{2}110]_{\alpha\text{-Zr}} \parallel [1\bar{1}01]_{\text{h-ZrO}}$.

7.4. Discussion

7.4.1. Formation mechanisms of h-ZrO suboxide

These results confirm that the structure of the h-ZrO phase formed in all the three materials matches the hexagonal structure with a sub-lattice of Zr atom positions similar to those in ω -Zr, in agreement with both earlier experimental observations [81, 301] and atomistic predictions [67, 68]. Extensive research has been undertaken to identify the mechanisms controlling the α to ω phase transformation in the transition metals Ti and Zr [304, 306-314]. I propose that understanding this transformation may also shed light on the formation mechanisms of h-ZrO during aqueous corrosion. Two orientation relationships between h-ZrO grains and the α -Zr substrate grains have been identified. The most common relationship, $(0002)_{\alpha\text{-Zr}} \parallel (\bar{1}011)_{\text{h-ZrO}}$ and $[\bar{2}110]_{\alpha\text{-Zr}} \parallel [10\bar{1}2]_{\text{h-ZrO}}$, is very close to that reported between α -Zr and ω -Zr [304, 306, 313, 314], or h-ZrO grown on thin α -Zr films during annealing at 700°C in the TEM [218]. Out of the 61 suboxide grains analyzed above, only one grain showed the $(0002)_{\alpha\text{-Zr}} \parallel (22\bar{4}\bar{1})_{\text{h-ZrO}}$ and $[\bar{2}110]_{\alpha\text{-Zr}} \parallel [1\bar{1}01]_{\text{h-ZrO}}$ relationship. A larger angular deviation in both crystal planes and directions can be seen between this relationship and that reported in the literature, $(0002)_{\alpha\text{-Zr}} \parallel (11\bar{2}0)_{\text{h-ZrO}}$ and $[11\bar{2}0]_{\alpha\text{-Zr}} \parallel [0002]_{\text{h-ZrO}}$ [218, 310]. Direct comparisons of orientations associated with the relationship reported in this study and that in the literature can be explored by the distribution of corresponding poles, Figure 7.9. A misorientation angle of $\sim 17^\circ$ can be seen for both planes and directions from the relationship proposed in the literature, Figure 7.9(a).

The selection of specific orientation relationships may be explained by the ab initio calculations by Trinkle et al. [310] that showed that the energy barrier for the α to ω transformation with the relationship $(0002)_{\alpha\text{-Ti}} \parallel (11\bar{2}0)_{\omega\text{-Ti}}$ is much higher than that for $(0002)_{\alpha\text{-Ti}} \parallel (\bar{1}011)_{\omega\text{-Ti}}$, and requires significantly more atomic shuffles [310, 314]. There is

also a relatively large mismatch between the second relationship identified in the current study and $(0002)_{\alpha\text{-Zr}/\alpha\text{-Ti}} \parallel (11\bar{2}0)_{\omega\text{-Zr}/\omega\text{-Ti}}$ reported in the literature [218, 306, 314], probably a result of higher level of accumulated stress required to trigger this less favourable transformation at the metal/oxide interface. In region 12 in Figure 7.4(b) the two tetragonal ZrO_2 grains highlighted by white arrows are only expected to be stabilised when the local stress levels are high [22, 297], and are observed immediately above the single suboxide grain with the $(0002)_{\alpha\text{-Zr}} \parallel (22\bar{4}\bar{1})_{\text{h-ZrO}}$ relationship. This may suggest that the formation of tetragonal ZrO_2 grains during aqueous corrosion depends on local strain/stress conditions which may be established by the orientation relationships between the underlying suboxide and the substrate.

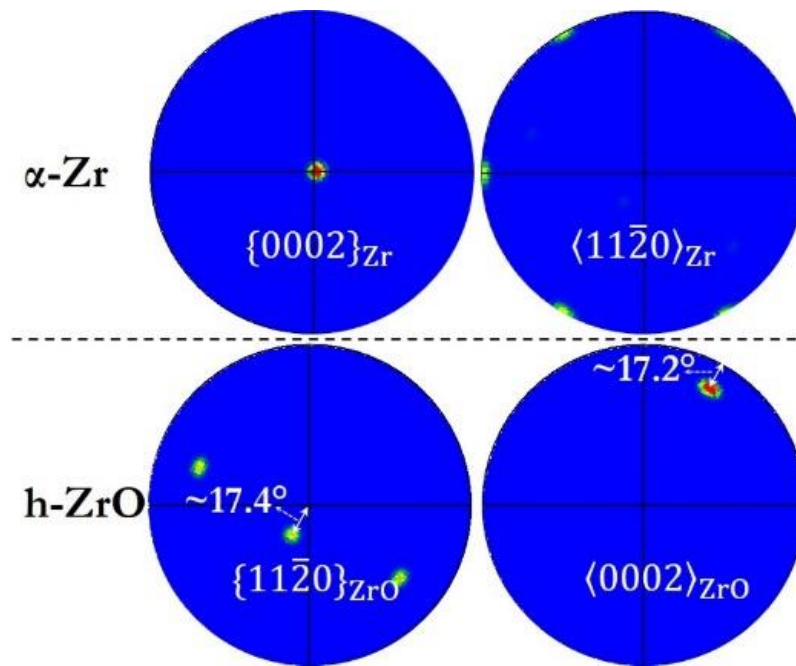


Figure 7.9 Contoured distributions of poles (half width 5°) comparing the position of $\{0002\}_{\text{Zr}}$, $\langle 11\bar{2}0 \rangle_{\text{h-ZrO}}$ and $\{11\bar{2}0\}_{\text{h-ZrO}}$, $\langle 0002 \rangle_{\text{h-ZrO}}$ from region 12 in the Zr-0.5Nb sample. The literature [27, 35] proposed that these poles are perfectly aligned.

The displacive transformation from $\alpha\text{-Zr}$ (or Ti) to $\omega\text{-Zr}$ (or Ti) under hydrostatic pressure has been shown to be controlled by time, pressure and impurities [308-310, 312, 315], so is not a simple diffusionless martensitic transformation. This behaviour is similar to

paraequilibrium transformations in which the larger atoms in the substitutional sites move in a military manner (without diffusion) whereas the interstitial atoms diffuse more easily and can partition between the phases [313, 316, 317]. This kind of transformation has been widely reported in the formation of Widmanstattern ferrite in steels, a displacive mechanism whose transformation rate is mainly controlled by the diffusion of carbon [316, 317]. Recalling the special Widmanstattern-type grain morphology of the h-ZrO suboxide formed during aqueous corrosion, I infer that the phase transformation mechanisms from α -Zr to ω -Zr and α -Zr to h-ZrO may share some common features, with oxygen diffusion playing a similar role to carbon in the paraequilibrium transformation, and controlling the formation of h-ZrO. The direct transformation from α to ω in both Ti and Zr requires pressures in the range 2-6 GPa [305, 308, 313, 318], although this can be significantly modified by the corrosion temperature [312, 313], residual stress levels and local strains [20, 22, 301] or alloying elements and impurities [307, 311, 313]. Accumulated stresses at the metal/oxide interface have been reported from both experimental measurements [22] and simulations [20], and corrosion temperatures around 300°C may decrease the pressure required to trigger the transformation.

7.4.2. The impact of α -Zr orientation on suboxide nucleation

The suboxide formed during aqueous corrosion generally has a acicular morphology, but not always as shown in Figure 7.6. The different morphologies of the suboxide could be a result of different underlying α -Zr orientations, as shown in Figure 7.10. When the underlying α -Zr grain is oriented with $\langle 0002 \rangle_{\alpha\text{-Zr}}$ parallel to the O/M interface, the suboxide formed tends to be more equiaxed and the O/M interface to be smoother, as shown on the left side of Figure 7.10. In contrast, when the underlying α -Zr grain is orientated with

$(0002)_{\alpha\text{-Zr}}$ parallel to the O/M interface, the suboxide generally shows an acicular shape as shown on the right of Figure 7.10.

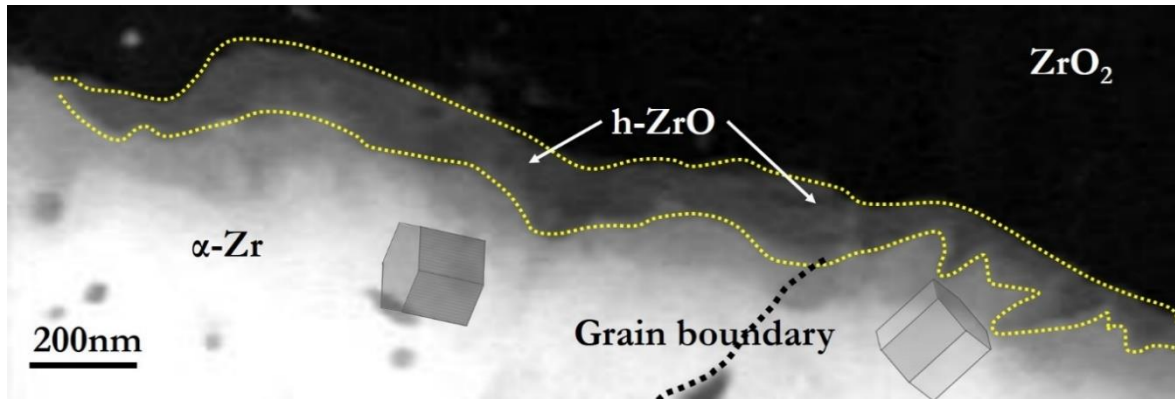


Figure 7.10 MLLS Fitted EELS spectra map showing the positions of oxide, suboxide and metal substrate on the Zr-1Nb alloy sample.

In order to explain this change in the suboxide grain morphology I have analysed the orientation of coherent or semicoherent facets at the $\alpha\text{-Zr/h-ZrO}$ interface that could provide a barrier to growth. Preferential movement of incoherent interfaces with higher mobilities than faceted coherent interfaces will lead to the formation of the sawtooth-like morphology observed. In Figure 7.11, I show the reconstructed atomic arrangements at the $\alpha\text{-Zr/h-ZrO}$ interface based on the orientation information extracted from one of the sawtooth-like suboxide grains from the Zircaloy-4 TKD map. The corrosion direction is close to $\langle 0002 \rangle_{\alpha\text{-Zr}}$, and the suboxide growth direction is close to $\langle 10\bar{1}4 \rangle_{\alpha\text{-Zr}}$. The residual facets will be the slow moving interfaces, and are nearly semicoherent, especially on the right-hand side. The atomic planes matching at bottom of the h-ZrO needle are close to $(0002)_{\alpha\text{-Zr}} \parallel (\bar{1}011)_{\text{h-ZrO}}$, which is an incoherent interface, and agrees with those Trinkle proposed for α/ω interfaces [310]. The $[\bar{2}110]_{\alpha\text{-Zr}}$ direction is parallel to $[10\bar{1}2]_{\text{h-ZrO}}$, Figure 7.11(b), and $\sim 15.6^\circ$ away from $[10\bar{1}1]_{\text{h-ZrO}}$ as proposed by Trinkle.

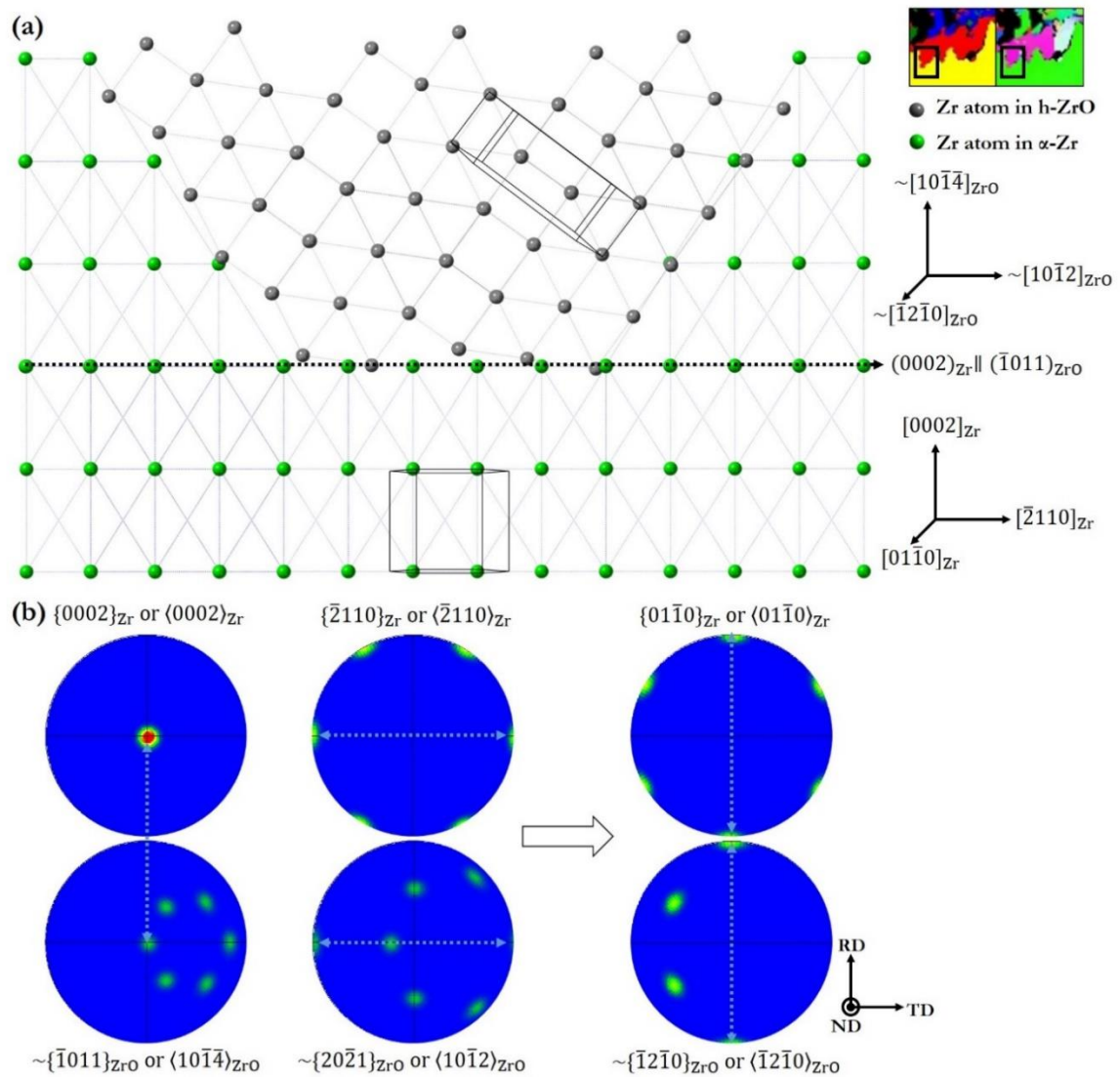


Figure 7.11 (a) Reconstructed atomic arrangements (single stacking plane shown) of the h-ZrO/α-Zr interface for the Zircaloy-4 sample based on TKD phase and IPF maps. (b) pole figures of the h-ZrO suboxide and α-Zr from the region of interest. To reveal the interface atomic arrangement more clearly, I have manually adjusted the Euler angles for both phases (from $\phi_1=11.4^\circ$, $\psi=100.5^\circ$, $\phi_2=30.7^\circ$ to $\phi_1=1.3^\circ$, $\psi=90.7^\circ$, $\phi_2=28.7^\circ$) so that the α-Zr grain can be orientated with (0002) in the centre of the stereographic projection.

When the underlying α-Zr grain is orientated with [0002] parallel to the O/M interface, the suboxide shows a less faceted morphology, Figure 7.6 and 7.10. This phenomenon can also be linked to the specific interface coherency, Figure 7.12, by reconstructing atomic arrangements at the h-ZrO suboxide/α-Zr interface in the Zr-1Nb sample. Here the h-ZrO suboxide and α-Zr grains are also orientated with $(0002)_{\alpha\text{-Zr}} \parallel (0\bar{1}1\bar{1})_{\text{h-ZrO}}$ and $[11\bar{2}0]_{\alpha\text{-Zr}} \parallel [01\bar{1}\bar{2}]_{\text{h-ZrO}}$, but the interface is close to the semicoherent $(1\bar{1}00)_{\alpha\text{-Zr}} \parallel (2\bar{1}\bar{1}0)_{\text{h-ZrO}}$.

facet. The thickening of the suboxide may thus occur primarily by a ledge growth mechanism [317, 319], leading to the plate-shaped suboxide morphology seen in Figure 7.10.

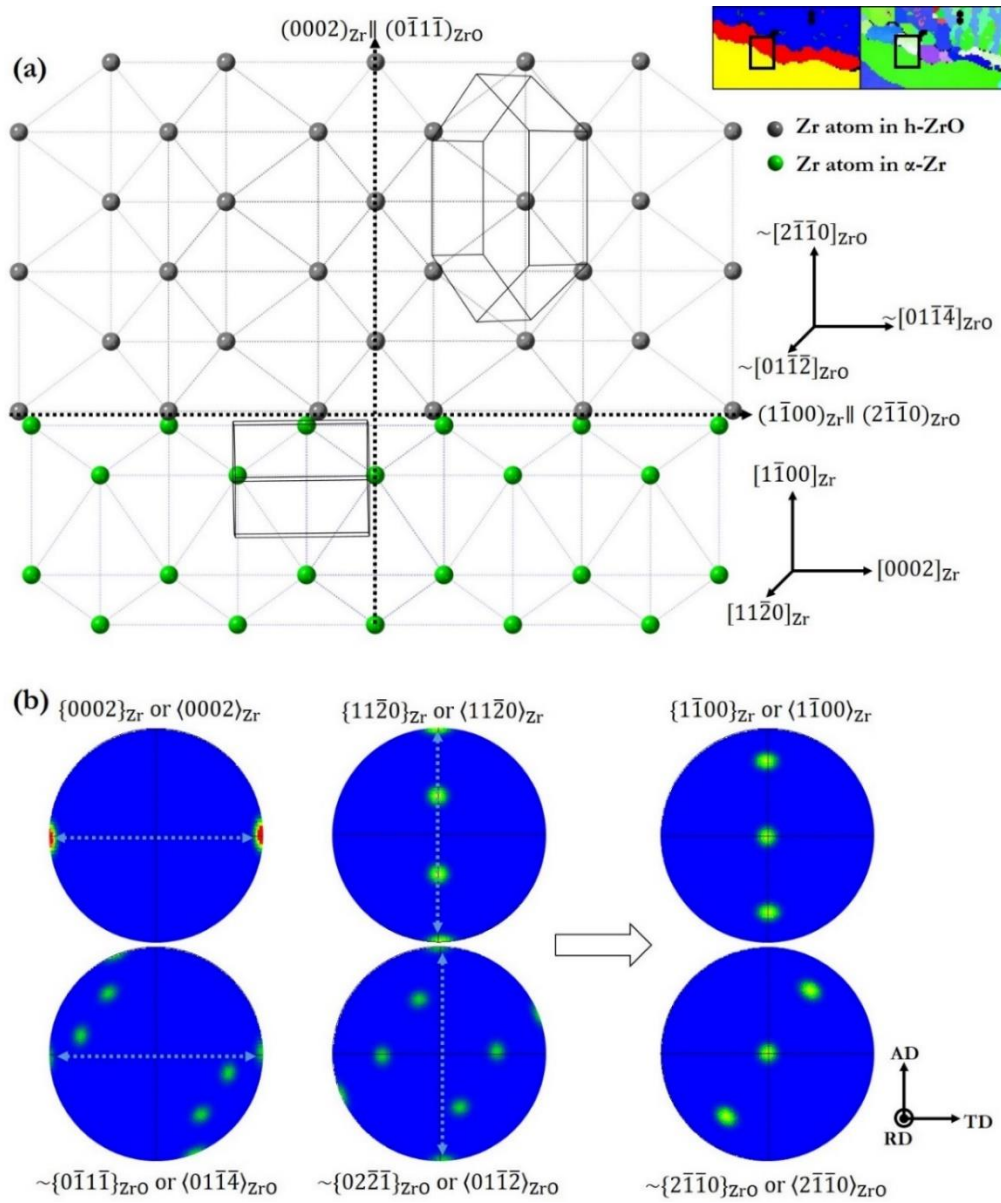


Figure 7.12 (a) Reconstructed atomic arrangements(single stacking plane shown) of the h-ZrO suboxide and α -Zr based on the TKD phase and IPF maps for the Zr-1Nb sample. (b) pole figures of the h-ZrO suboxide and α -Zr from the region of interest. To reveal the interface atomic arrangement more clearly, I have manually changed the Euler angles (from $\phi_1=77.8^\circ$, $\psi=104.1^\circ$, $\phi_2=3^\circ$ to $\phi_1=89.2^\circ$, $\psi=-89.6^\circ$, $\phi_2=59^\circ$) so that the underlying α -Zr grain can be orientated with $[0002]$ at the centre of the stereographic projection.

7.4.3. The effects of alloying elements on suboxide growth

The pressure required to induce the α - ω phase transition in Zr and Ti alloys has been observed to change with different types and concentrations of alloying elements or impurities [307, 311]. If the necessary space within the lattice to accommodate the lattice shear is occupied by interstitials, oxygen for example, the stress required for shear deformation is likely to increase [307]. For instance, 1.1 at.% oxygen can increase the barrier energy for the α to ω transformation in Ti by 10 meV/atom, but 3.8 at.% V can decrease the barrier energy by 3 meV/atom [311] (with the model assuming zero pressure and 0 K, the energy barrier from α -Ti to ω -Ti is 9 meV/atom [310]). Hennig et al. [311] reported that the addition of transition metals with more d electrons such as V and Fe can decrease the energy barrier for the α - ω transformation, whereas early transition metals and simple metals such as Al and non-metallic elements such as C, N and O favour α , increase the energy barrier and suppress the α - ω transformation. In commercial nuclear Zr alloys, Sn and/or Nb are the major alloying elements, with small amounts of Cr, Ni, Fe and H. According to the discussion above, we might expect these transition metal alloying elements to decrease the barrier energy for the transition from α -Zr to h-ZrO, and favour the formation of suboxide. Phase-field simulations have shown that anisotropy in the interfacial energy plays an important role in determining the morphology and formation rate of Widmanstätten ferrite in Fe-C alloys [320, 321] and the ω phase in Zr alloys [308]. Not surprisingly, the higher the anisotropy of the interfacial energy, the more acicular the product phase will be. This anisotropy of the interfacial energy can also be influenced by the presence of different types of alloying elements and impurities [322]. Here I have observed that the h-ZrO suboxide formed in Zircaloy-4 alloys with Sn as the main alloying element and small amounts of Fe and Cr tends to be more acicular than h-ZrO in alloys which have Nb as the main alloying element, Figure 7.13. The underlying α -Zr grains in these two maps have a similar

orientations, and so it is reasonable to infer that different morphology of suboxide may at least in part be explained by the different major alloying element in these two materials. Both Sn and Nb are energetically more stable on substitutional sites of the hexagonal close-packed lattice of α -Zr than at interstitial sites [323, 324], but Sn has a much higher solubility in α -Zr at 288°C (~4 at.%) than Nb (~0.3at.%) [324]. As a result, the concentration of Sn occupying substitutional sites will be higher in Zircaloy-4 (and other Sn-containing alloys) than in binary Zr-Nb alloys, and that this may be the dominant factor in controlling the anisotropy of the h-ZrO suboxide/ α -Zr interfacial energy, and hence the morphology of the corroding interface.

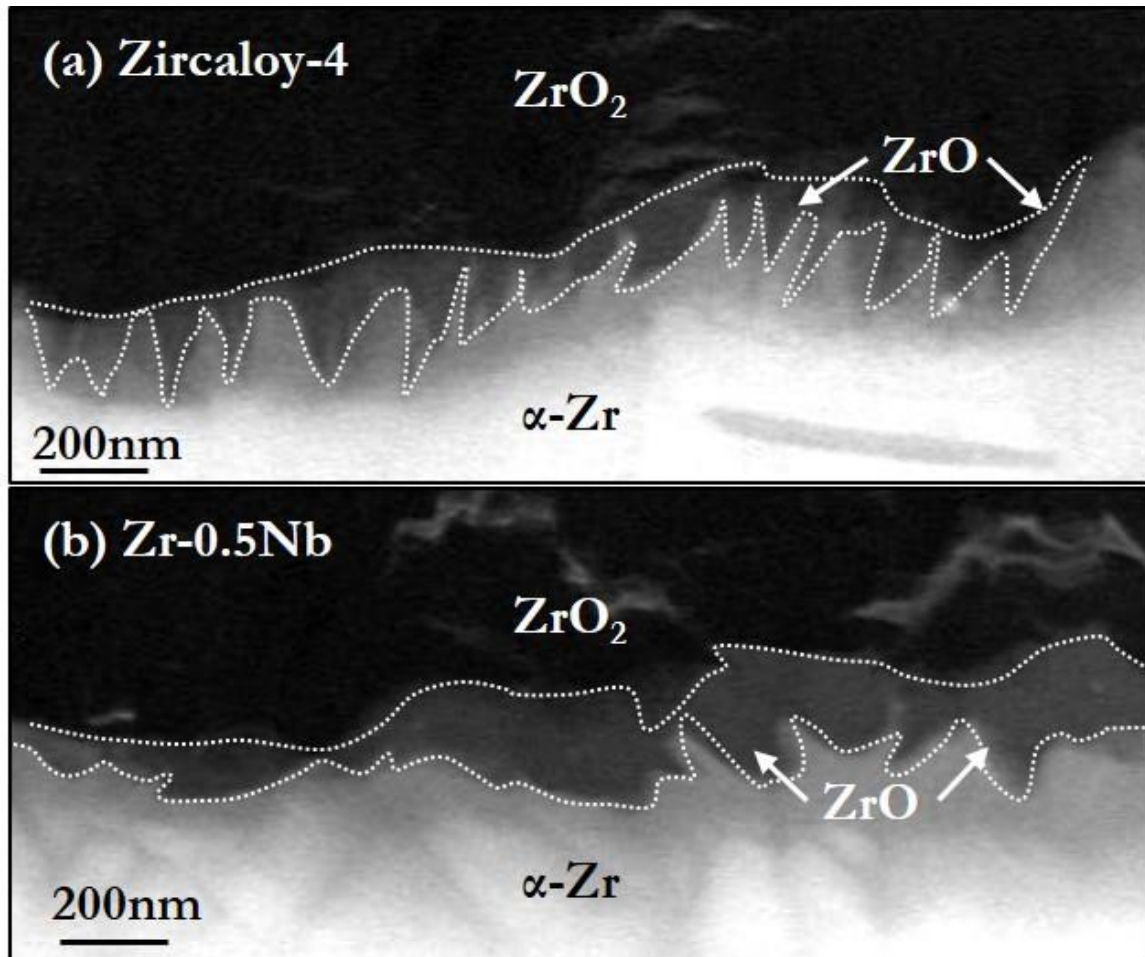


Figure 7.13 MLLS Fitted EELS spectra maps showing the shape of suboxide grains in different alloys, (a) recrystallized Zircaloy-4 sheet (106-day corrosion, oxide thickness ~2.6 μ m), (b) recrystallized Zr-0.5Nb tube (105-day corrosion, oxide thickness ~2.5 μ m).

