

Atomic-Scale Damage Induced in Zirconium Alloys by Neutron Irradiation, and the Effect on In-Reactor Corrosion



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Abstract

This thesis aims to understand the mechanisms of irradiation damage accumulation and in-reactor (in-pile) corrosion of cladding Zr alloys used in light water reactors using atomic- to μm -scale characterisation techniques, mainly atom probe tomography. These degradation mechanisms have been carefully studied in a range of valuable Zr alloys in the baseline, autoclave-corroded, irradiated, and in-situ irradiated and corroded conditions provided by collaborating company Westinghouse.

This thesis presents novel results that contribute to a deeper understanding of the degradation processes in Zr cladding materials in service. Direct evidence has been shown that both O and H segregate at and preferentially diffuse along the oxide grain boundaries, likely in the form of hydroxyl groups. During irradiation, Fe, Cu and other impurities are released from segregated sinks (second phase precipitates and grain boundaries), forming clusters and banding patterns in the bulk alloy. In-solution Sn and Nb are depleted to form Sn banding structures that are spatially out of phase with Fe bands, and growing Nb clusters, which I have shown to saturate at 40% Nb. At the same time, the Nb concentration in the cores of pre-existing β -Nb SPPs decreases from 90% to below 40% due to the intermixing of Zr atoms. The dose rate of neutron irradiation also affects the kinetics of these microchemistry changes, and for the first time it is observed that some of the Zr and Nb atoms transmute into Mo isotopes after severe irradiation, and that Li from the water chemistry can penetrate into the underlying metal and become trapped at irradiation-induced voids. During in-reactor corrosion, the oxidation front consumes the irradiated metal substrate. Most of the nano-scale solute segregation identified become randomly distributed once incorporated into the Zr(O) region, whereas Nb clusters can persist longer even after full oxidation, showing a

significant delayed oxidation behaviours like the pre-existing Nb-rich second phase precipitates.

These new results offer insights to the industrial partners developing of new alloys, and so contribute to the safe and more cost-effective operation of nuclear reactors. The sample preparation and data analysis methods developed in this thesis offer new approaches in the analysis with laser-mode atom probe tomography of H distributions in oxide materials and cluster analysis on peak-overlapping signals.

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谨以此献给我的家人和我的二十八岁。

19:38

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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 February 2023 and October 2025 under the supervision of Profs Chris G.M. Grovenor, Michael P. Moody and Paul A.J. Bagot. 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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International microscopy congress (IMC), Atomic-scale solute redistribution during high fluence neutron irradiation of a zirconium cladding alloy, **talk**, Liverpool, UK, August 2026.

TMS, Atomic-scale characterisation of the in-pile corrosion of ZIRLO and X2 Zr cladding alloys, **talk**, San Diego, USA, March 2026.

UK APT workshop, APT analysis of Nb clusters in the cladding Zr alloys induced by neutron irradiation, **talk**, Oxford, UK, November 2025.

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APT&M, Atomic-scale characterisation of irradiation damage in ZIRLO[®] alloy, poster Leuven, Belgium, September 2023.

Table of Contents

Abstract	ii
Acknowledgements.....	iv
Preface	vi
Table of Contents.....	ix
1. Introduction	1
2. Literature Review.....	4
2.1 Cladding Zr alloys	5
2.1.1 Zr properties	5
2.1.2 Alloy development	6
2.2 Irradiation	11
2.2.1 Microstructural defects	11
2.2.2 Microchemistry changes.....	13
2.2.3 Irradiation conditions.....	16
2.3 Corrosion	16
2.3.1 Cyclic corrosion.....	17
2.3.2 Corrosion of SPPs.....	23
2.3.3 Diffusion of corrosion species	24
2.3.4 Li accelerated corrosion.....	29
2.3.5 The O/M interface	32
2.3.6 In-pile corrosion	35
3. Experimental Methods.....	40
3.1 Materials	40
3.1.1 Baseline samples	41
3.1.2 Irradiated-only samples	42
3.1.3 Autoclave corroded Samples	43
3.1.4 In-pile corroded samples	45
3.2 Atom Probe Tomography	47
3.2.1 Field evaporation	49
3.2.2 Ion detection	50
3.2.3 Reconstruction	51
3.2.4 Laser-pulsed APT	52
3.3 APT data acquisition	53
3.3.1 Specimen preparation	53

3.3.2	Experiment design	58
3.4	APT data analysis	60
3.4.1	Voltage-based reconstruction.....	61
3.4.2	Mass spectrum analysis	62
3.4.3	Composition calculation	67
3.4.4	Cluster analysis.....	69
3.4.5	Trajectory aberrations	78
3.5	Other characterisation techniques.....	79
3.5.1	Electron Backscatter Diffraction	79
3.5.2	Energy-Dispersive X-ray Spectroscopy	79
3.5.3	Transmission Electron Microscopy	80
3.5.4	Secondary Ion Mass Spectrometry	80
4.	Baseline Zr alloys.....	82
4.1	Baseline W13 alloy.....	83
4.2	Baseline W10 alloy.....	90
4.3	Baseline X2 alloy	95
4.4	Baseline ZIRLO alloy.....	96
4.5	Discussion and conclusions	97
5.	Irradiation damage in Zr alloys.....	99
5.1	Irradiated W13 alloy	100
5.1.1	4.1 dpa	102
5.1.2	17.5 dpa	104
5.1.3	33.5 dpa	105
5.1.4	Composition analysis.....	108
5.1.5	W13 alloy summary	115
5.2	Irradiated X2 alloy.....	117
5.2.1	8 dpa	117
5.2.2	32 dpa	119
5.2.3	Composition analysis.....	121
5.2.4	X2 alloy summary	124
5.3	Irradiated ZIRLO alloy	125
5.3.1	8 dpa	125
5.3.2	16 dpa	125
5.3.3	24 dpa	125
5.3.4	32 dpa	127
5.3.5	Composition analysis.....	129
5.3.6	ZIRLO alloy summary	132
5.4	Discussion and conclusions	132
6.	Autoclave corrosion of Zr alloys	136

6.1	H ₂ O water corrosion	136
6.2	¹⁸ O-spiking	148
6.3	D-spiking	152
6.4	Discussion and conclusions	168
7.	In-pile corrosion of Zr alloys	170
7.1	Li ingress	170
7.2	Vogtle X2 alloy	186
7.3	Vogtle ZIRLO alloy	194
7.4	Discussion and conclusions	202
8.	Conclusions and future work	204
8.1	Conclusions	204
8.2	Suggestions for future work	209
9.	References	211

1. Introduction

Nuclear energy accounts for a substantial fraction of energy production, and new commercial nuclear reactors are being built in several parts of the world for electricity baseload and older plant being put back into operation to support the uninterruptable power needs of data centres. While benefiting from the reliable energy efficiency and output, the risks of fission power must not be neglected. As one of the most important materials in light water reactors (LWRs), Zr cladding alloys, in the reactor core, separate the nuclear fuel and coolant water. These tubes are the first barrier to escape of the fission products [1], and thus are significant to the safety of the whole nuclear plant.

By contacting the coolant water, aqueous corrosion forms an oxide layer on the outer surface of the cladding tube, which gradually becomes porous, providing limited mechanical support and resistance to further oxidation. H species from the dissociated water can diffuse through the oxide into the metal substrate and, once the ppm-level solubility limit at room temperature is exceeded, hydride precipitates can form which significantly embrittle the cladding. The cladding is also subjected to neutron irradiation, which accelerates the corrosion kinetics and introduces vacancies, dislocation loops and volume growth that undermines the structural stability. The combined effect of these factors degrades the cladding materials, posing a significant risk for operation of the whole reactor plant. The current strategy to mitigate this risk is early removal of the fuel rods to avoid cladding failure, but results in low burnup of the valuable UO_2 fuel, and generates unnecessarily high volumes of highly active waste that must be stored and disposed of.

The nuclear industry has endeavoured for decades to understand the irradiation damage and corrosion mechanisms to develop advanced Zr alloys that are more resistant in the service environment [2]. Because of the very fine scale of the microstructure in cladding alloys and

especially the oxide, high-resolution characterisation techniques to investigate cladding Zr alloys for many years. This thesis builds on the knowledge collected in previous DPhil projects at the University of Oxford by Drs Ni Na, Daniel Hudson, Jing Hu, Thomas Aarholt, Brian Setiadinata, Junliang Liu, Guanze He and Anne Callow. My project was also part of the Mechanistic understanding of Irradiation Damage in fuel Assemblies (MIDAS) Programme, involving the University of Manchester, Imperial College London, Westinghouse, Rolls-Royce, UK national nuclear laboratory (NNL), UK atomic energy authority (UKAEA) and EDF.