7.5. Conclusions

The present study has made extensive use of nano-scale orientation mapping by transmission Kikuchi diffraction to study reaction mechanisms at the oxide/metal interface. A thin layer of h-ZrO suboxide is observed in all the specimens characterized, although these are not always continuous, suggesting the aqueous corrosion of zirconium usually follows the pathway: $\text{Zr} \rightarrow \text{h-ZrO} \rightarrow \text{ZrO}_2$. The following conclusions can be drawn;

1. The formation of h-ZrO suboxide during aqueous corrosion has been discussed as a paraequilibrium displacive transformation, and two preferred orientation relationships between h-ZrO and α -Zr have been identified, $(0002)_{\alpha\text{-Zr}} \parallel (\bar{1}011)_{\text{h-ZrO}}$ and $[\bar{2}110]_{\alpha\text{-Zr}} \parallel [10\bar{1}2]_{\text{h-ZrO}}$ or $(0002)_{\alpha\text{-Zr}} \parallel (22\bar{4}\bar{1})_{\text{h-ZrO}}$ and $[\bar{2}110]_{\alpha\text{-Zr}} \parallel [1\bar{1}01]_{\text{h-ZrO}}$, where the first one is more commonly observed.
2. A fibre texture with the $(10\bar{4})_{\text{m-ZrO}_2}$ parallel to the metal/oxide interface is observed in the m-ZrO₂ phase in all these three materials studied, regardless of the underlying α -Zr orientations, and no specific orientation relationship between h-ZrO and m-ZrO₂ or α -Zr and m-ZrO₂ was identified. This suggests that the formation of the oxide texture during aqueous corrosion is not determined by the substrate texture. Our results are consistent with the explanation that the preferred oxide texture is related to the minimization of stress generated at the oxide/metal interface [88].
3. The suboxide morphology can be equiaxed, plate-like or sawtooth-like depending on the underlying α -Zr grain orientation. Alloying elements and impurities may also change the anisotropy of the interfacial energy, and further affect the suboxide grain morphologies. Equiaxed or plate-like grains may lead to more uniform stress distributions and a smoother metal/suboxide interface compared with the sawtooth-like h-ZrO grains often found in Sn-containing alloys. This may be a

contributing factor to the widely reported improved corrosion performance of the Sn-free binary Zr-Nb alloys under in-reactor conditions.

4. The detailed role of the h-ZrO suboxide in aqueous corrosion of Zr alloys is not clear, partly because some of the key properties of this phase have not been determined; the transport properties of either O or H through h-ZrO, or the reaction rates of $\text{Zr} \rightarrow \text{h-ZrO}$ and $\text{h-ZrO} \rightarrow \text{ZrO}_2$ at different oxygen partial pressures. However, I suggest that the presence of the suboxide layer of different morphologies, plate or sawtooth-like, can affect the overall corrosion performance of Zr alloys by influencing the roughness and local stress state at the oxide/metal interface, and so it is important to improve our understanding of the conditions under which h-ZrO is formed in service.

Chapter 8 The Role of Oxide Nano-Porosity in Hydrogen Transport

8.1. Introduction

Understanding the fundamental mechanisms of hydrogen pick-up is important to improve the stability of structural components in-service in nuclear reactors. This chapter describes TEM characterisation of nano-porosity in zirconium oxide films on different alloys using Fresnel imaging. Combining experimental observations and ab initio simulations leads to the proposal of the role of nano-porosity in hydrogen transportation.

The ab initio modelling work was carried out by Dr. Mikael Christensen, Dr. Walter Wolf and Dr. Erich Wimmer, Materials Design, USA.

8.2. Materials and Experimental Methods

Three materials were used in the experimental part of this work; Westinghouse RXA Zr-0.5Nb, commercial Zircaloy-4 and CNL SRA Zr-2.5Nb alloys. Detailed sample information and corrosion data have been described in section 4.3. The choice of these samples was to explore whether the distribution of nanoscale porosity was the same in oxides grown on different Zr alloys and at different stages of the oxidation process. The Zircaloy-4 sample was at a relatively early stage of aqueous corrosion, before the first kinetic transition. Two Zr-0.5Nb and three Zr-2.5Nb samples corroded for 75, 165, 150, 700 and 2000 days respectively were characterized to compare the evolution of distribution and morphologies of cracks with corrosion time. Cross-sectional transmission electron microscopy foils containing both the oxide layer and the metal matrix were prepared using the FIB lift-out method described in section 5.2. NanoSIMS specimens were prepared following the procedures defined in section 5.3.

8.3. Results

8.3.1. Characterisation of oxide cracks

Stress cracks were seen in all the oxides studied here, and show significantly different morphologies and distributions on different alloys, Figure 8.1, 8.2 and 8.3. The oxide layer thickness varies from 1.7 μm to 2.3 μm in the region of observation on the 61-day Zircaloy-4 sample, Figure 8.1(a). Even at a relatively early stage of aqueous corrosion, before the first kinetic transition, many lateral stress cracks 0.5-1 μm in length and 50-200 nm in width can be seen through the oxide depth, Figure 8.1(a). High-magnification Fresnel images revealing the distributions and morphologies of cracks/porosity in the outer oxide layer on the Zircaloy-4 sample are shown in Figure 8.2. The existing high density of interconnected micro-cracks and nano-porosity, Figure 8.2(a), and vertical cracks, Figure 8.2 (b), in the outer oxide layer enable the direct ingress of coolant water resulting in the loss of corrosion protection of the outer oxide layer. By comparison, both the oxide thickness and the oxide/metal interface are relatively uniform on the Zr-0.5Nb sample even after a much longer corrosion time, Figure 8.1(b and c). The distributions and morphologies of oxide cracks on the Zr-0.5Nb samples also differ significantly from those on the Zircaloy-4 sample, even though the as-received alloy grain microstructures and texture and corrosion conditions of these two alloys are similar. On the 75-day Zr-0.5Nb sample, only a few small stress cracks (length < 300 nm, width < 50 nm) can be seen. On the 165-day sample, a layer of lateral cracks can be seen above the oxide/metal interface, but their size is much smaller than those on the 61-day Zircaloy-4 sample. In addition, the occurrence of these lateral cracks on Zr-0.5Nb samples does not seem to lead to significant changes in corrosion rate, Figure 4.5.

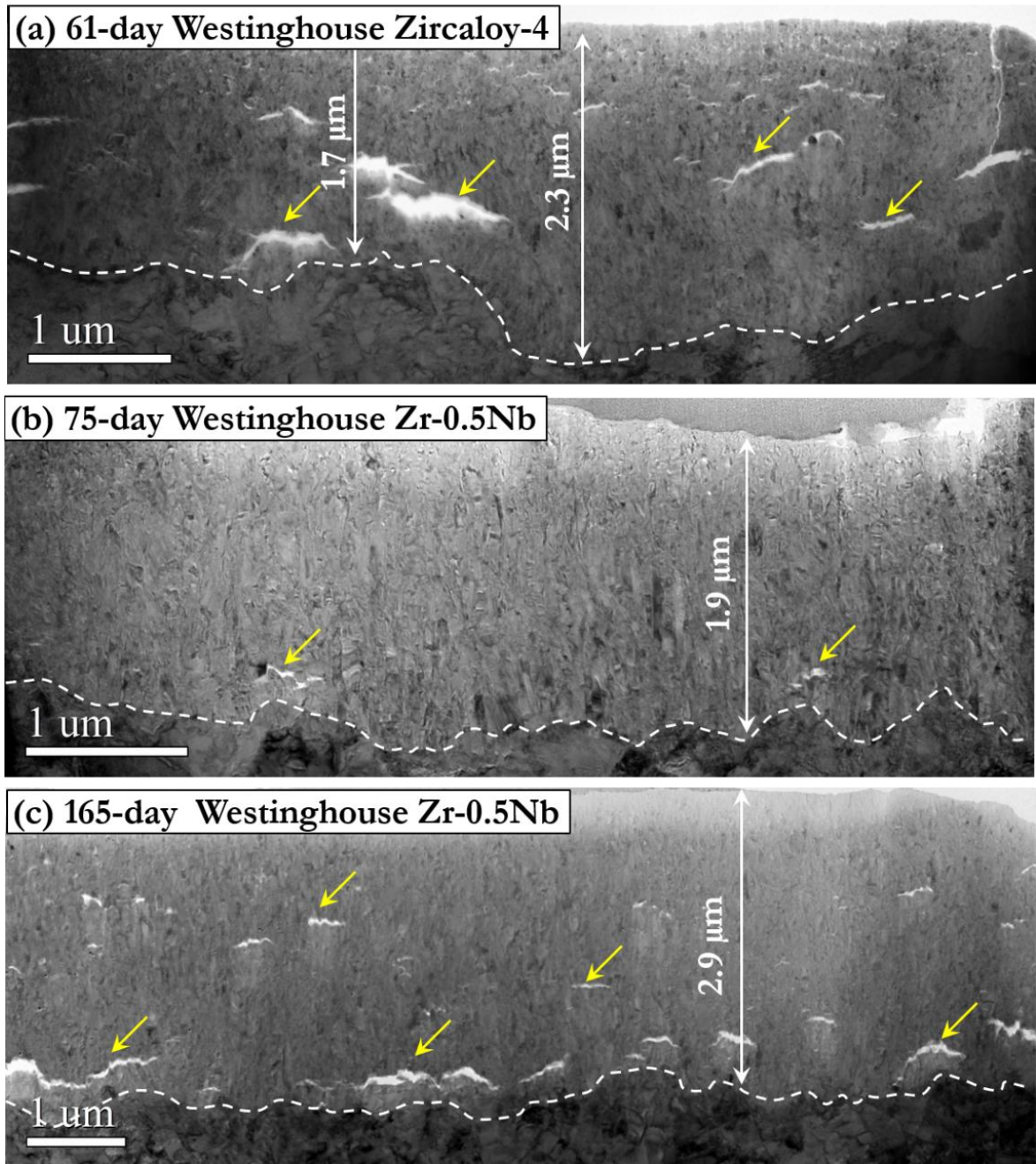


Figure 8.1 Morphologies and distributions of oxide cracks on (a) 61-day Zircaloy-4, (b) 75-day Zr-0.5Nb and (c) 165-day Zr-0.5Nb samples. The oxide/metal interfaces are indicated by dashed lines, and examples of cracks by yellow arrows.

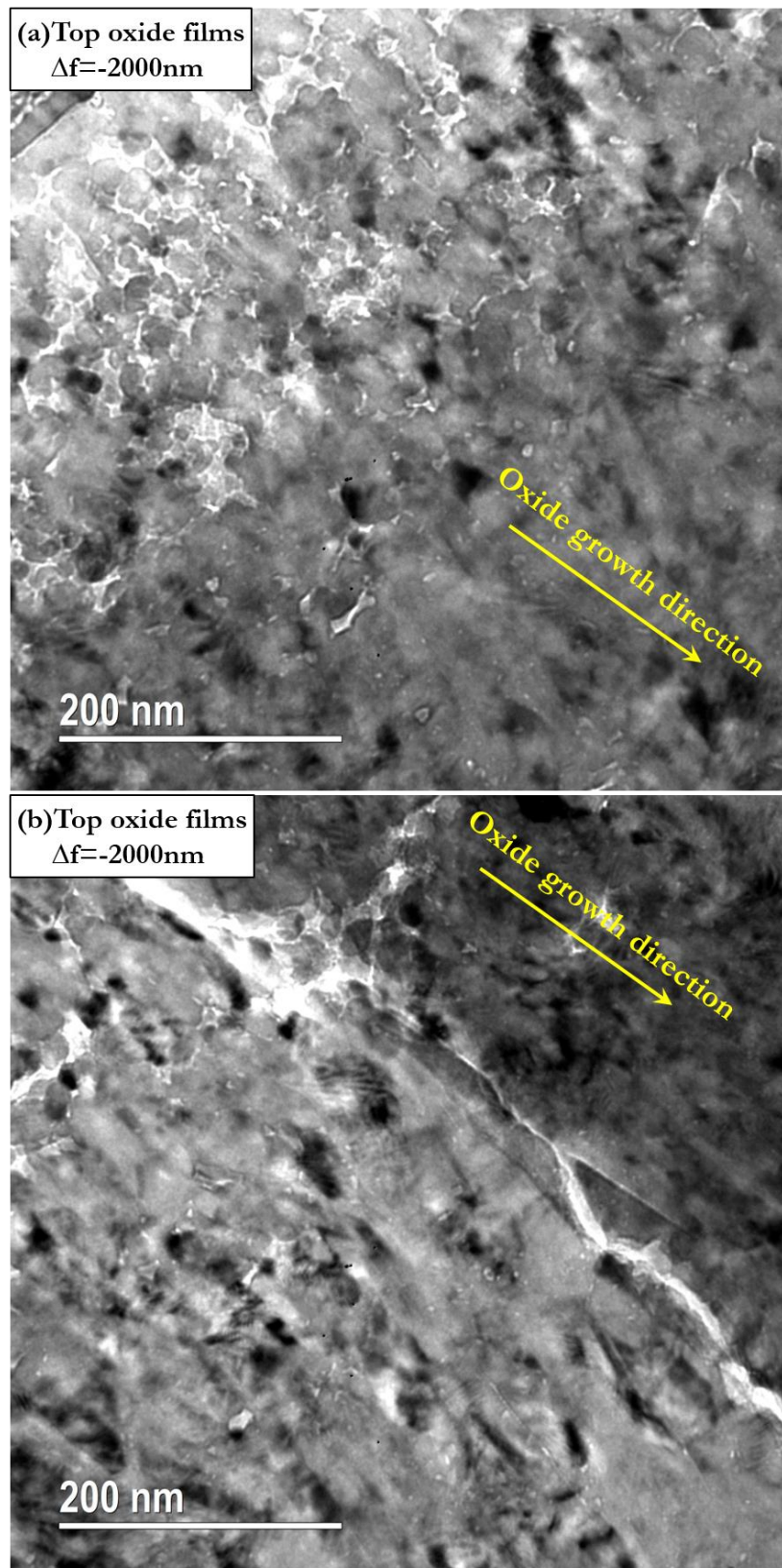


Figure 8.2 Morphologies and distributions of micro-cracks and nano-porosity in the outer oxide layer on the 61-day Zircaloy-4 sample

Compared with the commercial Zircaloy-4 and Westinghouse RXA Zr-0.5Nb alloys, the CNL SRA Zr-2.5Nb alloy shows a relatively better resistance to corrosion and hydrogen pick-up, Figure 4.5. This could be a result of different corrosion conditions used, but also can be due to the different microstructures (e.g. grain size, texture, distributions of second phases) in the as-received alloys. As a result, or possibly the cause of slow corrosion rates, CNL Zr-2.5Nb alloys also show a significantly different oxide morphology compared with that on the Zircaloy-4 and Zr-0.5Nb alloys.

Figure 8.3 shows the oxide morphology and distributions of cracks on Zr-2.5Nb samples corroded for 150, 700 and 2000 days respectively. The oxide thickness and oxide/metal interface is quite uniform even after a corrosion time of 2000 days. The oxide thickness is $\sim 1.6 \mu\text{m}$, $3.1 \mu\text{m}$ and $7.3 \mu\text{m}$ on the 150-day, 700-day and 2000-day samples respectively, indicating its corrosion rate is much slower than Zircaloy-4 and Zr-0.5Nb alloys. More importantly, the oxide cracks on these CNL Zr-2.5Nb samples are found to be much smaller in size than those on Zircaloy-4 and Zr-0.5Nb samples, Figure 8.1 and 8.3. A layer consisting of small lateral cracks can be seen $\sim 3 \mu\text{m}$ away from the oxide/metal interface on the 2000-day sample, where the first kinetic transition is supposed to occur. This kind of layer of lateral cracks has also been observed in other Zr alloys at the corrosion kinetic transition, e.g. ZIRLO and Zircaloy-4 [15, 59, 301], and its formation is linked to the large compressive stresses generated in the oxide by the volume expansion on oxidation.

Ni et. al. [15] have proposed that these lateral cracks are not generated as a result of transition, but that a process by which these cracks become connected through interconnected nanoporosity may be critical in controlling the overall rate of corrosion and kinetic transition. I thus compared the different morphologies and distributions of nano-porosity on these alloys.

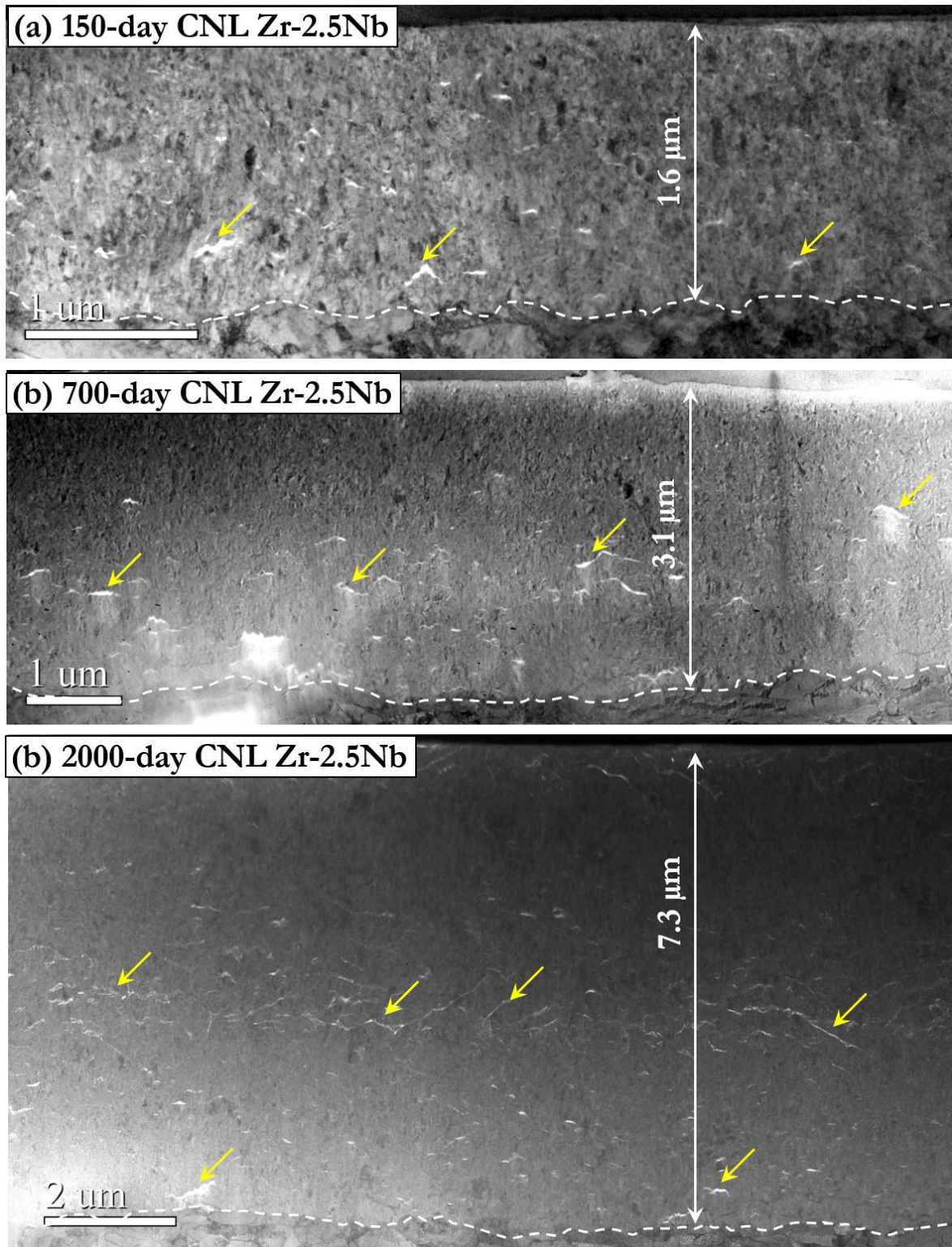


Figure 8.3 Morphologies and distributions of oxide cracks on (a) 150-day, (b) 700-day and (c) 2000-day CNL Zr-2.5Nb samples. The oxide/metal interfaces are indicated by dashed lines, and examples of cracks by yellow arrows.

8.3.2. Characterisation of oxide nano-porosity

A set of high-resolution Fresnel contrast TEM images showing the morphology and distribution of nano-pores and nano-pipes are shown in Figure 8.4 as function of depth through typical oxide layers grown on the Zr-0.5Nb and Zircaloy-4 samples. It is worth mentioning here that for each sample at least two TEM specimens were prepared, which generated thousands of TEM images, but only a small number of images have been selected to represent the typical observations for the studied samples.

Close to the metal-oxide interface, where I expect the oxide to be electrochemically protective (the so-called barrier layer [325-327], several different kinds of nanoscale porosity can be seen. At ~200 nm from the interface on the 75-day Zr-0.5Nb sample, Figure 8.4(a), some of the grain boundaries between the columnar oxide grains are decorated with a ‘string-of-pearls’ arrangement of interconnected porosity that Ni et. al. [15] have termed nano-pipes, Figure 8.4(a-3). The individual pores become gradually less well connected closer to the metal-oxide interface, Figure 8.4(a-2 and a-3), so that < 200 nm from the interface mostly isolated 1-3 nm pores are observed within the oxide grains, Figure 8.4(a-2). Individual pores are also observed in the ZrO suboxide layer, Figure 8.4(a-1). This kind of complex, partly interconnected porosity has been suggested to play an important role in the rate-determining oxygen transport processes during corrosion [24, 328]. In the present context, nano-porosity near the oxide-metal interface could provide pathways for the diffusion of molecular hydrogen, as will be discussed below.

Further from the metal-oxide interface, more continuous interconnected nano-pores/nano-pipes are observed along many of the grain boundaries, and some of these have evolved into larger micro-cracks, Figure 8.4(a-4). This confirms that in these samples the outer layers of oxide are short circuited in the overall electrochemical corrosion cell, so that the only

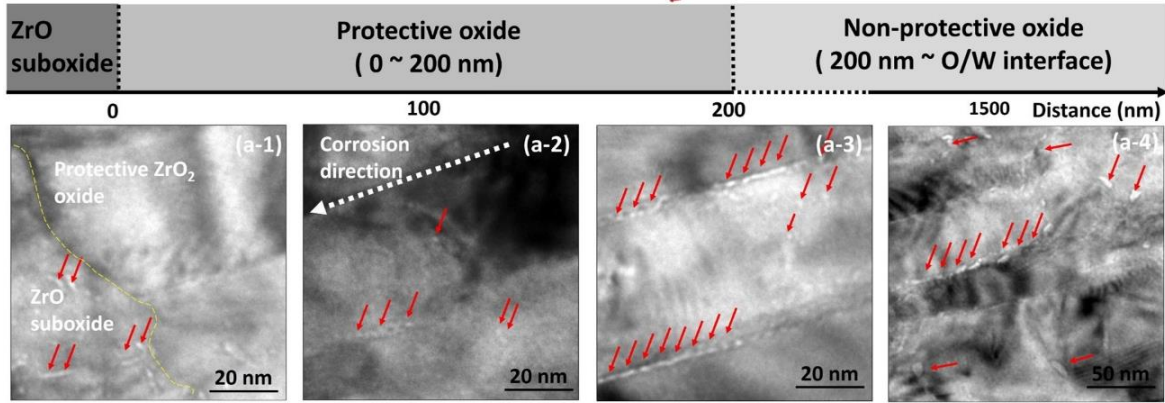
protective barrier layer will be the thin oxide layer between the nearest interconnected nano-pipes and the underlying metal.

Figure 8.4(b and c) show the results of the same through-depth porosity analysis for 165-day Zr-0.5Nb and 61-day Zircaloy-4 samples. In some regions near the oxide/metal interface, the 165-day Zr-0.5Nb sample shows similar oxide nano-structures, although some regions show more interconnected nano-pipes, Figure 8.4(b-1 and b-2). If we define the barrier layer as the region where only isolated pores can be identified, both of these two Zr-0.5Nb samples have a similar barrier thickness of ~ 200 nm, Figure 8.4(a and b). Above that layer, a porous structure with continuous interconnected nano-pores/pipes is observed, Figure 8.4(a-4 and b-4). The Zr-Nb alloys have better resistance to corrosion and hydrogen pickup than Zircaloy-4, Figure 4.5. The results in Figure 8.4(c) show that the apparent barrier layer in the oxide on Zircaloy-4 (the region free of interconnected porosity) is only ~ 100 nm thick, Figure 8.4(c-1 and c-2), and more continuous nano-pipes and nano-cracks can be found throughout the porous oxide, Figure 8.4(c-3 and c-4). This may be a result of the higher volume fraction of equiaxed grains seen in oxides on the Zircaloy-4 sample [34,46], and suggests an easy transport path for hydrogenic species that can explain the higher measured hydrogen contents for this material, Figure 4.5.