This thesis reports results primarily from atom probe tomography (APT), complemented by transmission electron microscopy (TEM), transmission Kikuchi diffraction (TKD), nanoscale secondary ion mass spectrometry (NanoSIMS) and nano-indentation carried out by my collaborators, to study a range of Zr alloys in different degraded states in order to understand the mechanisms of damage accumulation under irradiation and in-reactor corrosion at the atomic- to μm -scale. The chapters in this thesis focus on:

Chapter 2 reviews key findings about Zr cladding alloys and the mechanisms of degradation in irradiation and corrosion environments over the past decades.

Chapter 3 introduces the samples studied in this thesis, the arrangement of results in the following chapters, and consideration of APT experiments and data analysis.

Chapter 4 studies W13, W10, X2 and ZIRLO alloys in the baseline state, providing a starting point to compare with their degraded states.

Chapter 5 studies W13, X2 and ZIRLO alloys that have been subjected to neutron irradiation in the BOR-60 and Vogtle reactors. Comparison is made with their baseline states in Chapter 4 to understand the microchemistry changes and microstructural damage induced by neutron irradiation.

Chapter 6 studies oxides formed during autoclave corrosion to understand the microstructure and solute redistribution at the oxide/metal interface, and the in-diffusion mechanisms of corrosion species through the inner oxide during corrosion.

Chapter 7 studies X2 and ZIRLO alloys that have been in-situ irradiated and corroded (in-reactor/in-pile corrosion) in the Vogtle reactor to understand the degradation of cladding materials in the actual in-service environment and the potential effect of irradiation on the accelerated corrosion kinetic during in-pile corrosion.

Finally, **Chapter 8** summarises the results and contributions of this thesis and recommends future work that might be valuable to the nuclear industry.

2. Literature Review

Over the past few decades, nuclear energy has become an increasingly significant part of the global energy mix. In particular, nuclear power accounts for 12% of the electricity generated in the UK and 67% in France [3]. Most currently operating and planned commercial nuclear power plants are light water reactors (LWRs), which can be subdivided into boiling water reactors (BWRs) and pressurised water reactors (PWRs). The schematics for these two designs are displayed in **Figure 2-1**. The cooling water is circulated through the reactor core to absorb heat. This thermal energy is transferred to steam, which drives the turbine to generate electricity. BWRs directly use water in the reactor core to drive the turbines, while in PWRs, the cooling system (secondary circuit) is physically separated from the water in the primary circuit (primary water) to prevent the radioactive primary water contaminating structural components in the turbine. PWRs are the mainstream design for most of the current commercial fission nuclear reactors.

The nuclear reactor core, where the fission reaction occurs, consists of nuclear fuel and control elements. Uranium dioxide (UO_2) pellets are stacked end to end within the cladding tube to form a fuel rod, and hundreds of such fuel rods are bundled together to form a fuel assembly. The main role of cladding materials is to encapsulate fuel pellets and fission products, protecting them from the primary water, while enabling efficient heat transfer. The geometry of the PWR cladding tubes is usually tubes with 4 m in length, 10 mm in diameter, and 0.6 mm in thickness [4]. The cladding is exposed to highly corrosive environment of $\sim 300^\circ\text{C}$ temperature, 15-16 MPa pressure, and a high flux of neutron irradiation. Thus, the properties of cladding materials and their ability to withstand extreme in-service degradation are the key challenges for achieving higher fuel utilisation (defined as burnup in units of Giga Watt days per Metric Tonne of Uranium: GWd/MTU) and energy efficiency, which

reduces both the cost of the electricity generated and reduces the volume of highly active waste per MWh.