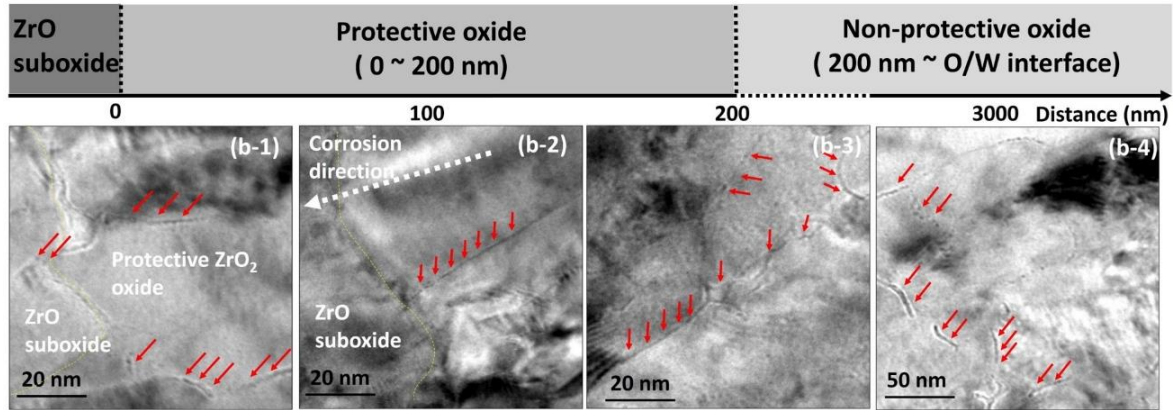
Later in this project, I found a method to stitch together a series of high-magnification Fresnel contrast TEM images and show the distributions of nano-porosity through the whole oxide thickness using the script developed by Preibisch et al [329]. An example of stitched Fresnel contrast ($\Delta f = -2000$ nm) TEM images revealing the distribution and morphologies of nano-porosity in the outer and inner oxide layer on the 700-day CNL Zr-2.5 sample is shown in Figure 8.5 and 8.6. In comparison with morphology of nano-porosity observed on the Zircaloy-4 and Zr-0.5Nb sample, Figure 8.4, fewer interconnected nano-pipes were seen on

the 700-day CNL Zr-2.5Nb sample. This compact oxide structure formed on Zr-2.5Nb alloys may thus explain its good resistance to hydrogen pick-up, Figure 4.5.

(a) Zr-0.5Nb, 75days, $\Delta f = -1000$ nm



(b) Zr-0.5Nb, 165days, $\Delta f = +1000$



(c) Zircaloy-4, 61days, $\Delta f = -1000$ nm

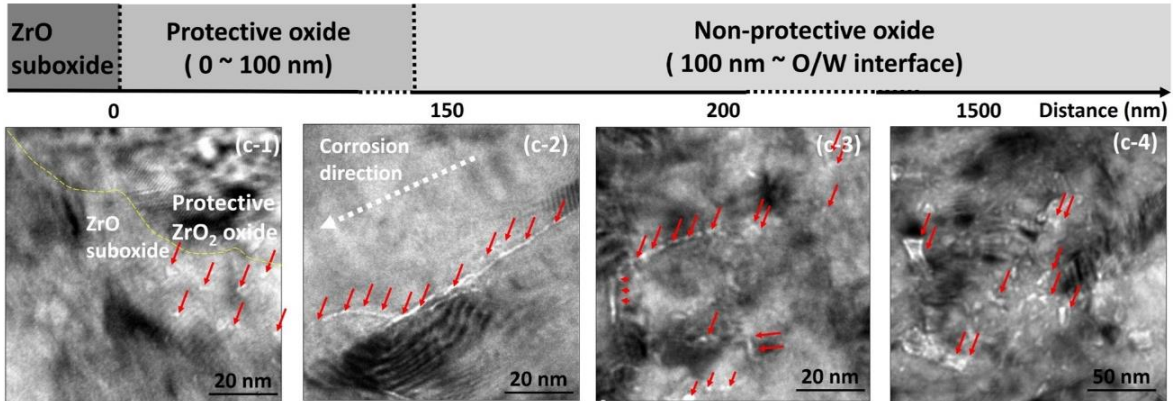


Figure 8.4 TEM Fresnel imaging showing the distributions of nano-porosity as function of depth in the oxide on three Zr alloys; (a) 75-day Zr-0.5Nb, (b) 165-day Zr-0.5Nb and (c) 61-day Zircaloy-4. Nano-pores/pipes are highlighted by red arrows and the metal-oxide interface is highlighted by the yellow dashed line. The proposed ranges of protective and non-protective oxide is marked on top of the images.

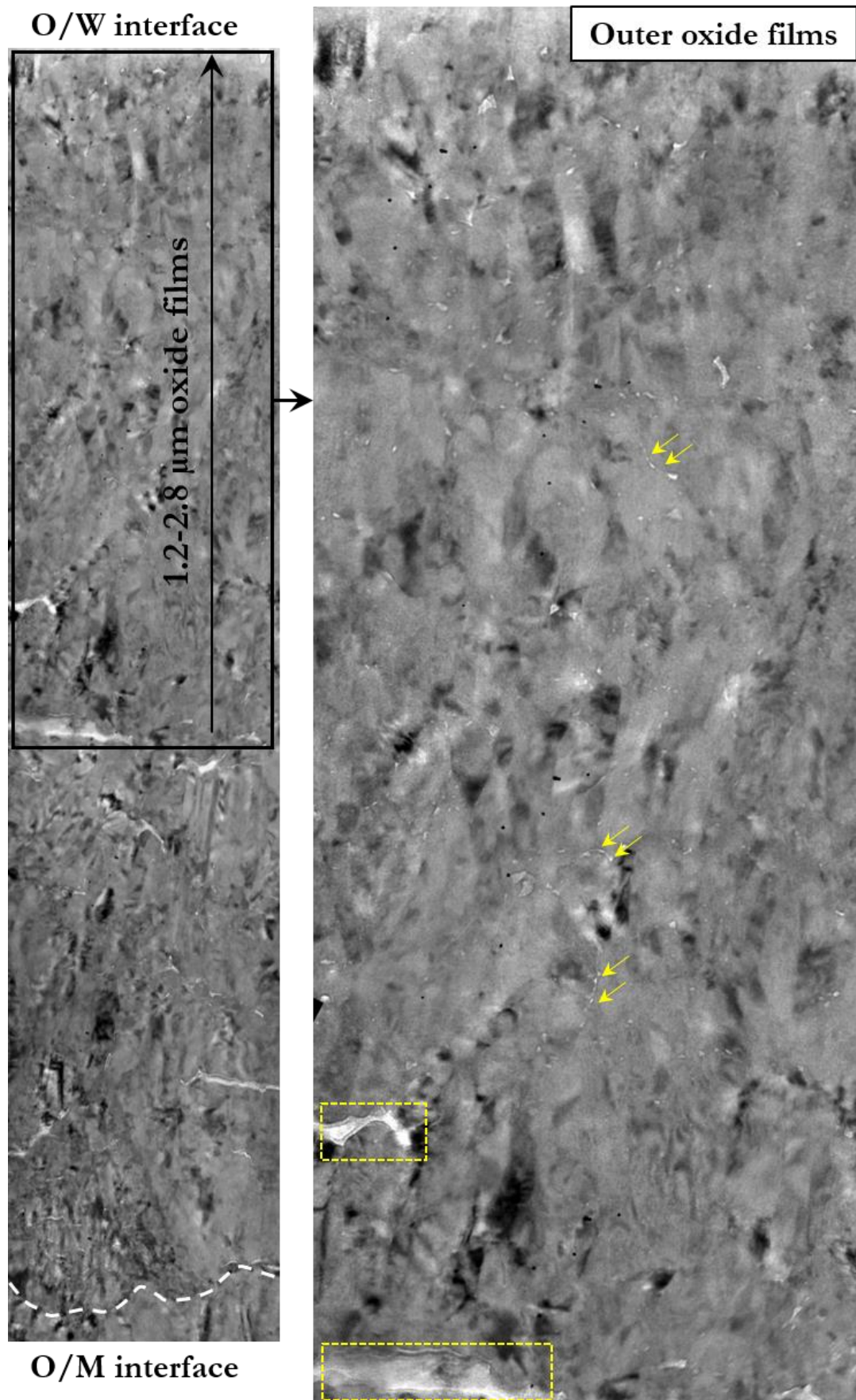


Figure 8.5 Stitched Fresnel contrast ($\Delta f = -2000\text{nm}$) TEM images showing the distribution and morphologies of nano-porosity in the outer oxide layer on the 700-day Zr-2.5 sample

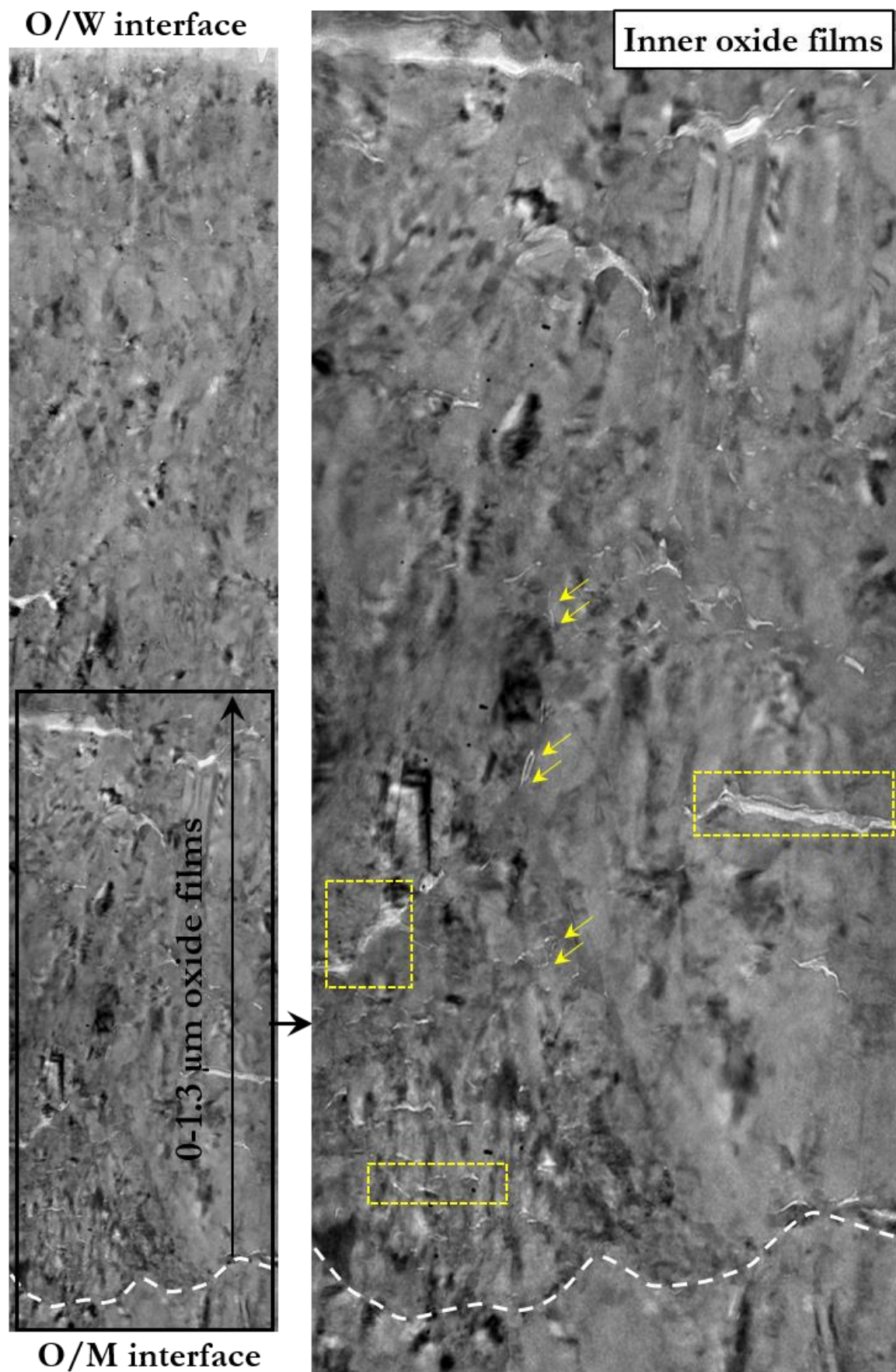


Figure 8.6 Stitched Fresnel contrast ($\Delta f = -2000\text{nm}$) TEM images showing the distribution and morphologies of nano-porosity in the inner oxide layer on the 700-day Zr-2.5 sample

Although this kind of porosity has been identified previously in similar samples [29], I have made the first attempt to measure this porosity quantitatively. This is only possible because the sample thickness is close to the width of individual oxide grains. When the Fresnel images are analyzed using ImageJ® I can extract the density of nanopores at different regions of each oxide, and the results are plotted Figure 8.7. The error bars in distance are from measurements of the pore density averaged over the areas studied, while the density error bars are from the variations in pore numbers identified in data sets from different areas of the images.

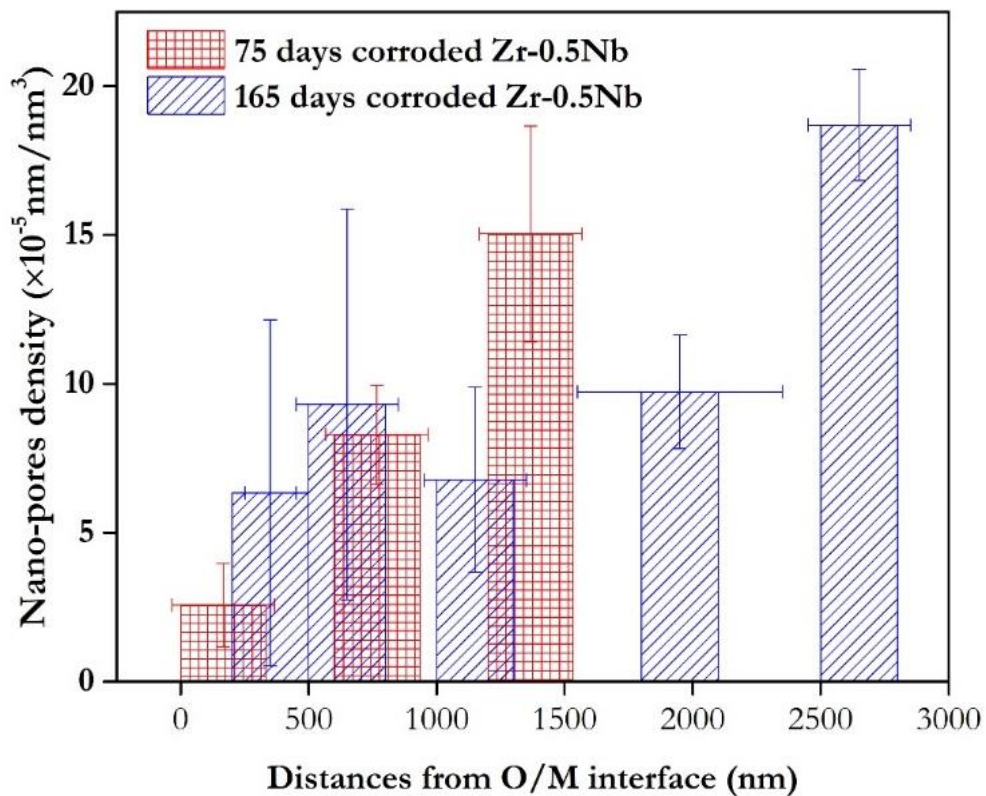


Figure 8.7 Nano-porosity density as function of the distance from the oxide/metal interface in Zr-0.5Nb samples exposed for 75 days ($\sim 2\mu\text{m}$ oxide thickness) and 165 days ($\sim 3\mu\text{m}$ oxide thickness).

The pore density obtained from these quantitative measurements increases significantly towards the oxide surface, confirming the visual impression of changes in pore concentration we gain from the images in Figure 8.1. Quantitatively, at least 3 times more porosity was

identified near the oxide/water interface than at the oxide/metal interface. As highlighted earlier, there is also a transition of pore shape from interconnected through most of the oxide layer to mostly isolated pores close to the oxide/metal interface [81, 330]. Secondly, a denser distribution of pores (by a factor of at least 2) is identified close to the oxide/metal interface for the 165-day sample than observed in the 75-day sample. This is direct evidence for an increase of porosity along the ZrO_2 grain boundaries as the oxide thickens. However, this increase in nano-porosity is not obviously related to an increase in corrosion rate, as observed in Figure 4.5, there is no acceleration in corrosion rate of the Zr-0.5Nb alloy at 165 days. I thus conclude that this nanoscale interconnected porosity is not an effective pathway for the rapid transport of oxygen anions.

8.4. Discussion

The key observation in this chapter is that there is a clear correlation between the measured increase in hydrogen pickup fraction and the observed increase in interconnected porosity in the oxide on both the Westinghouse and CNL Zr alloys, Figure 4.5, 8.4, 8.5 and 8.7.

In Figure 4.5, I have shown different hydrogen pick-up performance of these alloys at different corrosion stages. Compared with Zircaloy-4 and Zr-0.5Nb alloys, the CNL Zr-2.5Nb alloy shows relatively better resistance to hydrogen pick-up. For example, for a corrosion time of 200 days, the absorbed deuterium content in the CNL Zr-2.5Nb alloy is only around 1 wt. ppm, while it is ~20 wt. ppm H in the Westinghouse RXA Zr-0.5Nb alloy. The different resistance to hydrogen pick-up of these two alloys can be a result of the different morphologies of the second phase as shown in Figure 4.1, but also can be contributed by the different distributions of nano-porosity in their films as described above. The total hydrogen pickup fraction varies from 1% at 75-day corrosion to approximately 5% at 165-day corrosion on the Westinghouse Zr-0.5Nb samples. The pick-up fraction increases

by a factor of 5, while the pore density at the oxide/metal interface region increases by a factor of 2 as described above. Thus there is a clear correlation between the measured increase in hydrogen pickup fraction and the observed increase in interconnected porosity in the oxide. The increase in the number density of nano-porosity can provide more pathways for the transportation of hydrogen/deuterium through the oxide films to interact with the metal matrix, leading to a high HPUF.

A more detailed ab-initio molecular dynamics study carried out by collaborators, Dr. Christensen, Dr. Wolf and Dr. Wimmer, has recently shown that the reaction of water molecules with nano-pores and nano-pipes in the oxides may play a key role in the hydrogen pickup mechanism [143].

Quantum mechanical simulations have widely reported spontaneous dissociation of water molecules on metal or oxide surfaces reacting with water [330, 331]. This process is also observed through molecular dynamics simulations of zirconium oxides. Figure 8.8 shows molecular dynamics simulations of the ingress of water molecules into a nano-pipe in ZrO_2 and the generation of molecular hydrogen by reaction of water with vacancies in the side walls. When a water molecule reacts with an oxygen vacancy, the site is filled with the oxygen atom from the water molecule and two hydrogen atoms are released, which bind to two neighbouring sites. These two H atoms can recombine and escape as an H_2 molecule, Figure 8.8(c). These hydrogen molecules are able to diffuse through nano-voids as small as 0.5 nm in diameter, i.e. through nano-pipes and nano-pores which are too small for the diffusion of water molecules, Figure 8.8(d).

If the hydrogen molecules are formed close to the oxide/water interface, they are likely to escape into the aqueous phase. If, on the other hand, the reaction takes place deeper inside the oxide film, and if there is a network of nano-pores reaching the region of suboxide or

the metal-oxide interface, as shown in section 8.3, these hydrogen molecules can diffuse through nano-pores and further react with the interfacial suboxide or metal matrix.

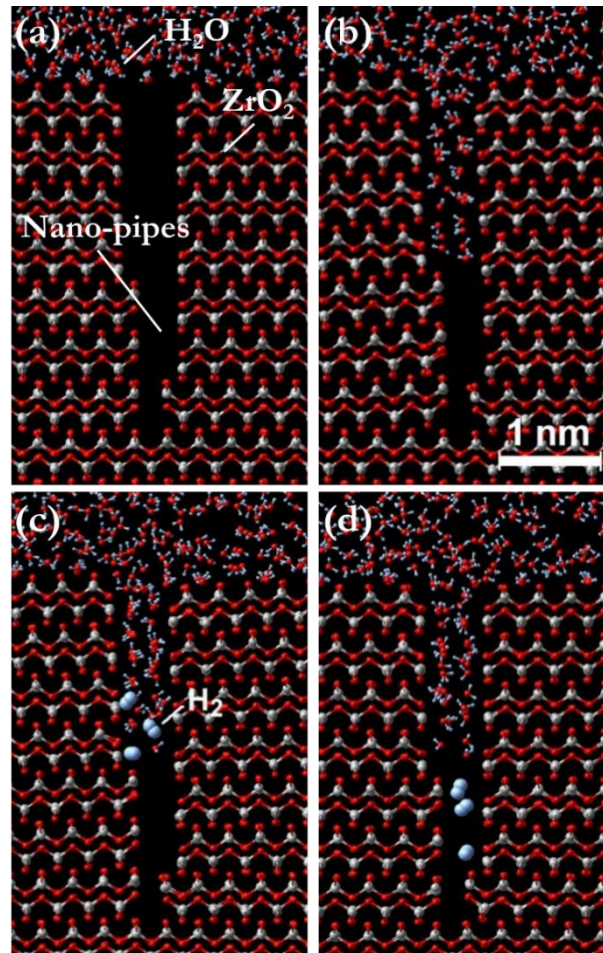


Figure 8.8 Ingress of water molecules into a nano-pipe of ZrO₂ and H₂ diffusion. (a) model of a nano-pipe in t-ZrO₂ with water at 550 K and 150 bar; (b) ingress of water into nano-pipes after 50 ps; (c) generation of molecular H₂ by reaction of water with vacancies in side walls; (d) diffusion of H₂ molecules into the nano-pipe of about 0.5 nm width [143].

As evident from Chapter 7 and results reported in the literature [53, 54, 67, 332, 333], a discontinuous layer of zirconium suboxide (ZrO) is often found, and a layer of oxygen-saturated α -Zr metal (Zr₃O) is always observed, in the interface region between the metal and the bulk oxide. The same modelling [143] also reveals that the suboxide and oxygen-saturated α -Zr metal can play a critical role in the pickup of hydrogen. On surfaces of ZrO, Zr₃O and Zr, molecular hydrogen can dissociate spontaneously releasing a significant amount of heat. As illustrated in Figure 8.9, the dissociation of an H₂ molecule on the

surfaces of ZrO , Zr_3O and Zr are strongly exothermic, -111, -94, and -111 kJ/mol, respectively. The next step in the hydrogen pickup process is the ingress of H atoms from the surfaces of suboxide or into the interior of these phases. The modelling demonstrates that this could be a rate-limiting step, especially if there is a layer of dense zirconium monoxide. The barrier for ingress of H atoms is as low as 20 kJ/mol for Zr_3O and highest for ZrO . However, these values of barrier energy hold only for isolated H atoms on the surfaces of Zr metal, oxygen-saturated $\text{Zr}(\text{O}_{\text{sat}})$, Zr_3O , and suboxide phases. As the coverage increases, the chemical potential of H atoms chemisorbed on these surfaces rises. Together with entropic effects, at a certain concentration it becomes favourable in terms of Gibbs free energy for H to migrate into the bulk phase rather than remaining as chemisorbed species. In fact, it is reasonable to assume that the “surfaces” underlying Figure 8.4 and 8.6 are in reality nano-scale small patches of suboxide adjacent to nano-pores, where the relative H concentration could be quite high, thus providing a thermodynamic driving force to overcome the barriers for H ingress. The calculations [143] also show that the high barrier for H ingress into stoichiometric hexagonal ZrO can be dramatically reduced from 200 kJ/mol to 65 kJ/mol with the presence of oxygen vacancies. It is reasonable to assume that at ZrO/ZrO_2 interfaces where the partial pressure of oxygen will be low both phases exhibit oxygen vacancies thus facilitating the ingress of hydrogen.

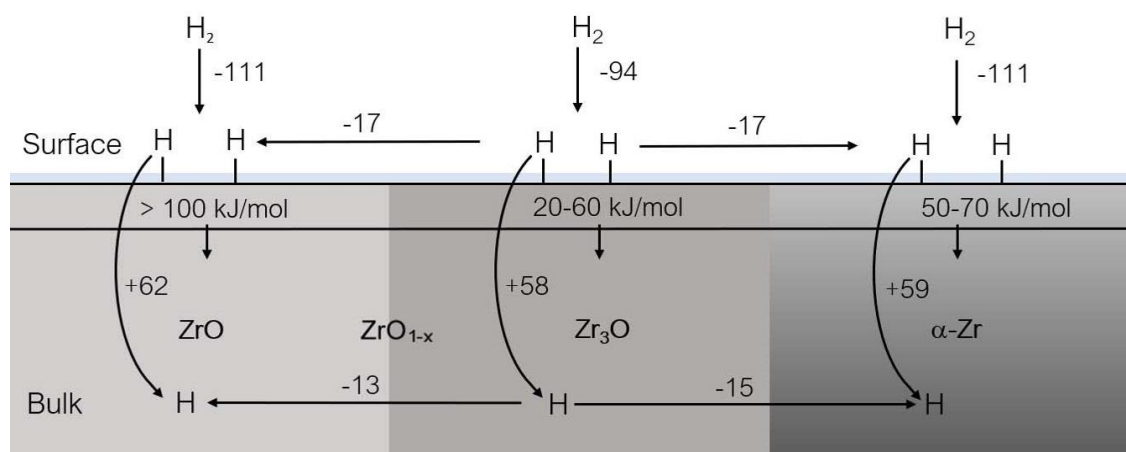


Figure 8.9 Energies of dissociation and barriers of H_2 into Zr and its suboxides [143].

8.5. Conclusions

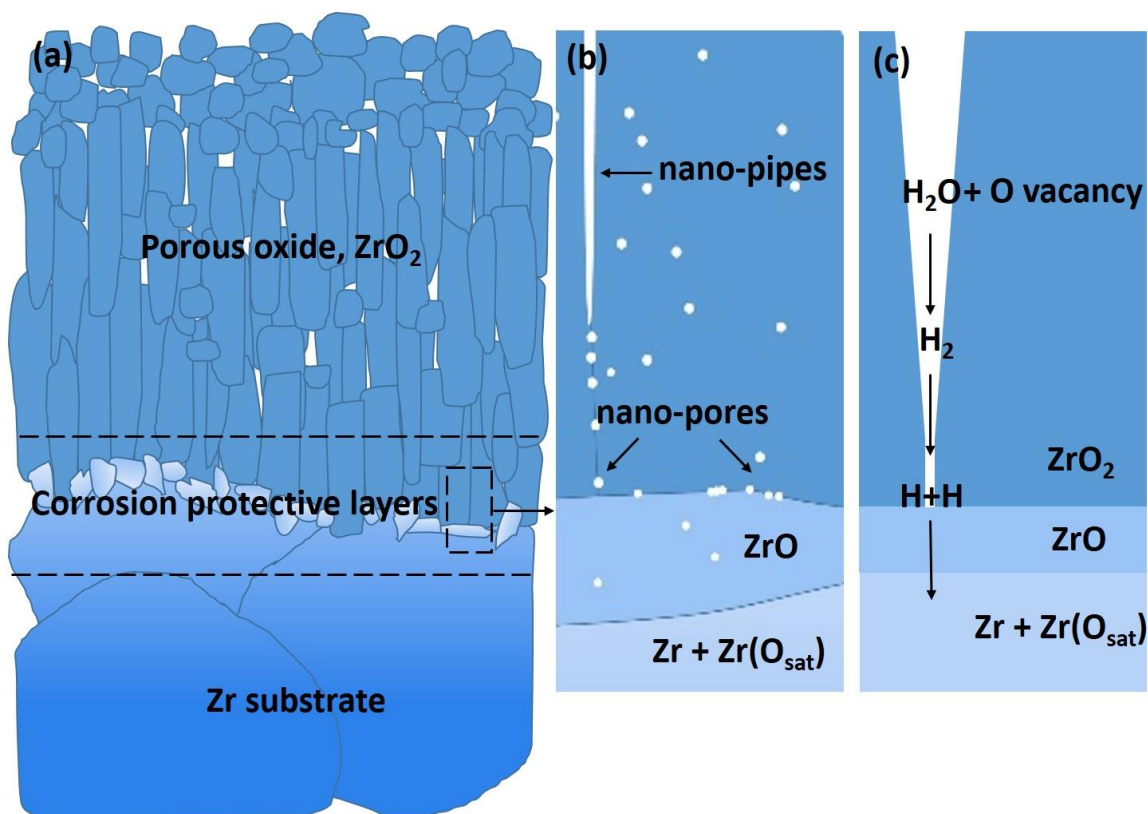


Figure 8.10 Nano-pores and nano-pipes distribution in ZrO₂ corrosion films. (a) Schematic of the nano-pore and nano-pipes size and distribution in the oxide layer. (b) shows magnified images of nano-pores and nano-pipes in the protective oxide near the metal-oxide interface. (c) shows the proposed mechanism for H uptake.

Combining the experimental observations in Figure 7.1, 8.4 and 8.5 and 8.6, my modelling collaborators and I have generated a schematic in Figure 8.10[143] to show possible processes of hydrogen pickup in zirconium alloys during aqueous corrosion. Water molecules can diffuse through nano-pipes reaching a region close to the metal-oxide interface as shown in Figure 8.10. In this region, ZrO₂ is likely to contain a relatively high concentration of oxygen vacancies. As the quantum mechanical calculations show, water molecules react strongly with vacancies releasing hydrogen, which recombines to form molecular H₂. The hydrogen molecules are able to diffuse through nano-voids as small as 0.5 nm in diameter, i.e. through these nano-pipes and nano-pores which are too small for the

diffusion of water molecules. From this one can infer that molecular hydrogen is likely to be present in nano-pores close to the metal-oxide interface with a diameter between 0.5 nm and 1 nm, which are not resolved in the TEM images, but would allow diffusion of molecular hydrogen. Atom Probe Tomography analysis of the metal-oxide interface region of Zr-2.5Nb alloys corroded in deuterated water [334] has detected deuterium in isolated nanopores of this size, but has not observed D in nano-pipes close to the suboxide region, perhaps emphasizing the relative rarity of these penetration paths. Molecular hydrogen may escape during sample preparation for APT while hydroxyl groups on the walls of nano-pipes are more strongly bounded and likely to persist.

Chapter 9 Distributions of Deuterium in Zirconium Oxides

9.1. Introduction

In this chapter, I have used Cameca NanoSIMS 50 and revealed the distribution of deuterium in oxides on Zr alloys formed under different conditions, e.g. autoclave and in-reactor, and correlated this to the role of nano-porosity in hydrogen transportation, with the aim to contribute to the understanding of the mechanisms controlling the hydrogen/deuterium pickup in zirconium alloys in service. The influence of sample preparation on the distribution of deuterium has also been discussed.

I would like to thank Dr. Kexue Li for training me in the operation of NanoSIMS and help with data analysis. Some of the NanoSIMS characterisations were carried out by him.

9.2. Materials and Experimental Methods

To explore the similarities and difference of hydrogen/deuterium distributions in oxides grown on different Zr alloys under different corrosion conditions and at different stages of the oxidation process, NanoSIMS characterisation has been carried out on several samples. Detailed sample information and corrosion data has been described in section 4.3. NanoSIMS specimens were prepared following the procedures defined in section 5.3.

9.3. Results and Discussion

In this study, some of the samples have been corroded in heavy water for periods ranging from 30 days to 2000 days, Table 4.3. Deuterium's natural scarcity (1.15×10^{-4} fraction of natural hydrogen) thus guarantees that nearly all the deuterium detected originates from the sample. Hydrogen (^1H and H_2) signals are primarily a contaminant from the sample surface and the high vacuum chamber ($\sim 1.3 \times 10^{-11}$ kPa). Thanks to the high mass resolution, clear

separation of $^2\text{H}^-$ and H_2^- signals around 2 Daltons using a mass resolving power of about 1300 can be seen in a typical NanoSIMS mass spectrum from a deuterated zirconium sample as shown in Figure 9.1[236]. Thus, unwanted contributions to a $^2\text{H}^-$ signal from H_2^- can be ignored under our typical analysis conditions.

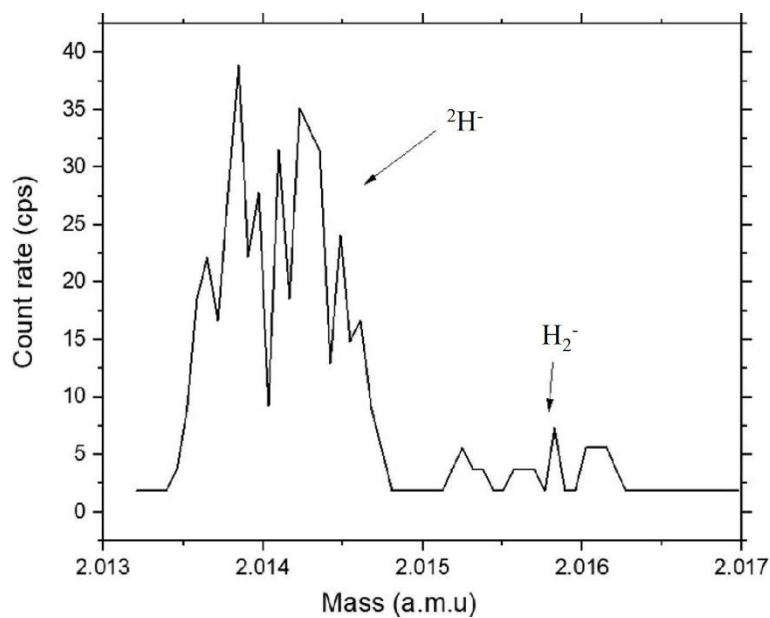


Figure 9.1 High-resolution mass spectra from a deuterated zirconium sample showing the separation of $^2\text{H}^-$ and H_2^- peaks [236].

9.3.1. Deuterium distributions in Zr oxides

Figure 9.2 shows the 3D distributions of $^2\text{H}^-$ and $^{18}\text{O}^-$ in the oxide films on the 61-day deuterated Zircaloy-4 sample. Figure 9.2(a) is a typical 1D depth profile, and a high concentration of $^2\text{H}^-$ is detected near the oxide/water interface (top 0.5 μm) with a rather uniform distribution, and then a gradual decrease in deuterium concentration from the outer part of the oxide towards the metal/oxide interface. Overlaid on this gradual decrease there are sharp spikes in the $^2\text{H}^-$ signal in Figure 9.2(a) that correspond to the apparently planar ‘hotspots’ in Figure 9.2(b). Figure 9.2(c) is a magnified image of the area marked with a red box in Figure 9.2(b), and over a distance of about 120 nm there is a suggestion of a vertical pathway connecting three $^2\text{H}^-$ hotspots. A similar pathway can be seen immediately below

the red box in the same dataset, Figure 9.2(b). Analysis of the 3D $^2\text{H}^-$ distribution from the 106-day Zircaloy-4 sample shows similar distribution of $^2\text{H}^-$ distribution through the oxide depth [236]. In comparison with a high density of sharp spikes shown in the Zircaloy-4 samples, a CNL Zr-2.5Nb sample shows quite uniform distributions of deuterium in its oxide layer, with fewer and smaller deuterium hotspots, Figure 9.3.

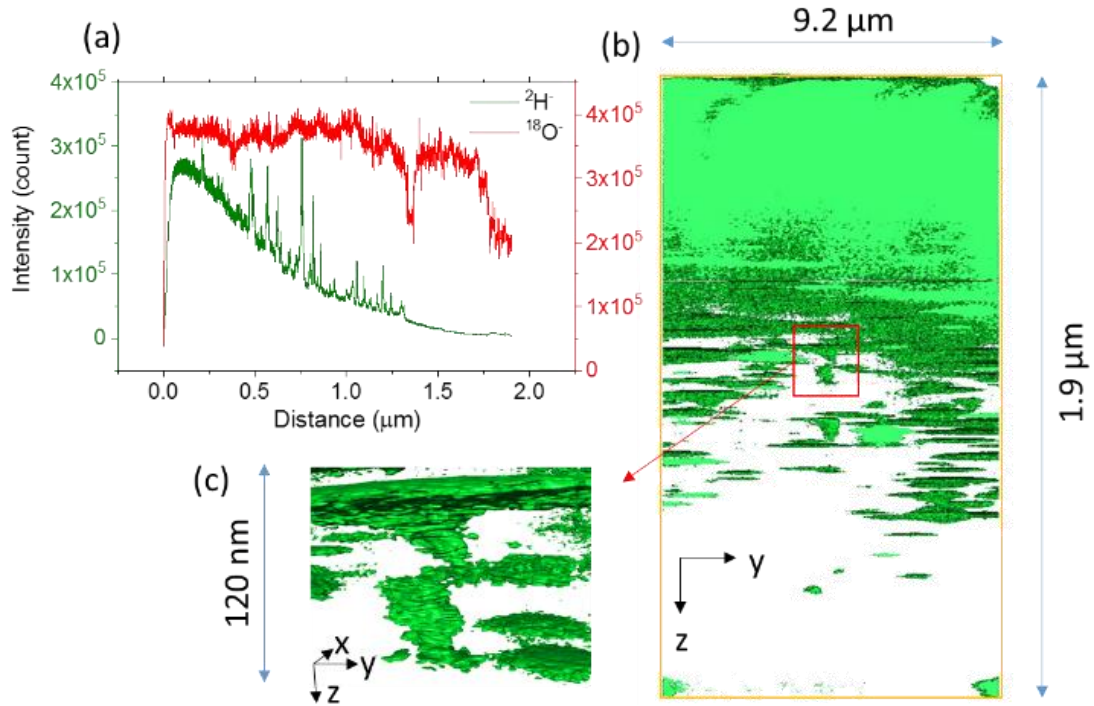


Figure 9.2 Distribution of $^2\text{H}^-$ and $^{18}\text{O}^-$ in a 61-day Zircaloy-4 sample (a) 1D depth profiles, (b) the 3D deuterium distribution and (c) is a magnified image from the red box in (b) showing the interconnected pathways for deuterium.

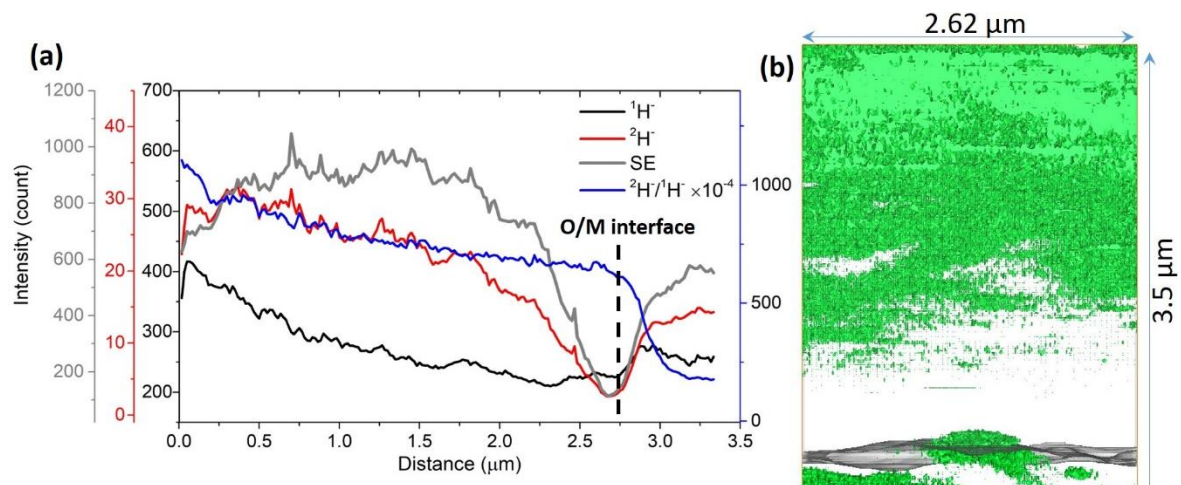


Figure 9.3 Distributions of $^1\text{H}^-$ and $^2\text{H}^-$ in a 700-day Zr-2.5Nb sample (a) 1D depth profiles, (b) the 3D deuterium distribution

To address the possibility of trapping deuterium by SPPs in the oxides, I have stopped a NanoSIMS measurement when clear deuterium hot spots were identified in the middle of the oxide layer on the 61-day deuterated Zircaloy-4 sample, and then analysed the exposed oxide surface by SEM/EDX mapping to determine the locations of SPPs and cracks, Figure 9.4. In the SE image in Figure 9.4(a), white arrows identify small cracks in the oxide layer (usually seen as small round pits), and a yellow circle marks a larger crack parallel to the metal/oxide interface that creates a significant roughening of the exposed surface. In Figure 9.4(b), EDX analysis shows the location of SPPs (Zr-Nb-Fe type) on the crater surface obtained by mapping the Fe L peak (using 5 keV incident electron beam energy to achieve ~ 10 nm lateral and ~ 80 nm depth resolution). Figure 9.4(c) is the summed $^2\text{H}^-$ ion images from the last 40 planes analysed (the accumulated counts from the sputtering of a volume of oxide ~ 20 nm thick), and the regions of enhanced deuterium counts are marked with red circles. Figure 9.4(d) is a similar summed $^2\text{H}^-$ ion image from only the last four planes analysed (~ 2 nm thick, so much closer to the surface analysed in the SEM), with regions of high deuterium intensity labelled by white circles. By comparing the locations of the SPPs in the EDX map and the red dotted and white solid circles of enhanced $^2\text{H}^-$ yield, it is clear that there is no correlation. Instead, we find that all the red and white circles contain at least one small crack, tens of nanometers in diameter (although there are also several small cracks with no sign of deuterium trapping). There is also no evidence for deuterium trapping at the single large crack in this image (yellow circle). This result on the lack of deuterium segregation to SPPs does not agree with several previous reports, e. g. Hatano et al. [335] suggested that hydrogen transport through oxide layers was via SPPs, which presumably requires preferential segregation to these features, and Bossis et al. [301] interpreted 1-D profiles of SIMS measurements as showing that hydrogen was transported to the metal through large SPPs.

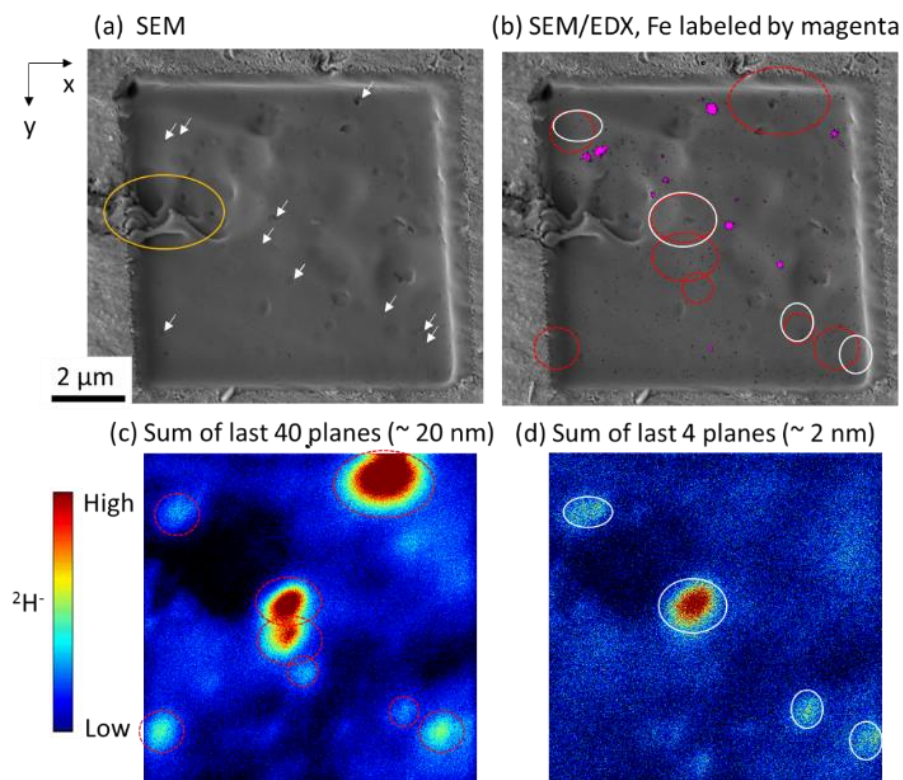


Figure 9.4 Correlating locations of deuterium hot spots, cracks and iron-containing SPPs.

(a) the SEM image of a crater bottom in the middle of the oxide layer on the 61-day deuterated Zircaloy-4 sample. (b) EDX mapping of the positions of iron-containing SPPs (magenta spots) on the crater surface in (a). (c) is an accumulated $^2\text{H}^-$ ion image from the last 40 planes (~ 20 nm thick). (d) from the last 4 planes (~ 2 nm thick).

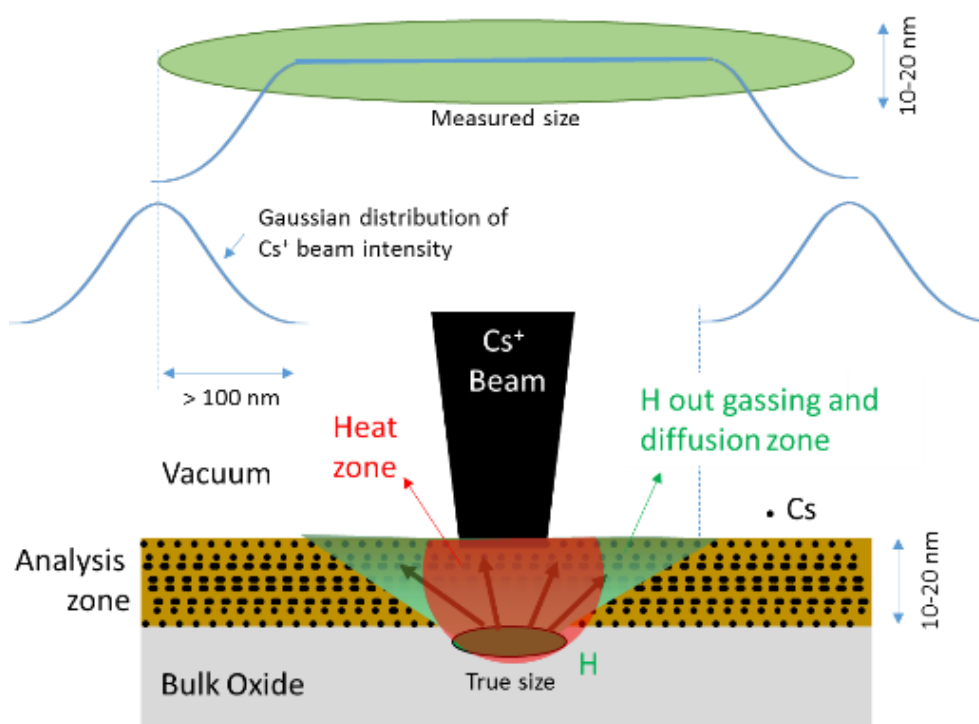


Figure 9.5 Schematic of suggested hydrogen outgassing and diffusion processes during Cs^+ primary ion bombardment. Courtesy of Dr. Kexue Li..

One possible explanation for the observation that not all the cracks in the SEM images show deuterium cracking is that the longer the crack is exposed to the primary Cs^+ beam the more chance there is for deuterium outgassing. Figure 9.5 is the schematic of the suggested processes of hydrogen outgassing and diffusion during Cs^+ ion bombardment that creates an ‘analysis zone’ where the primary beam modifies the sample surface. In a NanoSIMS measurement, heat accumulates in the region bombarded by the highly focused primary ion beam. Ishitani [336] and Schmied [337] predicted that the local temperature increase could be as high as hundreds of degrees in a sample with poor heat conduction, like zirconium dioxide. SRIM [222] simulations for 16 keV Cs^+ ions implantation suggest that the ion range should be around 20 nm in zirconium dioxide. Taking the incident beam size into consideration (~150-200 nm), the volume of material that will transiently experience a significant increase in temperature is estimated to be 3.5×10^5 to $6.3 \times 10^5 \text{ nm}^3$. Bringing these factors together, I can suggest that when the analysis zone reaches a region of the microstructure in which deuterium is trapped, as a result of a dramatic local temperature increase deuterium atoms will become mobile and diffuse to the surface. The area of the surface influenced by this outgassing and diffusion process is then convoluted with the incident Cs^+ beam size, resulting in the analysis of a deuterium enriched region with a horizontal diameter much larger than the scale of the original trapping site.

9.3.2. Effects of irradiation and sample preparation on deuterium distribution

Figure 9.6 shows the ratios of $^2\text{H}^-$ and $^1\text{H}^-$ intensities measured on different samples using different NanoSIMS analysis geometries, in-depth and cross-sectional, bulk sample and FIB lift-out. The isotope ratio is the value of total ion counts of $^2\text{H}^-$ divided by the total ion counts of $^1\text{H}^-$ in sample resin (for cross-sectional samples), oxide and metal, separately. ImageJ

[235, 338] was used to obtain the total ion counts by summing the counts in each pixel in each region. The isotope ratio of $^2\text{H}^-/^1\text{H}^-$ measured from the resin is about 1.5×10^{-4} , close to the natural ratio $\sim 1.15 \times 10^{-4}$ as expected.

In the oxides, the three in-depth analysis, either on bulk samples or FIB lift-out, show significantly higher $^2\text{H}^-/^1\text{H}^-$ ratios compared with the cross-sectional analysis, even measured on the same bulk samples. For example in the oxide films on sample 1F10, the in-depth analysis $^2\text{H}^-/^1\text{H}^-$ ratios are up to 40 times higher than the cross-sectional analysis. The differences within the $^2\text{H}^-/^1\text{H}^-$ ratios between in-depth and cross-sectional analysis are expected to be mainly caused by the sample preparation. As we know, the diffusivity of deuterium is sensitive to the environmental conditions, e.g. local temperature, strain and stress [57, 339, 340], which can be changed by the procedures involved in the sample preparation as described in section 5.3.

The cross-sectional analysis shows higher values of $^2\text{H}^-/^1\text{H}^-$ ratios in the metal matrix than those in the oxide films, and the values of $^2\text{H}^-/^1\text{H}^-$ ratios in the metal matrix increase with sample corrosion time (or the deuterium content, Figure 4.5) as expected. The differences of $^2\text{H}^-/^1\text{H}^-$ ratios between in-depth and cross-sectional analysis in the metal matrix are not as significant as those in the oxide films. One possible explanation could be the formation of stable Zr hydride in the metal matrix [341, 342], which has stronger bonding energy than the hydrogen/deuterium in the oxides, and can be less influenced by the sample preparation. The distribution of hydrogen/deuterium in the oxide layers is more sensitive to the environmental changes, e.g. temperature/stress changes induced by the sample preparation. Another key observation from Figure 9.6 is that there is a clear evidence of enhanced-ingress of hydrogen/deuterium into the Zr matrix in the in-flux sample, B56. Being corroded for similar time (190 days and 185 days), B56 (in-flux sample) and B82 (out-of-flux) formed similar thickness of oxides, 1.2 μm and 1.1 μm respectively. However, the deuterium content

in the in-flux corroded sample B56 is ~9.2 ppm, 8.5 times higher than in the out-of-flux corroded sample B82. The different content of deuterium absorbed by the metal matrix can also be seen in Figure 9.6 from the different $^2\text{H}^-/^1\text{H}^-$ ratios. The $^2\text{H}^-/^1\text{H}^-$ ratio in the metal matrix of the in-flux sample B56 is ~0.06, 10 times higher than that in sample B82, Figure 9.6. These results indicate that the magnitude of $^2\text{H}^-/^1\text{H}^-$ ratios measured through NanoSIMS is, within experimental error, proportional to the content of deuterium in the bulk samples. In the oxides, the $^2\text{H}^-/^1\text{H}^-$ ratio of the in-flux sample B56 is ~1.1, is around 10 times higher than that in the out-of-flux sample B82, Figure 9.6.

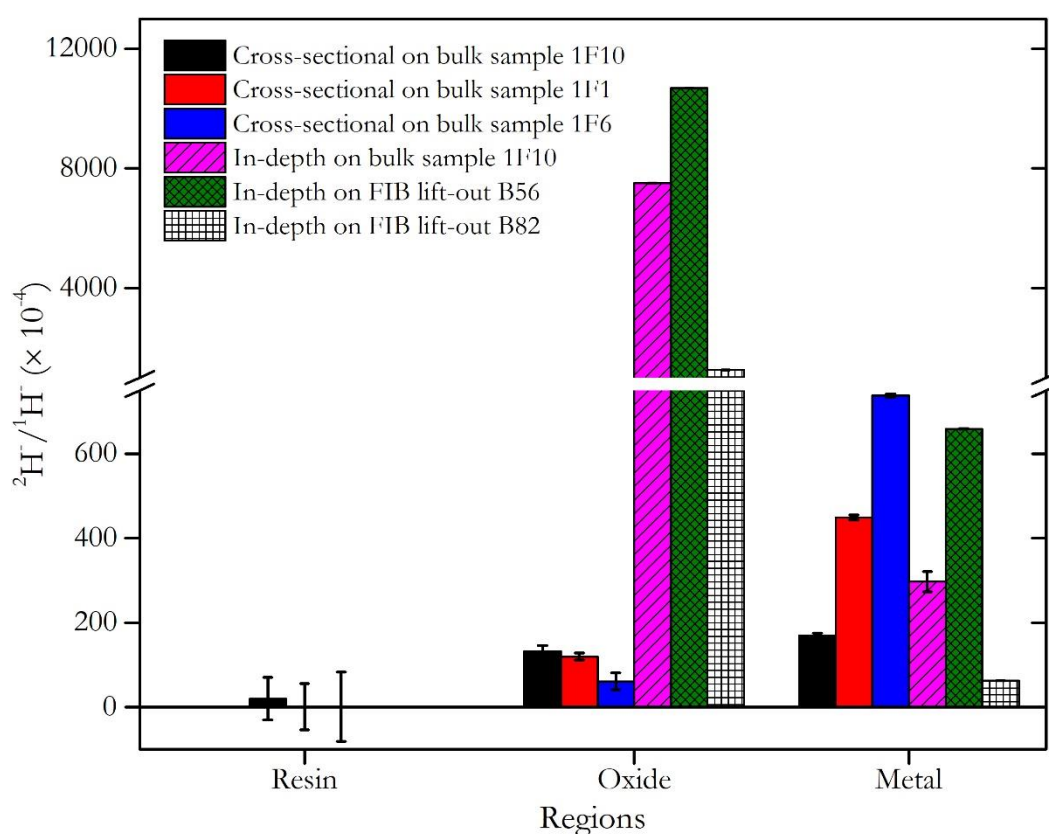


Figure 9.6 Intensity of $^2\text{H}^-/^1\text{H}^-$ ratios as a function of NanoSIMS analysis geometries (in-depth and cross-sectional) and materials. Note that the resin is only included in the cross-sectional samples. Plotting data supplied by Dr Kexue Li

In both oxides and metals, the isotope ratios differ by a factor of ~10 between the in-flux and out-of-flux samples. This can be a result of irradiation-enhance diffusion of hydrogen, but it is also possible that the in-flux formed oxides have more pathways/traps for deuterium

transportation. As described in Chapter 8, a clear correlation exists between the increase in the measured hydrogen pickup fraction and the increase in observed interconnected porosity in the oxide, and oxide nano-pipes have been proposed as a possible pathway for the transportation of hydrogen/deuterium through the oxide layers. Under irradiation, the nucleation and growth processes of textured oxides can be disrupted [54, 120]. The resulting increase in local porosity [29] and reduced cohesion between grains [103, 334] may then contribute to the diffusion of deuterium through the oxide layer. In Chapter 8, I have also described how modelling suggests that the occurrence of oxygen vacancies can significantly decrease the diffusion barrier for deuterium in both zirconium oxide and suboxide. In addition, it has been reported that point defects created by irradiation are strong H/D trap [343], which can then contribute to the observation of more deuterium in the in-flux samples in this work. More details about irradiation-induced defects will be discussed in Chapter 10.

9.4. Conclusions

A methodology using high-resolution secondary ion mass spectrometry to characterize with sub-micron resolution the 3D distribution of deuterium in corroded Zr alloys samples has been described.

The key observation in this chapter is experimental evidence showing the existence of deuterium trapping sites in zirconium oxides which would be part of a transportation pathway for hydrogen/deuterium through the oxide films into the metal matrix. Recalling the distributions and morphologies of oxide nano-porosity and the simulation results showing the role of nano-porosity in the transportation of hydrogen described in Chapter 8, these deuterium trapping sites or hot spots in NanoSIMS maps may be related to the oxide nano-porosity. Second phase particles (e.g. the Zr-Cr-Fe type) in the oxide films do not show trapping effects for the hydrogen.

The procedures included in sample preparation, e.g. mechanical polishing, can lead to obvious redistribution of hydrogen/deuterium in the sub-surface sample. In oxides, where the hydrogen/deuterium bonding energy is much lower than that in the metal matrix, the distribution of hydrogen/deuterium is more sensitive to the environmental conditions, e.g. temperature changes and local strain induced by the sample preparation. The NanoSIMS results show that the $^2\text{H}^-/^1\text{H}^-$ ratios from in-depth analysis on bulk samples (with minimum sample preparation involved) are up to 40 times higher than the cross-sectional analysis on the same sample but after mechanical polishing. It can then be concluded that the distribution of hydrogen/deuterium revealed by in-depth analysis may be more realistic compared with the cross-sectional analysis.

The distribution of deuterium in the in-reactor corroded Zr alloys and its oxides has been mapped using NanoSIMS in-depth analysis. The results indicate the $^2\text{H}^-/^1\text{H}^-$ ratios, in both in-flux oxides and metals, increases by a factor of ~ 10 compared with out-of-flux samples. The increasing content of the pickup deuterium in the in-flux corroded sample may be due to irradiation-enhanced diffusion of deuterium ions, and also could be a result of more available transportation pathways/traps for deuterium existing in the in-flux oxides.

Chapter 10 Irradiation Effects in Zirconium Oxides

10.1. Introduction

This chapter describes the results of irradiation damage in zirconium oxides including both direct characterisation of ex-reactor materials and in-situ radiation damage studies, leading to some suggestions for mechanisms controlling microstructural evolution in zirconium oxides under irradiation. These radiation-induced microstructural changes then need to be considered as possible processes affecting the transportation of oxidation species across oxide films that can occur in reactors, and lead to enhanced corrosion rates.

The in-situ irradiation experiments were accomplished thanks to help from Dr. Anamul Haq Mir, Dr. Jonathan Hinks and Prof. Stephen Donnelly at the University of Huddersfield and Dr. Jing Hu, Dr. Mark Kirk, Dr. Meimei Li, Mr Ed Ryan and Mr Pete Baldo at Argonne National Laboratory. I would also like to thank Mr. Guanze He, Dr. Zhao Shen and Dr. Mohsen Danaie for their assistance on the advanced microscopy analysis.

10.2. Materials and Experimental Methods

CNL Zr-2.5Nb samples corroded in-flux for 190 days were selected to study neutron-irradiation effects. The samples used in in-situ irradiation study were prepared from an autoclave-corroded Westinghouse Zr-0.5Nb model alloy. Detailed sample information and corrosion data have been described in section 4.3. Cross-sectional transmission electron microscopy foils containing both the oxide layer and the metal matrix were prepared using FIB lift-out method described in section 5.2. The in-situ irradiation experiments were carried out using the Intermediate Voltage Electron Microscopy (IVEM)-Tandem Facility at Argonne National Laboratory and the MIAMI2 facility at University of Huddersfield. Details of the irradiation parameters used at the IVEM and MIAMI2 facilities are presented

in section 3.6. TKD characterisation was carried out to generate information on the oxide texture, phase distributions, grain morphologies. More detailed information about the TKD configurations and setup have been presented in sections 2.2 and 5.2.

10.3. Results and Discussion

10.3.1. Characterisation of oxides formed in reactor conditions

Typical TKD band contrast and texture component maps of Zr-2.5Nb samples corroded in-flux, out-of-flux and in an autoclave are compared in Figure 10.1. The grain morphologies of oxides formed out-of-flux or in the autoclave (without the impact of n-irradiation) in the pre-transition stage of oxidation, Figure 10.1(b and c), are similar to those previously reported [59, 81], showing most of the oxide layer has well aligned columnar grains with a few small equiaxed grains. The thicker, post-transition oxides seem to have a more complicated, and more equiaxed, grain structure, Figure 10.1(d). By comparison, a more heterogeneous microstructure in reactor-formed oxides was seen, with reduced columnar grain growth and less textured structure compared to the autoclave formed oxides.

As presented in section 2.2 and 7.3, oxides formed by aqueous corrosion of nuclear Zr alloys have been widely reported to have a strong fibre texture with the majority of the m-ZrO₂ grains with directions between $(10\bar{2})_{\text{m-ZrO}_2}$ and $(10\bar{6})_{\text{m-ZrO}_2}$ lying along the surface normal [62, 65]. The texture component maps in Figure 10.1(middle column) are coloured according to the orientation deviation of oxide grains away from the $(10\bar{4})_{\text{m-ZrO}_2}$ || RD fibre component. The statistical distributions of the frequency of textured oxide grains as a function of angular deviation away from the fibre component are also plotted in Figure 10.1(right column), together with the $(104)_{\text{m-ZrO}_2}$ pole figures.

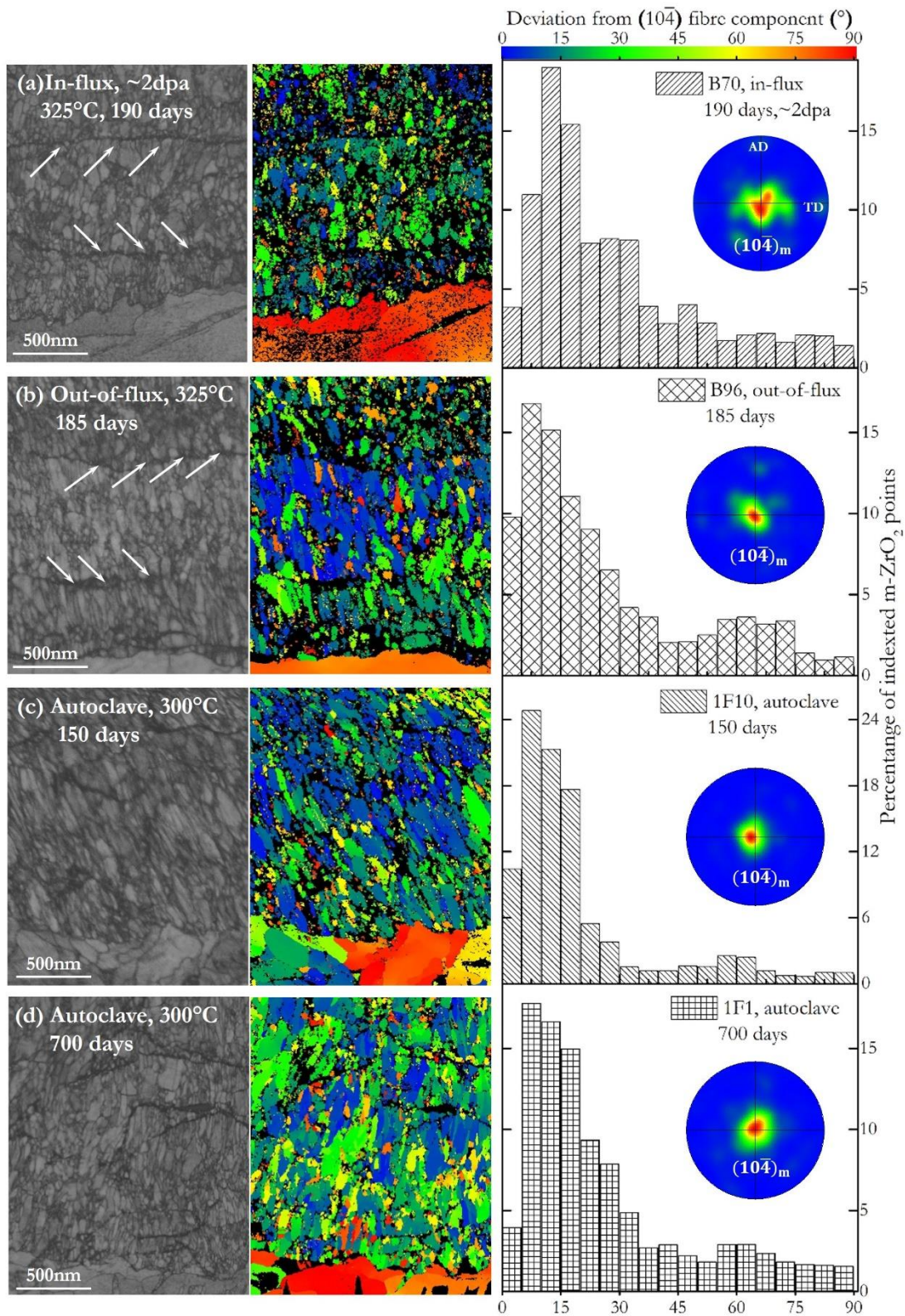


Figure 10.1 TKD band contrast (left column) and texture component (middle column) maps for oxides formed on CNL Zr-2.5Nb tubes (a) In-flux, 190 days, 7.6×10^{20} n.cm⁻², (b) Out-of-flux, 185 days, (c) autoclave, 150 days and (d) autoclave, 700 days. The white arrows in (a and b) show the regions of oxidised β -Zr. The grains in the texture component maps are coloured according to the angular deviation of their $(10\bar{4})_{m-ZrO_2}$ poles from the RD. $(10\bar{4})_{m-ZrO_2}$ pole figures and statistics showing the frequencies of grains with the $(10\bar{4})$ poles deviating with specific angular ranges away from the RD are shown in the right column.

In all these specimens, with or without irradiation, pre- or post-transition, more than 50% of the indexed m-ZrO₂ grains are observed with $(10\bar{4})_{\text{m-ZrO}_2}$ texture lying within 30° of the surface normal. The colour in the orientation maps changes gradually with depth in the oxide, with a stronger texture in the outer few microns that decreases in strength towards the oxide/metal interface. This is thought to be due to stress accumulation near the oxide/metal interface [22, 60, 88], and possibility exists that the interface roughness may change the oxide growth direction and further affect the texture orientations. The Nb-enriched layers that are the residue of the original β -Zr phase decorating the grain boundaries (also clearly seen in the pattern quality maps in the left column of Figure 10.1) seem to result in a sharp change in the texture strength. Below each of these layers the oxide is better aligned with $(10\bar{4})_{\text{m-ZrO}_2}$, Figure 10.1(a and b). More studies will be required the roles of these Nb-enriched layers during the corrosion processes of CNL Zr-2.5Nb alloy.

The oxide layer formed in-flux, Figure 10.1(a), clearly differs from that formed under out-of-flux or autoclave conditions, Figure 10.1(b and c), in terms of both grain morphology and texture strength. Figure 10.1(a) shows the oxide contains more small, equiaxed grains, some with an irregular shape. A $(10\bar{4})_{\text{m-ZrO}_2}$ texture can also be seen from the texture component map, but the grains show larger angular deviations from the texture component compared with the oxides formed out-of-flux or in an autoclave, as can be clearly seen from both the statistical distribution of the frequency of textured oxide grains and the $(10\bar{4})_{\text{m-ZrO}_2}$ pole figure, Figure 10.1(right column). These results show the formation of oxides that are less well textured and with a more disrupted grain structure in-reactor, as has been previously reported [103]. It seems likely that these changes in grain morphology and texture in the oxide layers can contribute to the accelerated corrosion observed in these samples in-flux.

Under irradiation, crystallite nucleation and growth processes are likely to be disrupted by the high concentration of defects at the M/O interface [78, 120]. This can lead to an increase

of porosity and reduced cohesion between grains [30]. An increased oxygen diffusion rate through the damaged oxide could also lead to enhanced nucleation of ZrO_2 grains at the interface, and the development of a more equiaxed, irregular grain structure [104, 144, 344]. At the same time, the direct effects of radiation on the oxide microstructure should also be taken into consideration.

10.3.2. Ion-irradiation induced damage in the ZrO suboxide

Here I focus on the direct experimental observation of irradiation-induced damage to the ZrO suboxide formed at the metal/oxide interface. Figure 10.2(a and b) show in-situ observations of the oxide/metal interface, and in (d) an EELS O/Zr atomic ratio map of the initial sample in which we can identify the ZrO_2 (bright white), Zr metal matrix (dark grey), and the intermediate contrast of h-ZrO grains and the oxygen-saturated metal ($\alpha\text{-Zr}(\text{O}_{\text{sat}})$). The reverse contrast variations in the HAADF image in (c) are a result of changes in average atomic mass in the same phases. Based on (c) and (d), the location of suboxide grains can be identified precisely in Figure 10.2(a and b), and lie between the dotted and dashed lines. The columnar m- ZrO_2 grains are clearly seen above h-ZrO suboxide grains $\sim 30\text{nm}$ in diameter which separate the $\alpha\text{-Zr}$ matrix and the bulk oxide along most of the O/M interface. Previous work has suggested that the loss of diffraction contrast in bright field TEM images is a useful indication of local amorphisation [345], and considerable changes in local contrast around the metal/oxide interface were observed during the relatively early stages (10^{14} ions. cm^{-2}) of the in-situ experiment at 50 K. Interpreting these changes in contrast in-situ is complicated due to the unavoidable slight bending of the sample during irradiation which alters the diffraction conditions, so rather than rely on in-situ analysis of contrast changes I have carried out post-irradiation HRTEM analysis.

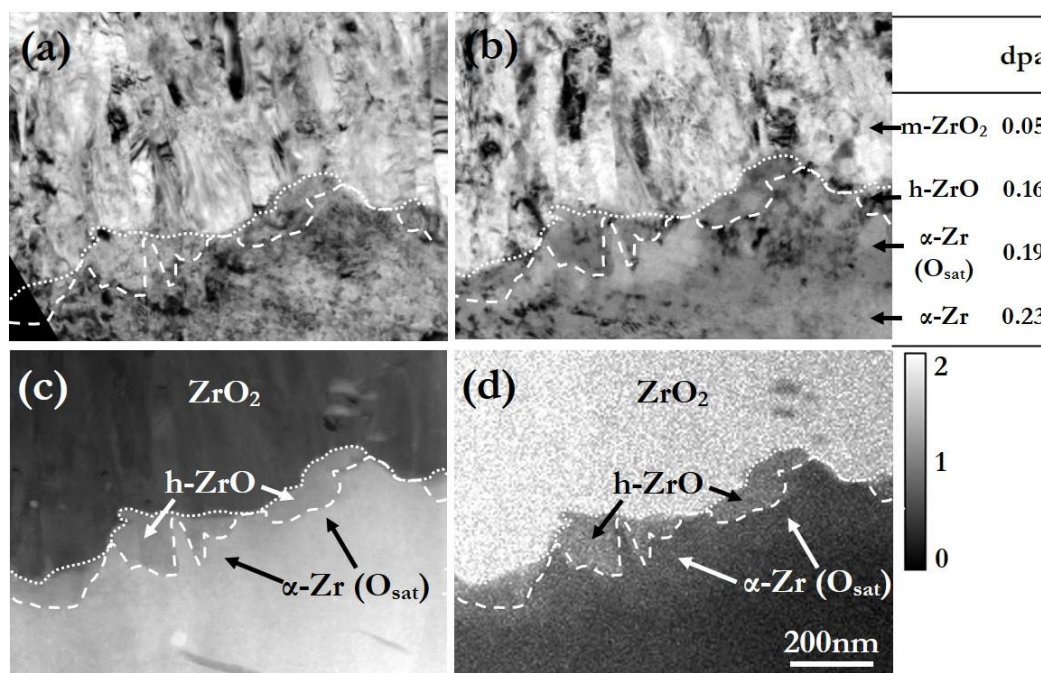


Figure 10.2 In-situ TEM images showing the microstructure of oxide, suboxide and metal substrate in the Zr-0.5Nb alloy (A-9) at different damage levels: (a) pre-irradiation (b) 10^{14} ions/cm², the corresponding damage levels in dpa are also shown on the right, (c) pre-irradiation HAADF STEM image and (d) O/Zr atomic ratio map from EELS analysis of the region followed during in-situ irradiation.

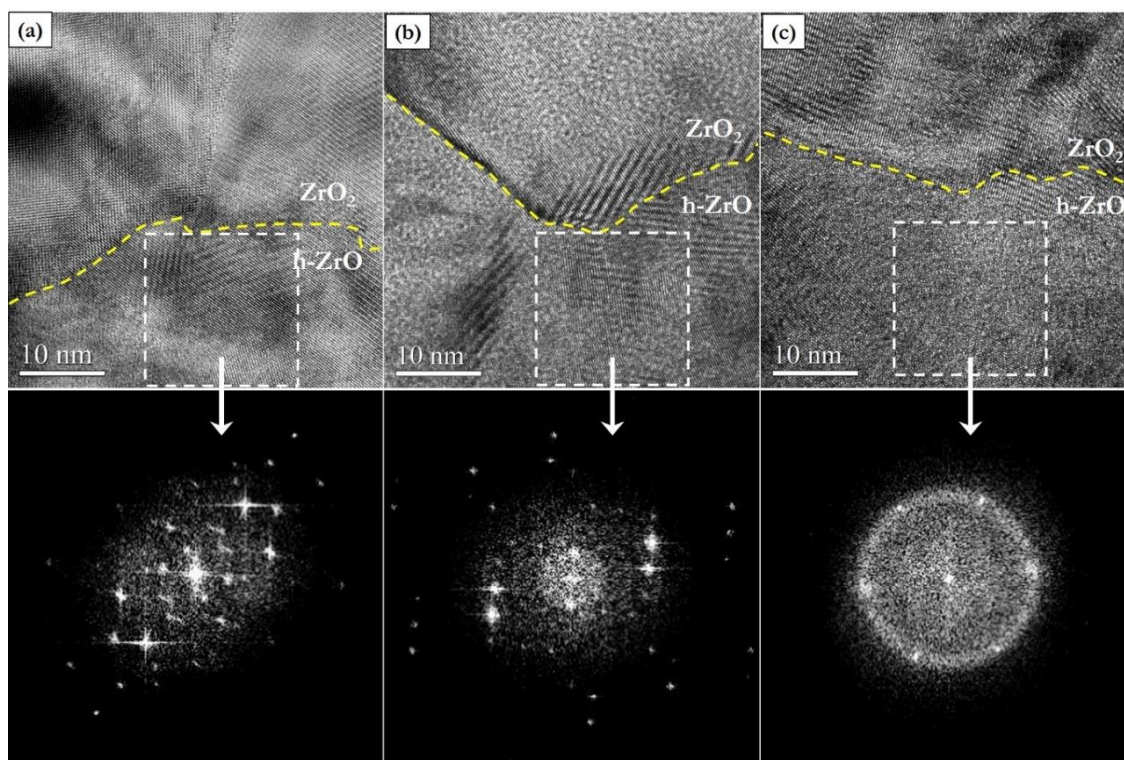


Figure 10.3 HRTEM images and FFTs from the O/M interface regions on Zr-0.5Nb samples (A-9), (a) pre-irradiation, (b) irradiated at 293 K to 1.9×10^{16} ions.cm⁻² and (c) irradiated at 50 K to 4×10^{15} ions.cm⁻².

Figure 10.3(a) shows a typical pre-irradiation HRTEM image of the crystalline phases at the oxide/metal interface. Complete amorphisation of the h-ZrO grain was seen in the specimen irradiated at 50 K up to 4×10^{15} ions.cm⁻², Figure 10.3(c), while in other samples the h-ZrO grains remained crystalline when irradiated at room temperature even up to a much higher dose of 1.9×10^{16} ions.cm⁻². These results suggest that irradiation-induced amorphisation of the ZrO suboxide is strongly temperature-dependent. A more detailed HRTEM analysis on adjacent α -Zr or ZrO₂ grains is shown in Figure 10.4. The dioxide still stay crystalline after ion irradiation, Figure 10.4(b), while the suboxide goes fully amorphous Figure 10.4(d). The oxygen saturated regions in the metal just beneath the h-ZrO suboxide layer showed some changes in contrast under irradiation, Figure 10.2(b), but post-irradiation HRTEM characterisation revealed that these oxygen saturated regions did not become fully amorphous, Figure 10.4(c). More evidence showing the preferential amorphization of the h-ZrO suboxide is shown in Figure 10.5.

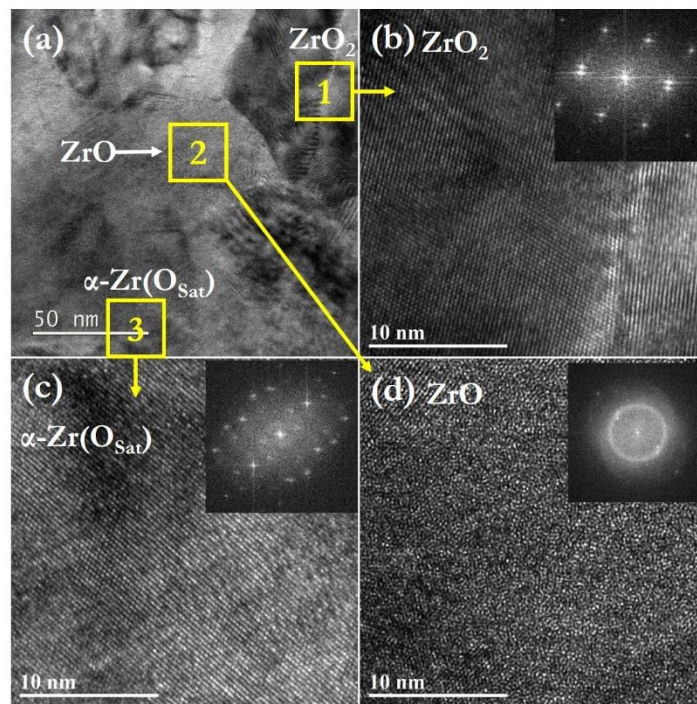


Figure 10.4 (a) low magnification bright field TEM image showing the m-ZrO₂, h-ZrO suboxide and α -Zr(O_{Sat}) after irradiation to 8.4×10^{15} ions/cm² (13dpa in h-ZrO) on Zr-0.5Nb alloy (A-9). (b) HRTEM and FFT from the region of m-ZrO₂ identified in (a). (c and d) HRTEM and FFT from the identified regions of α -Zr(O_{Sat}) and h-ZrO suboxide.

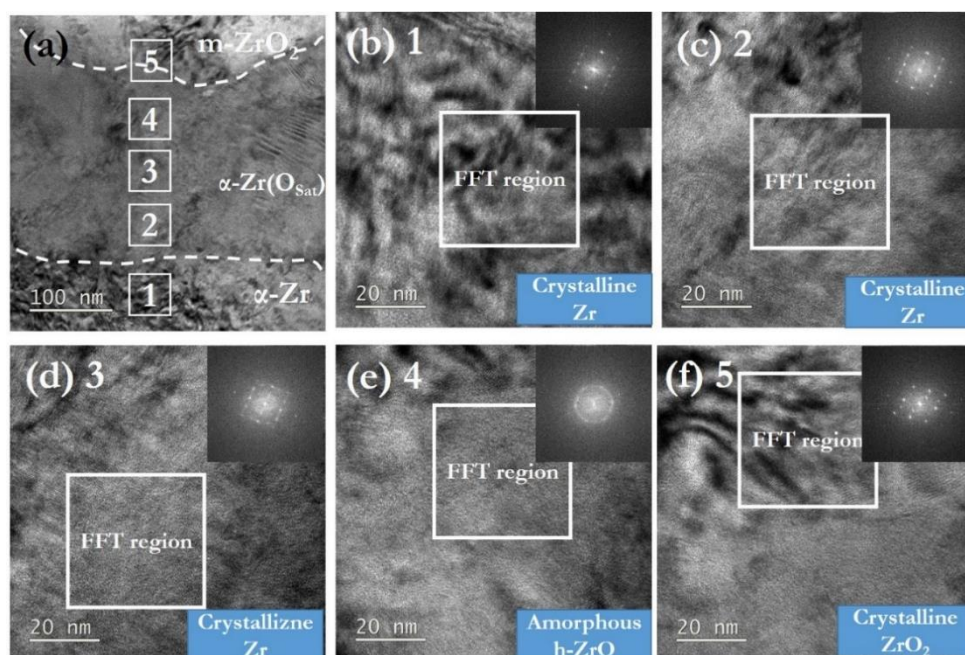


Figure 10.5 HRTEM analysis after irradiation to 8.4×10^{15} ions/cm² showing the occurrence of amorphization only in the h-ZrO grain on the Zr-0.5Nb alloy (A-9).

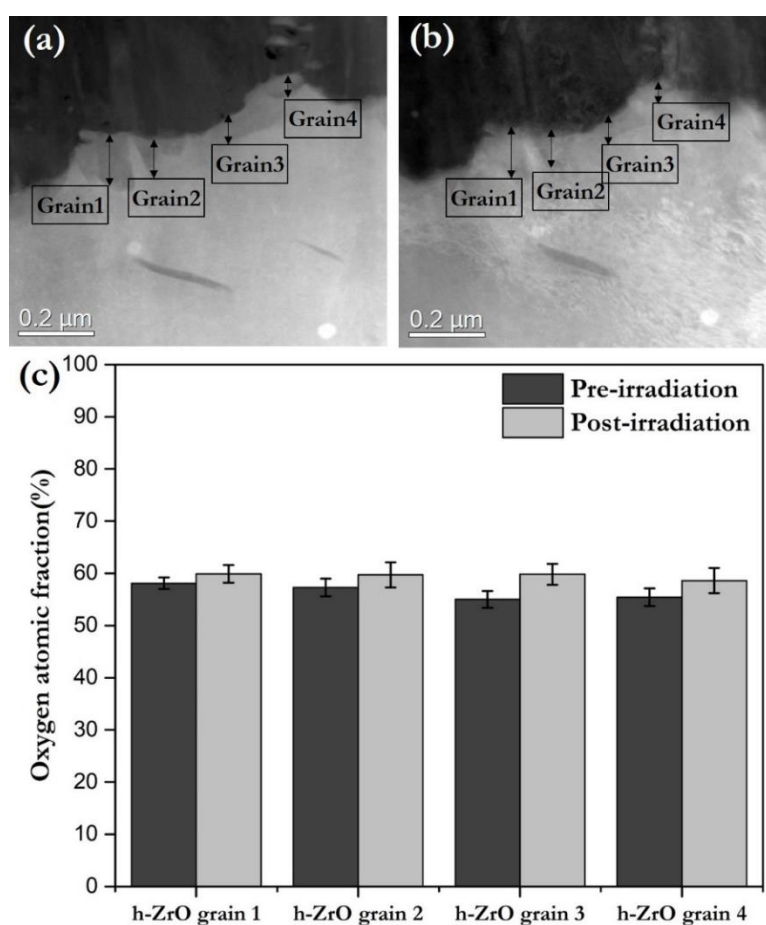


Figure 10.6 HAADF STEM images from the same area of (a) pre-irradiation and (b) post-irradiation samples, Zr-0.5Nb alloy (A-9). (c) Comparison of oxygen concentrations in the suboxide grains pre- and post-irradiation calculated from EELS spectra acquired

The post-irradiation samples were further characterized using EELS to determine the composition after ion irradiation, and the results in Figure 10.6 indicate that the O content in the suboxide is, within experimental error, the same as before irradiation, so the heavy ion bombardment has not released the interstitial O to the microscope vacuum.

The h-ZrO suboxide is more susceptible to irradiation damage than the adjacent α -Zr and ZrO₂ grains. I have proposed mechanisms for this irradiation-induced amorphization behaviour in h-ZrO based on the previous literature [346-348]. The first signs of amorphization of the suboxide grains appeared at a fluence of $\sim 10^{14}$ ions/cm², corresponding to 0.16 dpa in the h-ZrO. This behaviour is consistent with the homogeneous amorphization model of Motta and Olander [348, 349]. The basic postulate is that as the local concentration of point defects increases, a critical value is reached at which the lattice becomes unstable and collapses into an amorphous structure. In order to better understand the critical defect concentration at which amorphization occurs, a value of surviving defect fraction is required. Averback [350, 351] and Stoller [352] studied point defect production in Al, Cu and Fe at cryogenic temperatures ($T \leq 100\text{K}$), and based on their results the value of surviving defect fraction can be estimated to be $\sim 30\%$. By applying this value to our experimental conditions, a critical defect concentration in the h-ZrO can be estimated to be 0.047 at a fluence of $\sim 10^{14}$ ions/cm² (0.16 dpa), in good agreement with that proposed by Swanson [353] who reported a defect concentration between 0.02 and 0.04 is required for collapse of the lattice into an amorphous state.

The local defect concentrations, particularly in the h-ZrO grains that became fully amorphous, will be a result of several competing factors. We have estimated that the damage rate in the suboxide is as high as 0.0012 dpa/s, Table 2.3. The oxygen atoms in the interstitial positions are displaced more easily than Zr, so an ordered interstitial arrangement of O atoms is damaged particularly fast, resulting in a high local defect concentration [347]. However,

irradiation-induced thermal spikes will induce thermal recombination and lead to the annihilation of point defects. Free surfaces and grain boundaries can also serve as strong sinks for point defects, although the rate of both defect migration and annihilation processes will be reduced to some extent by the choice of 50K for the sample temperature during irradiation. Thermodynamic modelling shows that the h-ZrO suboxide phase, which is absent in the traditional Zr-O binary phase diagram [64], is actually an equilibrium phase over a very narrow oxygen partial pressure window [68]. Ab-initio studies predict the h-ZrO to have a structure similar to the high-pressure ω -Zr phase, but with the oxygen in an ordered arrangement [67, 68]. Assuming that this ordered interstitial structure plays a role in stabilizing the metastable h-ZrO [67], we can explain the observed amorphization behaviour as destruction of the ordering in the preformed h-ZrO grains in the TEM sample by ion-irradiation to the high dpa levels used here.

Under reactor conditions, the ongoing corrosion process means that suboxide grains are constantly reformed as the oxide layer thickens, such that the damage accumulated in each h-ZrO grain is limited. Using the kinetic data in [5] to estimate the rate at which h-ZrO grains are formed and consumed at the metal-oxide interface and a damage rate of 10^{-7} dpa/s [124, 125], the maximum damage accumulated in any individual suboxide grain can be estimated to be around 0.1dpa. Thus although amorphisation of the suboxide is unlikely to occur under reactor conditions, in agreement with the observation of crystalline h-ZrO layers in both neutron- and ion-irradiated samples in the literature [103, 299], we have observed that the h-ZrO is more susceptible to radiation damage than the surrounding phases. Although more study is needed to address the evolution in-reactor of the microstructure and defect content of this interface suboxide region, and its impact on the corrosion kinetics, some specific aspects to focus on can be suggested from consideration of previously reported irradiation effects in other materials. At the in-reactor temperature, ~ 270 - 360°C , the higher mobility of

radiation-induced defects can result in the nucleation and growth of defects clusters, e.g. dislocation loops and voids, in the hexagonal suboxide, and especially the voids can have a strong effect on local transport of oxidizing species. Other effects such as irradiation-induced growth and swelling may also occur preferentially in the interfacial suboxide phase, and the related strain and density changes can affect phase transformations as the underlying metal oxidized to bulk ZrO_2 . All these effects can modify local diffusion rates, the nucleation and growth process of new h-ZrO and ZrO_2 grains, and give rise to increased porosity, and so be a potent mechanism for radiation-assisted acceleration of the overall corrosion rate. The model proposed in this work may also be applied to explain the irradiation-induced amorphization of some other intermetallic compounds in zirconium alloys. For example, it has been widely reported that crystalline-amorphous transformations occur in intermetallic precipitates such as $\text{Zr}(\text{Nb},\text{Fe})_2$, $\text{Zr}_2(\text{Fe}, \text{Ni})$ and $\text{Zr}(\text{Cr},\text{Fe})_2$ under electron, ion and neutron irradiation over a large temperature range [348, 349, 354-356]. These Fe-enriched precipitates are known to have interstitial iron ordering to form superlattice structures [354, 357, 358], which may then be easily amorphized under irradiation. On the other hand, irradiation-induced amorphization has never been reported in β -Nb precipitates which do not have an ordered interstitial structure.

10.3.3. Ion-irradiation induced damage in ZrO_2

10.3.3.1. In-situ observation of irradiation-induced phase transformation

In this study ZrO_2 was observed to have a high resistance to irradiation-induced amorphisation up to a fluence of $1.9 \times 10^{16} \text{ ions.cm}^{-2}$ at room temperature, but a gradual evolution of microstructure in the bulk oxides can be seen in long term in-situ irradiation experiments, as shown in Figure 10.7. The resistance of zirconia to irradiation-induced

amorphisation has been widely reported over a wide range of both temperatures and damage levels [54, 359]. Strong diffraction contrast can be seen in the pre-irradiation image, Figure 10.7(a), from the characteristic nanocrystalline grain structure in a corrosion scale grown on a Zr alloy under simulated reactor conditions [29, 59], and the complex selected area diffraction (SAD) patterns are also characteristic of the textured ZrO_2 layer [58, 65, 188]. The diffraction contrast in the bright field micrographs gradually changed under irradiation, and we observed fewer but brighter spots in the diffraction patterns. We can perhaps also see some indication of grain growth in the oxide under irradiation in the in-situ TEM images, but the areas examined are small and grain boundaries in some regions are no longer discernible due to the larger number of defects, so it is hard to be sure of the statistical significance of this observation.

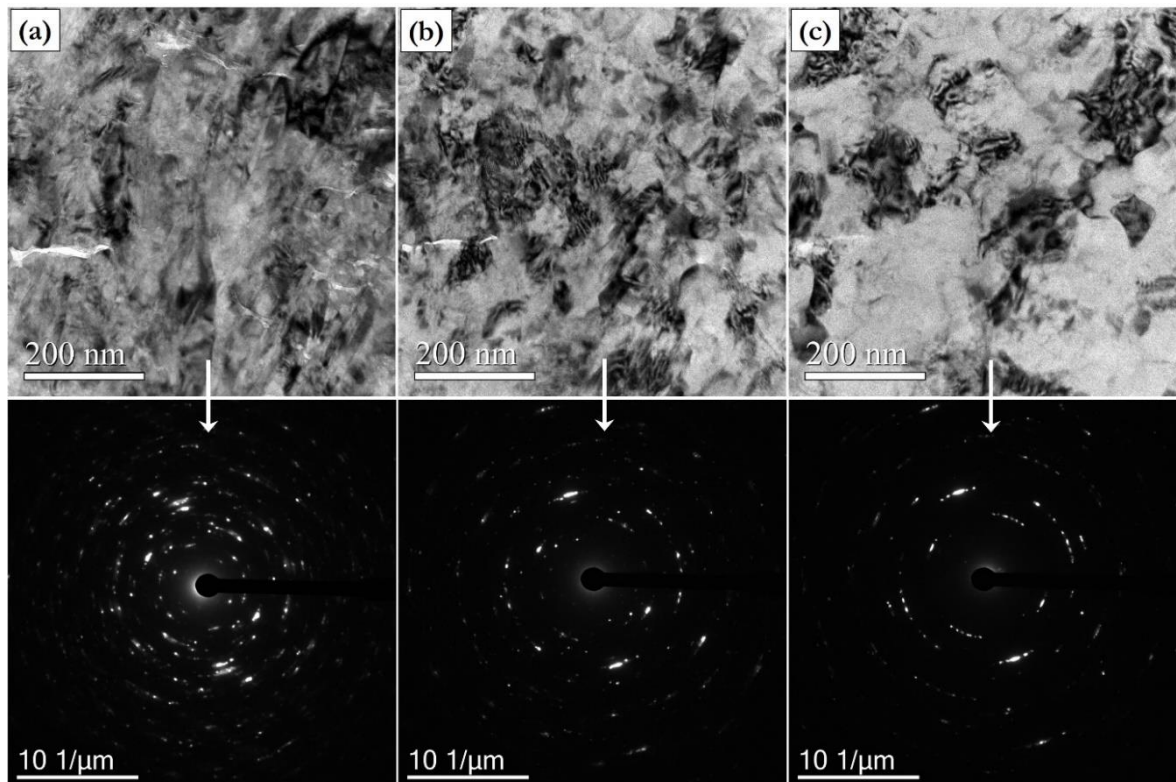


Figure 10.7 BF TEM images and corresponding SAD patterns showing the microstructural evolution of the oxide on Zr-0.5Nb sample (A-16) under 700 keV Kr^{++} irradiation at 293K (a) 0 dpa, (b) 3 dpa ($5.6 \times 10^{15} \text{ ions.cm}^{-2}$) and (c) 10 dpa ($1.9 \times 10^{16} \text{ ions.cm}^{-2}$).

However, irradiation-induced phase transformations can be also studied from the evolution of diffraction patterns like those shown in Figure 10.7. These patterns from only a limited number of individual small oxide grains and, especially when there is strong crystallographic texture [58, 65, 188], are very difficult to interpret. To make them easier to index, the patterns were rotationally averaged using the Difftool developed by Michell [360], which transforms the two-dimensional electron diffraction pattern into a one-dimensional profile, similar to a normal x-ray diffraction pattern. The background in the diffraction profiles was subsequently removed using the OriginPro software package. Simulated diffraction patterns, Figure 10.8(a), for monoclinic-ZrO₂, tetragonal-ZrO₂ and cubic-ZrO₂ were generated using the CrystalMaker and CrystaDiffract software packages using the standard lattice parameters summarised in Table 3.2. Indexing and interpretation of the TED patterns can then be conducted through a direct comparison between the experimental and simulated diffraction profiles.

Typical rotationally averaged in-situ diffraction patterns acquired at different damage levels are presented in Figure 10.8(b). As we would expect, the pre-irradiation profile matches well with that simulated for monoclinic-ZrO₂, in agreement with previous studies showing that more than 97% of the oxide in the thin lamella lifted out from a water-corroded Zr alloys is monoclinic [193]. Some peaks from the monoclinic phase are missing in the experimental spectrum as a result of the strong oxide texture [58, 65, 188]. With increasing damage from 0 dpa to 3 dpa, strong peaks from the monoclinic phase, e.g. (011)_m and (112)_m, decrease in intensity, and after 10 dpa all the peaks characteristic of the monoclinic phase have disappeared, Figure 10.8(b).

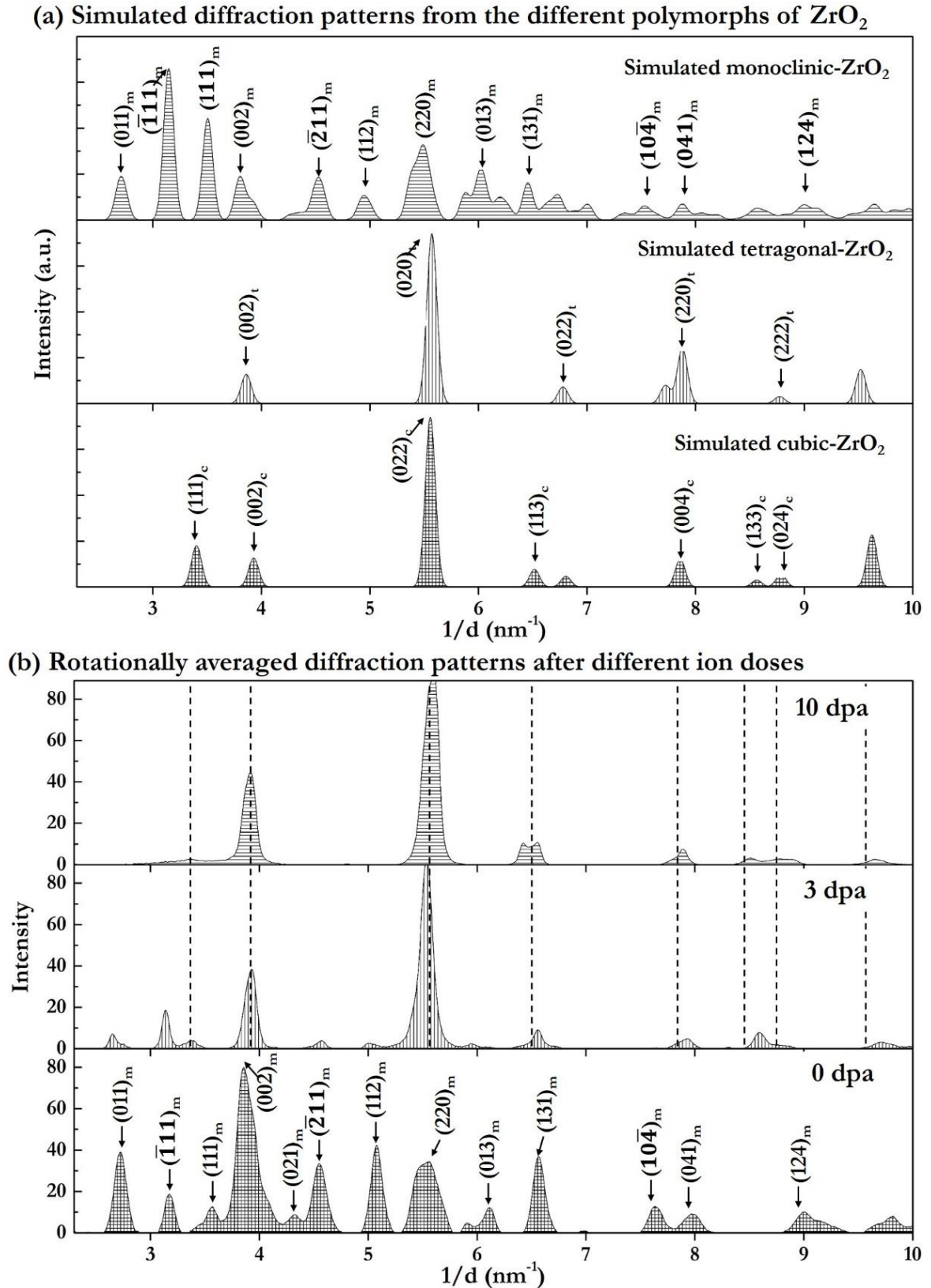


Figure 10.8 Electron diffraction profiles of (a) simulated crystals and (b) experimental patterns after specimens are irradiated by 700 keV Kr^{++} at 293 K to different damage levels; pre-irradiation, $5.6 \times 10^{15} \text{ ions.cm}^{-2}$ (3 dpa) and (c) $1.9 \times 10^{16} \text{ ions.cm}^{-2}$ (10 dpa)

This radiation-induced phase transformation can be followed by the evolution of these diffraction patterns, but there have previously been arguments in the literature about the crystalline nature of the product phase because the diffraction profiles from the tetragonal-ZrO₂ and cubic-ZrO₂ structures are very similar, Figure 10.8(a), with several peaks overlapping. A monoclinic-to-tetragonal transformation under ion irradiation has been reported by some authors [142, 145, 150-153], while others claim that the transformation is monoclinic-to-cubic [147, 154, 155]. To explore the crystalline nature of the product phase, we have thus analyzed the SAD patterns from a single grain in the irradiated zirconia together with measuring its lattice parameters through atomically resolved high angle annular dark field (HAADF) STEM images.

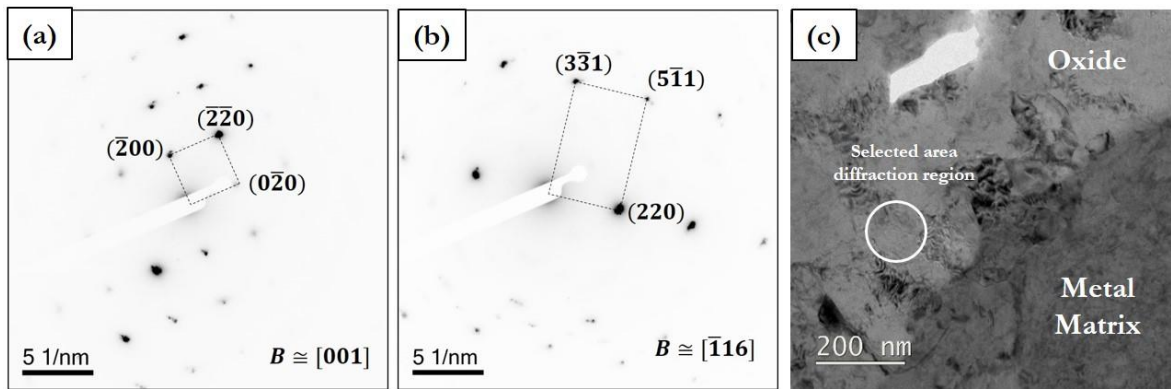


Figure 10.9 Two examples of SADs acquired at different tilt angles, (a) $T_x=3^\circ$, $T_y=-1.8^\circ$, (b) $T_x=-7.6^\circ$, $T_y=3.5^\circ$ and (c) the BF TEM image showing the corresponding SAD region from the oxides on the Zr-0.5Nb sample (A-16), 1.9×10^{16} ions.cm⁻² (10 dpa).

The methodology for unknown phase identification in TEM has been described in [361, 362], and relies on the acquisition of several diffraction patterns along different zone axis, and comparison of both these diffraction patterns and the tilt angles between them with the theoretical values from possible phases. Following this methodology, three SADs along selected zone axis were captured from a single grain in the post-irradiation specimen (10 dpa, 1.9×10^{16} ions.cm⁻²) by using the smallest selected area aperture (effective diameter ~130 nm). Two of the SADs and the associated bright field TEM images showing the

location from which the SAD was required are shown in Figure 10.9. The SADs in Figure 10.9(a) and (b) are indexed to be cubic zirconia with zone axes close to $[001]_{\text{cubic}}$ and $[\bar{1}16]_{\text{cubic}}$ respectively, separated by 13.26° and close to the experimental tilt angle between these two orientations of $\sim 12^\circ$. The identification of the cubic polymorph is further confirmed by atomically resolved high angle annular dark field (HAADF) STEM observations as shown in Figure 10.10. The lattice parameter measured from the atomic-resolution STEM image in Figure 10.10(b) is $5.15\text{\AA}$ in both directions and close to that reported in the literature of $5.09\text{\AA}$ for cubic zirconia [200].

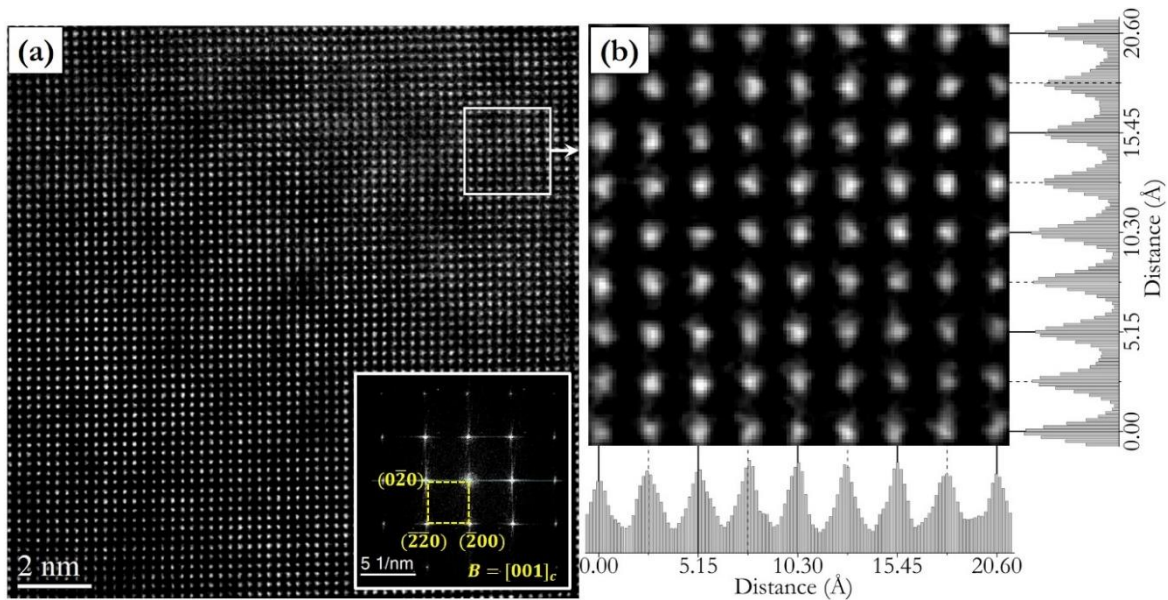


Figure 10.10 (a) Atomic-resolution HAADF STEM image from an oxide grain post-irradiation, $1.9 \times 10^{16} \text{ ions.cm}^{-2}$ (10 dpa), with corresponding FFT from the whole region, (b) direct measurement of lattice parameters based on the HAADF STEM images.

10.3.3.2. Phase fraction and grain size evolution under irradiation

The evolution in diffraction peak intensity is clearly dependent on damage dose, Figure 10.8(b), indicating that the irradiation-induced phase transformation behaviour is a function of accumulated defects. However, it is difficult from this SAD data to accurately extract quantitative values for the fractions of the different phases because factors such as variations in electron beam illumination and sample bending can also induce changes in relative peak

intensity. I have thus used TKD analysis on these ion-irradiated samples, which can generate statistical information simultaneously on grain morphology, phase and orientation.

Figure 10.11 shows pattern quality and phase maps of specimens in-situ irradiated to different doses at 293 K. The crystal structure information used here for TKD indexing is the same as we have used for SAD indexing, Table 3.2. In the pre-irradiation oxide film most of the small aligned columnar grains are found to be monoclinic-ZrO₂ as expected [58, 65, 188], and a small volume fraction (~2.5%) of tetragonal-ZrO₂ grains are found scattered throughout the oxide, Figure 10.11 (a) and (d). This tetragonal phase fraction is significantly lower than reported by bulk measurement techniques like laboratory and synchrotron XRD analysis where studies of oxide layers formed on similar alloys reported the tetragonal phase fraction to lie in the range 3–15% [22, 65]. The non-destructive nature of these measurements should preserve the stress state in the oxide, while stress relaxation is expected to occur during the preparation of thin TEM samples which may lead to transformation of some of the stress-stabilized tetragonal grains into the equilibrium monoclinic phase [297].

Both the grain morphology and the phase distribution are observed to change substantially under irradiation, and the volume fractions of indexed oxide phases at different doses are summarized in Table 10.1. After 4 dpa, the majority of the oxide film has already transformed into the cubic phase, and only a few surviving monoclinic-ZrO₂ grains can be seen, Figure 10.11 (e). After 10 dpa the volume fraction of surviving monoclinic-ZrO₂ is only 0.4%. A similar fraction of tetragonal phase is observed in both the 4 dpa and 10 dpa specimens, but instead of being observed as isolated grains like those in the pre-irradiation oxide, the tetragonal phase in the post-irradiation maps, Figure 10.11 (e) and (f), is mostly indexed as small clusters of a few isolated pixels within larger cubic-ZrO₂ grains, possibly as a result of mis-indexing. After 4 dpa, many small grains can still be seen in the regions

containing a mixture of c-ZrO₂ and untransformed m-ZrO₂, but after 10 dpa the average grain size has increased quite significantly, Figure 10.11(b and c). This kind of irradiation-induced grain growth behaviour has previously been reported in nanocrystalline c-ZrO₂ [359], but not in m-ZrO₂. From these observations, I suggest that the monoclinic-to-cubic transformation occurs in the early stages of irradiation, with small cubic grains being nucleated initially, and once the monoclinic to cubic transformation is complete then grain growth can proceed. The high-temperature c-ZrO₂ phase is supposed to be stabilized by a high density of irradiation-induced defects [74, 158] or free surfaces [363-365], both of which are available under these experimental conditions.

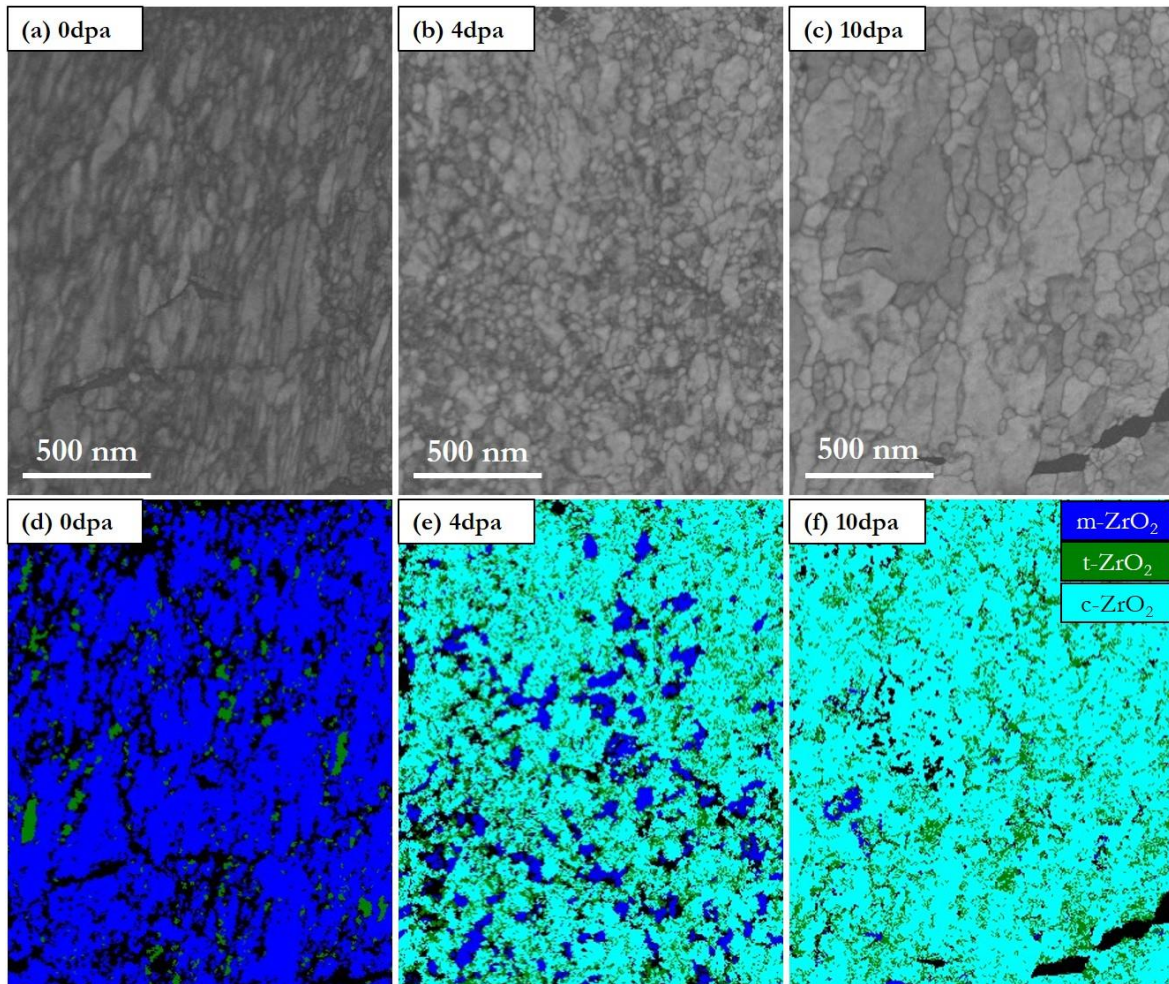


Figure 10.11 TKD pattern quality and phase maps from typical regions of in-situ irradiated oxides on the Zr-0.5Nb specimens (A-16). (a and d) 0 dpa, (b and e) 4 dpa, 7.4×10^{15} ions.cm⁻² and (c and f) 10 dpa, 1.9×10^{16} ions.cm⁻².

Table 10.1 TKD indexed phase fractions and grain size [366] measured at different doses

	0 dpa	4 dpa	10 dpa
monoclinic	97.5%	10.5%	0.4%
tetragonal	2.5%	4.1%	4.4%
cubic	0	85.4%	95.2%
Horizontal grain size (nm)	63±6	66±11	97±24
Vertical grain size (nm)	142±28	76±13	162±49
Aspect ratio (vertical/horizontal)	2.3	1.1	1.7

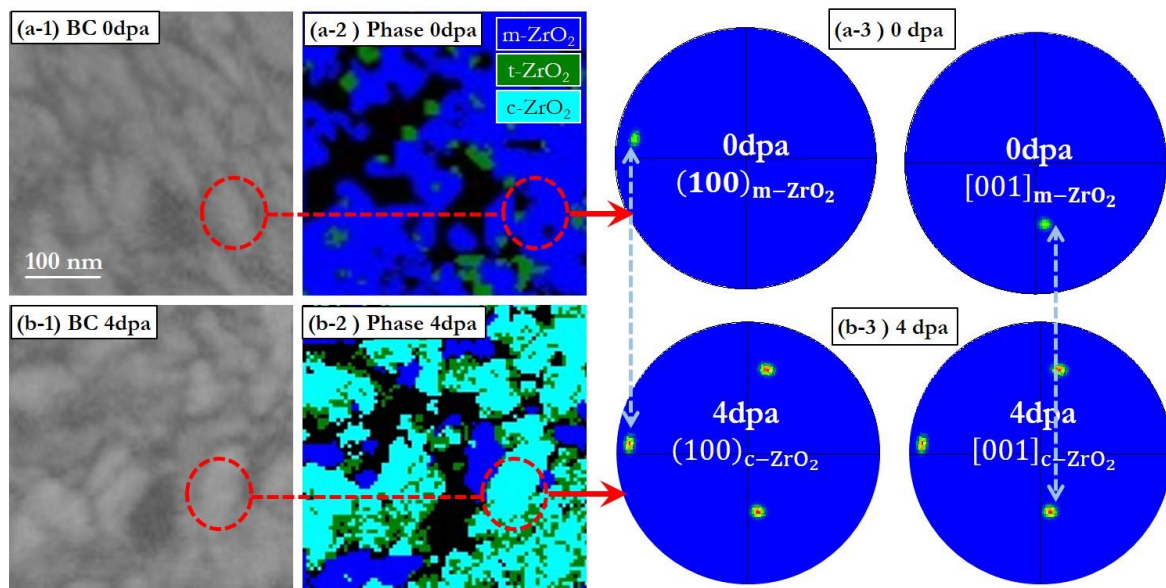


Figure 10.12 TKD pattern quality, phase maps and pole figures and stereographic projections (half width 5°) of the same region before and after in-situ irradiation. (a) 0 dpa, (b) 4 dpa, 7.4×10^{15} ions.cm⁻².

As well as providing information about grain and phase distributions, TKD also has the capability to analyze orientation relationships. The same region of oxide has been mapped by TKD before and after irradiation, and the corresponding pattern quality and phase maps are shown in Figure 10.12 along with orientation map for grains of both monoclinic and cubic ZrO₂. The alignment of low index poles of parent and product phases have been compared systematically in 3-dimensions to reveal their orientation relationships. Examples of contoured maps of the distribution of the (100)_c, [001]_c poles of cubic-ZrO₂ and the (100)_m, [001]_m poles of monoclinic-ZrO₂ are plotted in Figure 10.12(c) for the same grain before and post irradiation. Contoured pole figures from the whole region in the pre-irradiation

specimen and the post-irradiated specimen are shown in Figure 10.13. It can be seen that $(100)_m$ and $[001]_m$ are aligned with one of the corresponding poles or directions in the cubic- ZrO_2 , indicating a $(100)_m \parallel (100)_c$ and $[001]_m \parallel [001]_c$ crystallographic relationship in agreement with the prediction of Cayron et al. [367].

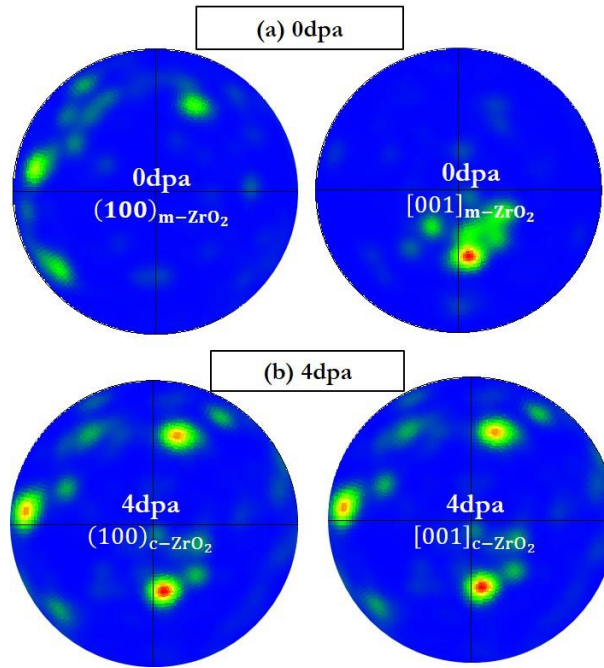


Figure 10.13 Contoured pole maps and stereographic projections from (a) (100) and $[001]$ monoclinic- ZrO_2 in the pre-irradiation specimen compared to (b) (100) and $[001]$ cubic- ZrO_2 in the post-irradiated specimen (4 dpa, $7.4 \times 10^{15} \text{ ions.cm}^{-2}$) from all the grains shown in Figure 10.12, half width 10° .

10.3.3.3. Irradiation-induced void formation

Figure 10.14 shows a set of Fresnel contrast images taken during the in-situ irradiation process. A high density of small void-like cavities (for convenience these will simply be called voids below) with an average diameter less than 0.5 nm begin to be detectable at 1 dpa, Figure 10.14(b). Continuous growth of the voids is seen with increasing dose, and at 10 dpa the average diameter is ~ 1.5 nm, Figure 10.14(c). Similar observations on the formation and growth of voids under ion irradiation have been reported in yttria-stabilized zirconia [368, 369] and other materials [370-372].

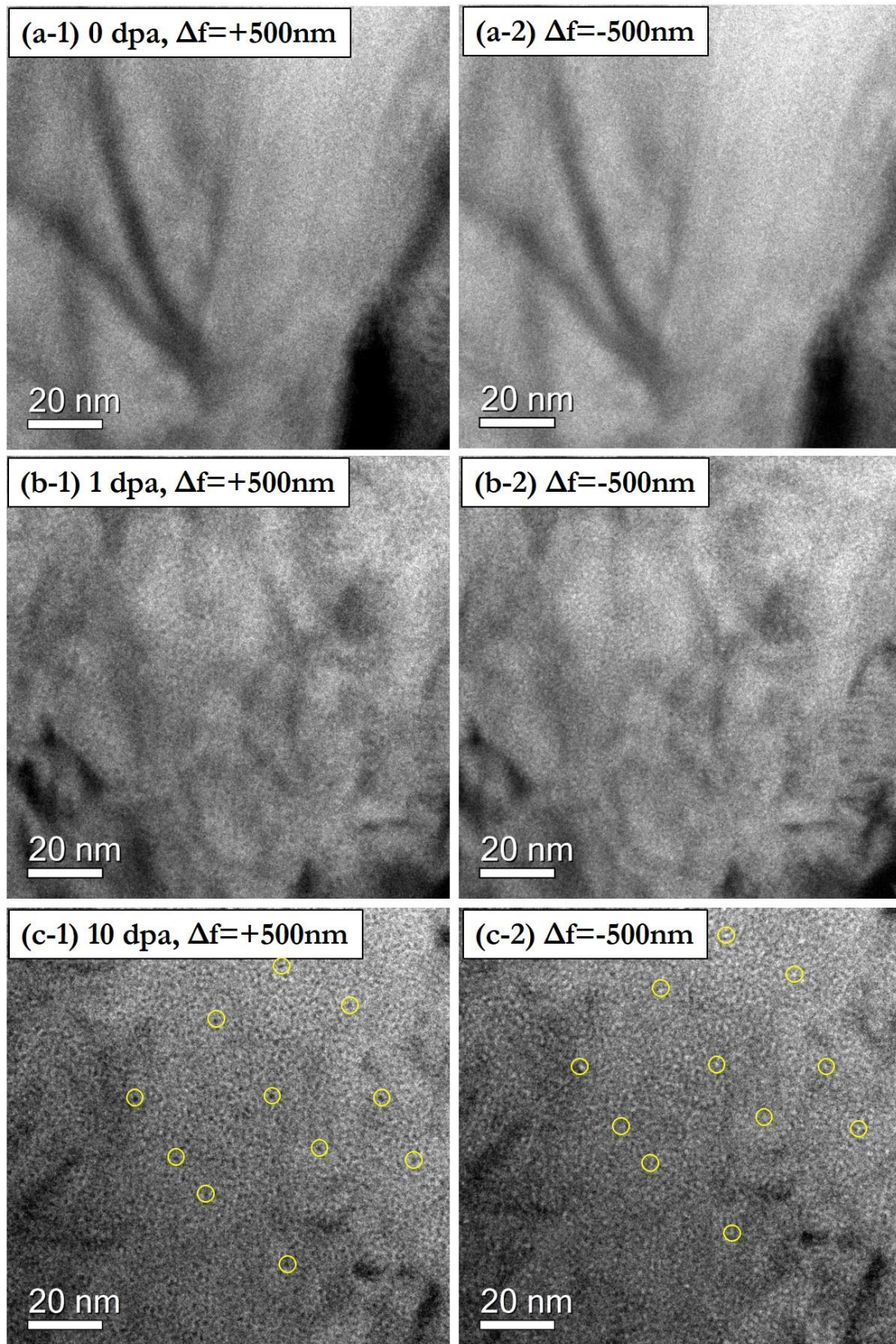


Figure 10.14 Fresnel contrast ($\pm 500 \text{ nm}$) bright field TEM images of the same region in the oxides on the Zr-0.5Nb specimen (A-16) showing distributions of voids at different in-situ irradiation doses; (a) 0 dpa, (b) 1 dpa, $1.9 \times 10^{15} \text{ ions.cm}^{-2}$ and (c) 10 dpa, $1.9 \times 10^{16} \text{ ions.cm}^{-2}$. Examples of voids are highlighted by yellow circles in both the overfocused and underfocused images of the 10 dpa sample.

Extended ion tracks can be produced in ceramics irradiated by heavy ions with energies of hundreds to thousands of MeV, but only in materials with relatively high electronic stopping powers [373]. In our study, the electronic stopping power is estimated by SRIM to be only ~ 0.3 keV/nm, and the incident ion energy is much lower, so I believe that these irradiation-induced features are voids rather than ion tracks. The formation of inert gas bubbles in materials irradiated with He or Kr has been reported previously [104, 134, 374] and have essentially the same behaviour under Fresnel contrast conditions, but the voids seen in this study do not contain sufficient gas to be classed as bubbles. Based on Fell and Murphy's calculation [375], at least 50 atoms are required to nucleate bubbles 0.5 nm in diameter. As mentioned earlier, more than 99% of the implanted 700 keV Kr^{++} ions will pass through TEM foils that are 15-50 nm in thickness. After a dose of 1 dpa (1.9×10^{15} ions. cm^{-2}) the residual concentration of Kr is estimated to be 0.005 at% and the ratio of the number of retained Kr ions to the number of observed voids can thus be estimated to be <1 , far below what is required to nucleate the features we observe. This is also confirmed by the energy dispersive X-ray (EDX) spectra in Figure 10.15 taken from two adjacent regions, one containing at least one void and the other avoiding all the obvious voids. The same analysis conditions (pixel size, dwell time and mapping area) are chosen so that these two spectra have similar background intensities. Ga peaks are observed due to Ga implantation during FIB sample preparation. Cu peaks are the result of fluorescence from the Cu-supporting grid. No detectable signal from Kr was observed, and the intensities of the Zr and O signals from the region covering the void features are $\sim 20\%$ lower than those from the nearby matrix. With an average void diameter of 1.5 nm and a foil thickness of 15 nm these observations could be explained by the superposition of two voids through the foil thickness.

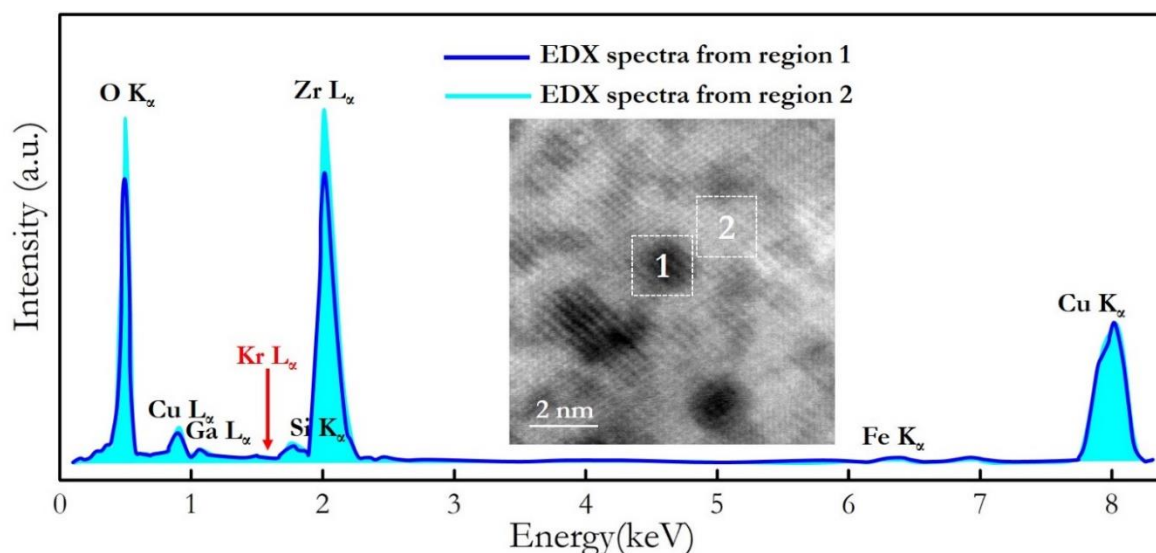


Figure 10.15 High-magnification HAADF image showing irradiation-induced voids and the corresponding EDX spectra from a void and an adjacent region of the matrix in the 10 dpa specimen (voids are darker in the dark field mode because the surrounding area has a higher average atomic mass).

10.3.3.4. Mechanisms of irradiation-induced phase transformation

Although a large number of point defects may recombine immediately after formation of a damage cascade, the remaining defects can lead to the accumulation of radiation damage and are a key parameter for understanding irradiation-induced processes, like the irradiation-induced void formation, phase transition and grain growth observed in the current study.

The results presented above confirm that nano-crystalline monoclinic-ZrO₂ grains in a thin TEM foil (~15-50 nm thick) are transformed into the higher symmetry cubic phase under in-situ ion irradiation, without any evidence for the formation of an intermediate tetragonal phase. The mechanisms of phase transformations between monoclinic and tetragonal or tetragonal and cubic zirconia upon deformation or thermal treatment have been widely studied [376-379]. Direct m-to-c transformation has only been observed under irradiation [147, 154, 155, 380], and is supposed to occur in a displacive manner [142, 148, 381], but the mechanisms controlling this displacive phase transition under irradiation are not clearly understood. To explore the nature of this transformation it is necessary to analyze the

orientation relationship between the two phases, predicted to be $(100)_m \parallel (100)_c$ and $[001]_m \parallel [001]_c$ [367], and also observed in this work. Figure 10.16 shows the reconstructed atomic arrangements of the (100) planes in the monoclinic and cubic phases respectively, and a high degree of coherency will be achieved at a $(100)_m \parallel (100)_c$ interface. Transformation from the monoclinic to cubic phase induces a strain of approximately -4.7% along the $[001]_m$ direction parallel with the $[001]_c$ direction and -2.7% along the $[010]_m$ direction. Since an angular misfit exists between the $[001]_m$ and $[100]_c$ directions ($\beta_m=99.25^\circ$ and $\beta_c=90^\circ$) a larger strain might be expected along $[100]_m$. In other words, the cubic-ZrO₂ structure could be obtained from the monoclinic phase by a uniform shear transformation along one of the principal axes, probably along $[001]_m$, of the monoclinic-ZrO₂ structure plus small contractions along the three principal axes.

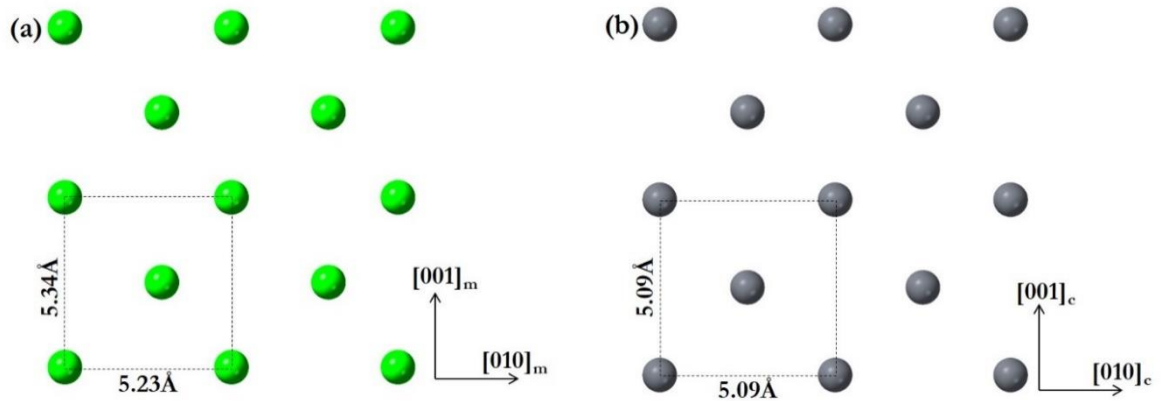


Figure 10.16 Reconstructed atomic arrangements (only Zr cations are shown) in the (100) plane of (a) monoclinic-ZrO₂ and (b) cubic-ZrO₂. The lattice parameters for the monoclinic phase are taken from [202] and for the cubic phase from experimental measurements in the current work.

10.3.3.5. Stabilizing mechanisms for cubic-ZrO₂

When irradiated by either 60 keV or 4 MeV Kr⁺⁺ at room temperature, bulk monoclinic-ZrO₂ has been reported to transform into a tetragonal phase [141, 152], but here monoclinic-ZrO₂ thin foils were seen to transform into the cubic phase. Both the tetragonal and cubic

phases are thermodynamically metastable at room temperature, so the obvious question is what is stabilizing these irradiation-induced metastable phases?

The stabilization of t- and c-phases of ZrO_2 by using substitutional cation dopants such as CaO , MgO and Y_2O_3 etc. have been widely studied [382-384]. Although a lot of studies have also been carried out to explore the stabilizing effect of Nb oxide in t- or c- phases of ZrO_2 , there does not seem to be much agreement. Ray et al [385]. reported that Nb oxide has a stabilizing capability, while Kim [75] and Li et al. [76] thought the addition of Nb oxide to be unfavourable for stabilization of the metastable ZrO_2 phases. In the current study, the oxides formed by water corrosion contains a small amount of Nb oxide (<0.5 mol%). I believe this small amount of alloying oxide will not be a primary factor stabilizing or destabilizing the metastable phase, and this possibility was not pursued here.

Both experimental and modelling results indicate that differences in surface energies of possible phases can favour the formation of a particular polymorph [363-365]. Modelled at 0 K, the surface energy of cubic- ZrO_2 is generally lower than that of tetragonal- ZrO_2 , e.g. 1193 mJ.m^{-2} for $(111)_{\text{cubic}}$ and 1315 mJ.m^{-2} for $(111)_{\text{tetragonal}}$ [386]. A major difference between a TEM thin foil (15-50 nm thickness) and bulk material is the strong influence of the free surfaces, and especially the additional surface energy contribution. The high-density of irradiation-induced voids also contributes significantly to the total surface energy in our samples. All these factors suggest that formation of the cubic phase may be favoured to reduce the surface energy when monoclinic- ZrO_2 thin foils are irradiated.

From modelling studies, Fabris et al. [158] and Raza et al. [74] have also shown that oxygen vacancies alone can stabilise the cubic phase at room temperature without the need for any cation doping. Anionic point defects generate stronger strain fields than Zr point defects [387], and the structural distortions around oxygen vacancies can affect the relative stability of the cubic phase [388, 389]. Incorporating oxygen vacancies at concentrations as low as 3

at% is suggested to stabilize the high-temperature cubic phase at room temperature [74]; a concentration that we can expect to achieve under in-situ ion-irradiation conditions. An attempt to quantify the concentrations of defect in irradiated zirconia has been carried out by Devanathan and Webb [390] using molecular dynamics simulations. In their simulations a 30 keV Zr recoil can create 0.0016 dpa and around 0.08 at% interstitials and 0.08 at% vacancies in the cascade. Most of these radiation-induced vacancies will recombine with interstitials and rapidly annihilate, but a steady state of ~ 0.002 at% vacancies (40% cation vacancies and 60% anion vacancies) is proposed [390]. If we assume that the concentration of vacancies at steady state increases linearly with the damage level, a concentration of 3 at% vacancies can be achieved at 3 dpa. An additional factor to consider is the effect of the strain induced by irradiation defects. Moll et al [391] have measured irradiation-induced strain as function of fluence in cubic-ZrO₂ irradiated by 4 MeV Au ions, and indicated that the small defect clusters formed in the low dose regime ($<10^{15}$ ions.cm⁻²) can lead to a sharp increase in elastic strain up to 0.5%. The local strain buildup during irradiation may also contribute to the stabilization of the cubic phase under our experimental conditions.

10.3.3.6. Mechanisms of void formation and grain growth

Irradiation damage in zirconia will create both cation Frenkel pairs ($Zr_i^{\bullet\bullet\bullet}$ and $V_{Zr}^{\bullet\bullet\bullet}$) and anion Frenkel pairs ($O_i^{\bullet}$ and $V_O^{\bullet}$). Calculations on fluorite structures such as UO₂, ZrO₂ and CeO₂ predict that the oxygen defects have significantly lower migration energies and hence higher mobilities than cation defects [137, 138]. For instance, the migration energies in cubic-ZrO₂ calculated by Aidhy et al [138] for $Zr_i^{\bullet\bullet\bullet}$, $V_{Zr}^{\bullet\bullet\bullet}$, $O_i^{\bullet}$ and $V_O^{\bullet}$ point defect are 5.9 eV, 6.2 eV, 0.7 eV and 0.3 eV respectively. Similar modelling results suggest that a system with completely separated vacancies has a very high energy and is not stable [139]. As a result, the formation of Schottky defects is favoured and lowers the system energy [136].

A Schottky defect in ZrO_2 involves two O vacancies and one Zr vacancy, and the evolution of randomly distributed vacancies into Schottky defects involves the diffusion of the mobile anion vacancies to the less mobile cation vacancies, $2V_{\text{O}}^{\bullet\bullet} + V_{\text{Zr}}^{\bullet\bullet\bullet} \rightarrow \text{Schottky defect}$. Simulations have shown similar evolutions of these vacancy clusters in CeO_2 and UO_2 [140, 392]. The Schottky defects may then lead to the nucleation of voids like those shown in Figure 10.14 and 10.15. These Schottky defects sequester vacancies, thereby making them unavailable for vacancy-interstitial recombination, and lead to an extra interstitial concentration leading either to the formation of interstitial clusters or a net flux of interstitials to any available defect sinks like the free surfaces or grain boundaries. Due to high migration energies of the interstitials [138], especially $\text{Zr}_i^{\bullet\bullet\bullet}$, they are rather immobile, and if they are created far enough from sinks, most of the surviving interstitials will exist as isolated defects or in small clusters (the modelling indicates the largest stable interstitial cluster in zirconia is consistently between 3 and 4 interstitials regardless of PKA energies [140]), which are difficult to image using TEM. Compared with the high density of vacancy clusters, interstitial clusters (e.g. dislocations) are rarely observed in these irradiated samples up to a fluence of $1.9 \times 10^{16} \text{ ions.cm}^{-2}$ (10 dpa) in the current study. These results are in agreement with those obtained in heavy ion irradiated nano-grain zirconia [141, 142].

Both simulations [393] and experimental studies [141] reveal that grain boundaries and free surfaces are effective sinks for irradiation-induced defects. The sink strength of a grain boundary can be described as $k_{\text{gb}}^2 = 15f(\theta, \gamma)/R^2$ [134], where $f(\theta, \gamma)$ is a function of grain boundary energy (γ), and misorientation angle (θ), and R is the grain radius. Clearly, the smaller the grain size, the greater the sink strength. When the grain size approaches the mean diffusion distance of defects created during the cascade events, the role of grain boundaries in the alleviation of radiation damage becomes significant, and as a result more defects will be absorbed by these sinks. Irradiation-induced grain growth behaviour has previously been

reported in nanocrystalline c-ZrO₂ [359], and has been described as a defect-driven mechanism resulting from the absorption of the cascade defects nearby the grain boundaries. This is a possible mechanism for the migration of grain boundaries and the associated grain growth I have shown in Figure 10.11.

10.3.3.7. Influence on in-service Zr alloys

It has been long known that the nanostructure of oxides formed on Zr alloys plays an important role in affecting their corrosion rates in service [188, 193]. Acceleration of the corrosion rate by up to factors of 6 has been reported as a result of neutron irradiation [96], but the mechanisms of this accelerating effect are still not well understood. The in-reactor acceleration has been correlated with specific in-reactor electrochemical conditions or irradiation-induced redistribution of alloying elements in the metal matrix [11, 394], but rather little attention has been paid to the influence of changes in the oxide microstructures. There are several factors we need to take into account when trying to relate our in-situ observations to more realistic damage conditions in service. Under typical in-reactor conditions the damage rate is of the order of 10^{-7} dpa/s [124], which is 4 orders of magnitude lower than that induced by ion irradiation in the current study. As discussed above, different surface energies can also favour the formation of a particular ZrO₂ polymorph, and the large surface areas associated with thin TEM foils may help stabilise particular structures in a way that cannot happen in bulk oxides. As a result, formation of the tetragonal phase instead of cubic phase may be favoured under in-reactor conditions in agreement with previous studies [103] stating that Zr oxides formed under in-reactor conditions contain a higher fraction of tetragonal phase compared with that formed in an autoclave.

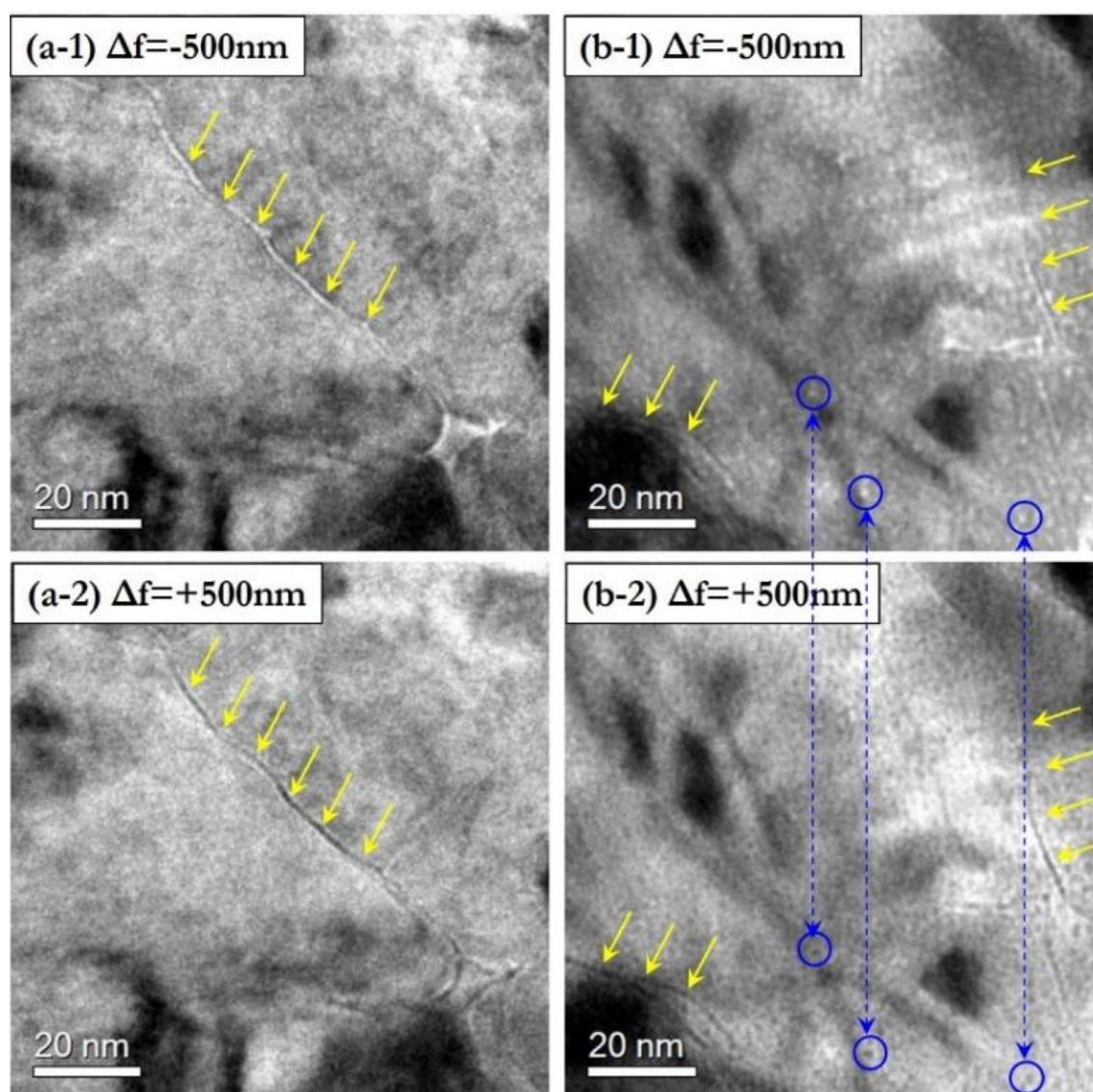


Figure 10.17 Fresnel contrast ($\pm 500 \text{ nm}$) bright field TEM images showing distributions of nano-porosity and voids in zirconia oxides formed on Zr alloys (a) 2000-day autoclave-corroded samples and (b) 2700-day in-reactor corroded sample ($10^{22} \text{ n.cm}^{-2}$, $\sim 8 \text{ dpa}$). Examples of grain boundary nano-porosity formed during corrosion are highlighted by yellow arrows and irradiation-induced voids in the grain interior by blue circles.

More importantly, in our experiments a high density of vacancies (and so clusters) can be formed at a very early irradiation stage, e.g. after $1.9 \times 10^{15} \text{ ions.cm}^{-2}$ (1 dpa) as shown in Figure 10.14(b). This damage level is achievable in high-burnups cladding materials, and an example of similar small vacancies clusters observed in the oxide on an in-reactor corroded Zr alloy is shown in Figure 10.17(b). These features are not observed in the autoclave-corroded samples after similar corrosion times, Figure 10.17(a), and so must be considered

to be the result of the irradiation. This evidence for the formation of mobile vacancies under both ion and neutron irradiation conditions is significant because calculations showing that diffusion of oxidising species can be enhanced by the presence of nano-pores/oxygen vacancies [136, 143, 395] and can provide a key mechanism to explain enhanced in-reactor corrosion rates.

10.4. Conclusions

I have used both in-situ radiation damage techniques and direct observations of ex-reactor materials to study radiation damage mechanisms in zirconium oxides. The following conclusions can be drawn;

1. Comparing ion and n-irradiated materials, I have observed the formation of oxides that are less well textured and with a more disrupted grain structure in-reactor, which I suggest to be a combination of irradiation-enhanced oxygen diffusion and also the direct effects of radiation on the oxide microstructure. In-situ ion-irradiation experiments reveal the susceptible nature of the ZrO suboxide to radiation damage which can generate high concentrations of defects at the oxide/metal interface that can then affect the nucleation and growth processes of new oxide grains, and lead to an increase of porosity and reduced cohesion between grains. As a result, oxides formed in reactor are more porous, less columnar and less textured – all of which can lead to enhanced in-reactor corrosion rates.
2. Irradiation-induced formation of voids, phase transformations and grain growth in monoclinic-ZrO₂ oxide scales on a model nuclear zirconium alloy have been confirmed, and all of these microstructural changes can be related to the evolution and interactions of irradiation-induced point defects. The formation of voids sequesters vacancies, thereby making them unavailable for vacancy-interstitial

recombination events and lead to a net flux of interstitials to be absorbed by defect sinks, e.g. grain boundaries, which will further lead to grain boundary migration and growth of the nanocrystalline grains.

3. More studies will be required to reveal the effects of in-reactor irradiation on the structure of Zr oxides, but the results reported above at least suggest that we must consider the possibility of radiation-induced stabilisation of metastable phases and formation of voids as one possible process that can occur in the oxides formed on in-reactor Zr alloys, which can enhance its corrosion rates and serve as one possible degradation mechanism limiting their in-service time.
4. The high-resolution transmission Kikuchi diffraction orientation mapping technique was used in combination with in-situ irradiation TEM for the first time in the current study. TKD can clearly show the evolution of grain size, texture and phase content in irradiated nanocrystalline materials, which is challenging for transitional TEM imaging as the grain boundaries may be no longer discernible owing to the large number of defects and the time-consuming nature of manual TEM orientation analysis. This combination has been shown to be a powerful method to probe the fundamental mechanisms controlling irradiation-induced microstructural evolution.

Chapter 11 Conclusions and Future Work

The broad aim of this work was to investigate the irradiation damage of oxide microstructure under irradiation. The main conclusions from each chapter are now summarized and used to form a theory for understanding the in-reactor oxide degradation mechanism and its effect on corrosion performance and hydrogen pickup. Finally, this chapter ends with suggestions for future work.

11.1. Conclusions

I have applied a range of high-resolution microstructure characterisation techniques to study the microstructure of zirconium oxides formed under different corrosion conditions. Based on the experimental observations, the following conclusions can be made:

- A thin layer of h-ZrO suboxide is observed in all the specimen characterized, not continuous in few cases, suggesting the aqueous corrosion of zirconium follows the pathway: $\alpha\text{-Zr} \rightarrow \text{h-ZrO} \rightarrow \text{ZrO}_2$. The transformation from $\alpha\text{-Zr}$ to h-ZrO follows a displacive mechanisms, and the suboxide grains can be equiaxed, plate-like or sawtooth-like depending on the orientation of the underlying $\alpha\text{-Zr}$ grain orientation. Alloying elements and impurities may also change the anisotropy of the interfacial energy, and further affect the suboxide grain morphologies. The equiaxed or plate-like grains may lead to a more uniform stress distribution, and thus the metal/suboxide interface of lower roughness compared with the sawtooth-like grains. The presence of this suboxide layer of different morphologies, plate or sawtooth-like, can affect the overall corrosion performance of Zr alloys by influencing the O/M interface roughness.

- The ZrO₂ oxide formed in an autoclave are observed with a similar texture on the model Zr-0.5Nb and commercial Zircaloy-4 alloys, with the $(10\bar{4})_{m-ZrO_2}$ parallel to the metal/oxide interface regardless of the underlying α -Zr orientations, and no specific orientation relationship was identified between h-ZrO and m-ZrO₂ or α -Zr and m-ZrO₂, which suggests that the formation of local oxide texture is not determined by the substrate texture. The nature of the formation of oxide texture is proposed to be related to the stress generated by the oxidation at the oxide/metal interface, since the oxide orientations (the preferred $(10\bar{2})_{m-ZrO_2}$ to $(10\bar{6})_{m-ZrO_2}$ planes for example) occupying a smaller area at the metal/oxide interface are favourable in order to reduce the compressive stress [88]. However, the oxide layers on model Zr-0.5Nb alloy contain more aligned columnar grains, while they tend to be more equiaxed on the commercial Zircaloy-4, which may be one of the factors responsible for the better corrosion resistance of the model Zr-0.5Nb compared with Zircaloy-4.
- The oxide microstructures formed in-reactor are more heterogeneous with a higher content of metastable tetragonal-ZrO₂, disrupted grain morphologies and less textured grains. All these in-reactor changes in oxide microstructures may facilitate the ingress of corroding species through the oxide layer and result in an accelerated corrosion rate. The heterogeneous oxide microstructure can be a combined effect of irradiation. The interfacial h-ZrO is observed to be susceptible to irradiation damage, perhaps by the accumulation of high concentrations of defects at the oxide/metal interface, which can affect the nucleation and growth processes of new oxide grains and further lead to an increase of porosity and reduced cohesion between grains. As a result, oxides formed in reactor are more porous, less columnar and less textured – all of which can lead to enhanced in-reactor corrosion rates. The direct effects of

radiation on the oxide microstructures were also confirmed, including irradiation-induced phase transformation and grain growth, which thus needs to be considered at high burnups in reactors. Another important observation is the irradiation induced vacancy clusters in both ion- and neutron-irradiated zirconium oxide samples. These small defects may also be responsible for the enhanced in-reactor corrosion rates as ab initio calculations suggest that diffusion of oxidising species can be enhanced by the presence of oxygen vacancies [136, 143].

- The role of oxide nano-porosity on hydrogen pick-up has been investigated experimentally and by modelling. Using TEM Fresnel imaging, the density of nano-pores in the oxide corrosion layers has been successfully quantified for the first time as function of both depth-position in the oxide and exposure time. The pore density obtained from quantitative measurements increases significantly towards the oxide surface. A clear correlation has been identified between the locations of small cracks/nano-pores (TEM Fresnel images) and hydrogen/deuterium trapping sites (NanoSIMS) in oxide films. The trapping sites may serve as transportation pathways of hydrogen/deuterium through the oxide films and contribute to the hydrogen pickup. The SPPs (e.g. the Zr-Nb-Fe type) in the oxide films do not show trapping effects for hydrogen. Combining the simulation results [143] and the present experimental observations, a possible mechanism of hydrogen pickup resulting from the oxidation of a metal by water has been drawn, and can be simply described as a three-step reaction. First, water molecules enter the oxide via the continuous interconnected nano-pipes/cracks in the outer layer of the oxide, and then dissociate to fill oxygen vacancies which leads to H atoms spontaneously forming molecular hydrogen. These hydrogen molecules dissociate spontaneously on suboxides into H

atoms and then diffuse into the interior of the unoxidized metal, finally forming thermodynamically stable zirconium hydrides.

- The distribution of deuterium in the in-reactor corroded Zr alloys and its oxides has been mapped using in-depth NanoSIMS analysis. The results indicate the $^2\text{H}^-/^1\text{H}^-$ ratios in both in-flux oxides and metals are higher by a factor of ~ 10 than that of the out-of-flux samples. The increasing content of the pickup deuterium in the metal matrix in the in-flux corroded sample may be due to irradiation-enhanced diffusion of deuterium ions, and also could be a result of more available transportation pathways for deuterium in the in-flux oxides. This thesis has demonstrated that NanoSIMS is a powerful technique for identifying the locations of hydrogen/deuterium in zirconium alloys and their oxides. The methodology using NanoSIMS to characterize with sub-micron resolution the 3D distribution of deuterium in zirconium alloy samples can also provide a useful tool in the analysis of the distribution of hydrogenic species in other engineering materials.
- In this thesis, TKD has been extensively used in the characterisation of zirconium oxides at the nano scale. To my knowledge, the TKD orientation mapping technique was used in combination with in-situ irradiation TEM for the first time. TKD can clearly show the evolution of grain size, texture and phase content in irradiated nanocrystalline materials, which is challenging for transitional TEM imaging. This combination has been shown to be a powerful method to probe the fundamental mechanisms controlling irradiation-induced microstructural evolutions.
- This thesis has also demonstrated several improved sample preparation methodologies, which have been proved to have the capability for preparing suitable samples for in-situ irradiation and NanoSIMS analysis, and can also be used to study other materials.

11.2. Suggestions for Future Work

In order to fully understand the in-reactor corrosion and hydrogen pickup mechanisms and to design better alloys for future cladding in nuclear reactors, some suggestions for future work are listed:

- The detailed roles of the h-ZrO in aqueous corrosion is not clear, as some of its key properties are not known, like its transport properties for either O or H, or the reaction rates of $\text{Zr} \rightarrow \text{h-ZrO}$ and $\text{h-ZrO} \rightarrow \text{ZrO}_2$ under different oxygen partial pressures. More experiments and modelling should be performed in this area.
- The sensitivity of the suboxide to irradiation damage can lead to phase changes and the accumulation of defects near the oxide/metal interface, which needs to be taken into account in the development of mechanistic models addressing radiation-assisted acceleration of corrosion rates in zirconium alloys.
- To better understand the evolution of oxides under irradiation, more experiments with different irradiation species, damage doses, dose rates and irradiation temperatures need to be performed. It would also be interesting to compare the responses of thin TEM foils and bulk oxide samples to irradiation.
- The role of alloying elements, e.g. Nb, Fe and Cr, in oxides during irradiation has not been precisely investigated. It is useful to carry out more experiments and modelling to reveal their interactions with irradiation-induced defects.
- The Nb-enriched β -Zr layers in CNL Zr-2.5Nb alloy play important roles during the corrosion processes. It will be useful to carry out isotopic tracer ($^2\text{H}^-$ and $^{18}\text{O}^-$) experiments in combination with SIMS to understand the specific roles of the Nb-enriched layers, e.g. their effects on the diffusion of oxidising species.

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