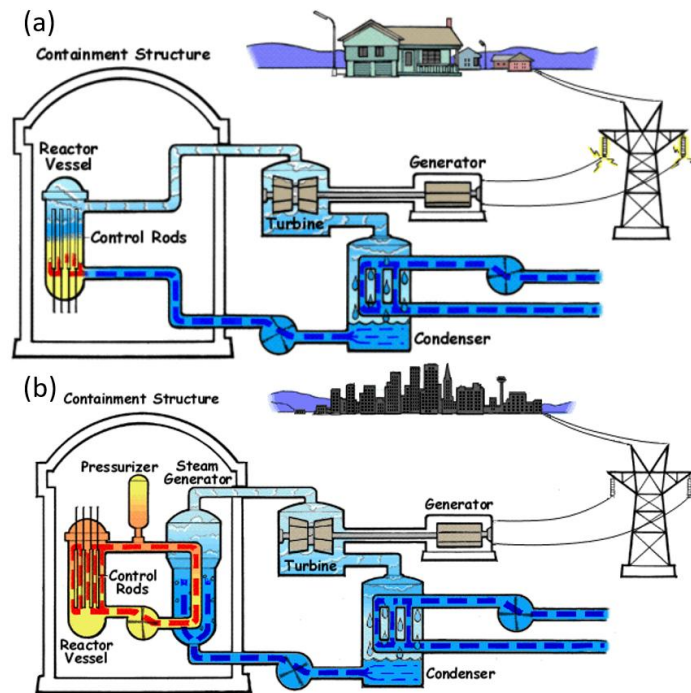


Figure 2-1. Simple schematics of (a) BWR and (b) PWR [5].

2.1 Cladding Zr alloys

Zirconium (Zr) alloys have been the most popular cladding material since the 1950s because of their outstanding neutron transparency, and an acceptable combination of mechanical properties and corrosion resistance [6]. To understand the degradation mechanisms of Zr alloys and improve the material design, a fundamental understanding of the metallurgy of Zr alloys is essential.

2.1.1 Zr properties

Zr is the 12th most abundant element on the Earth's crust and is primarily found in the minerals zircon (ZrSiO_4) and baddeleyite (ZrO_2). These natural sources contain ~2% of hafnium (Hf) which has a neutron adsorption cross section 1000 times greater than that of Zr. Zr also has strong affinities for hydrogen, oxygen and nitrogen, and trace amounts of

these elements will significantly affect the chemical and mechanical properties. Considerable costs are spent during processing to eliminate these elements [7].

Pure zirconium exists as α phase with hexagonal closed packed (HCP) structure at lower temperature, transforms to β phase with body centred cubic (BCC) structure above 850 °C, and becomes liquid phase above around 1850 °C [8]. The HCP structure has lattice parameters of $a=0.323$ nm and $c=0.515$ nm, with a slightly low c/a ratio of 1.593 (the ideal ratio is 1.633). The highest atomic density per unit area is on the prismatic plane, and prismatic $\langle a \rangle$ type slip (1-100) [11-20] is the dominant deformation system. The β to α transformation on cooling follows the Burger's relationship of $\langle 111 \rangle_{\beta} \parallel \langle 11-20 \rangle_{\alpha}$ and $(110)_{\beta} \parallel (0001)_{\alpha}$ [9].

2.1.2 Alloy development

The lifetime of the cladding materials limits the fuel utilisation in a PWR. Out of safety concern, less than half of the fuel can be utilised before prematurely becoming nuclear waste. Also, the refuelling process requires outgassing and suspension of reactor operation [10], leading to huge economic losses. Therefore, for decades the nuclear industries have been endeavouring to develop more robust Zr alloys by modifying alloying elements, and thermomechanical processing routes, to potentially prolong the lifetime.

Cladding-coolant aqueous corrosion is the major degradation mechanism of the cladding. The corrosion resistance of pure Zr is poor, however it can be substantially improved with addition of almost any element [11]. Two alloy systems were initially developed in the 1950s, Zr-Sn alloys, Zircaloy-1 to Zircaloy-4 (denoted as Zr-x hereon) [6], and Zr-Nb alloys, E110 and E635 [12, 13]. Sn was originally introduced to mitigate the detrimental effects of N [4]. It can also improve the strength and creep resistance by solid strengthening in α -Zr [14], but is kept at ~ 1 wt% to avoid formation of intermetallic precipitates. Sn solubility in α -Zr

decreases from ~8.2 at% at 900 °C [15] to 5 at% at 300 °C [16], and the addition of less than 1 wt% Sn should be fully soluble in the α -Zr matrix. Low levels of Fe also provide corrosion resistance in lithium hydroxide solutions [17], even though very limited Fe can exist in solid solution in the α -Zr matrix. Nb significantly improves the corrosion resistance because the Nb⁵⁺ oxidation state in the Zr oxide acts as n-type dopant that can reduce the oxygen vacancies and thus limit the in-diffusion rate of oxygen ions through the existing oxide layer. When exceeding the solubility in α -Zr of ~0.4 wt%, Nb forms β -Nb and, with the addition of Fe, Zr(Nb,Fe)₂ second phase precipitates (SPPs) [4], which are more noble than the surrounding Zr matrix showing delayed oxidation and providing improved corrosion resistance. Nb also has a low neutron cross section of 1.15 barn [12].

With this understanding, the ZIRLO[®] alloy [17] was developed by Westinghouse during the 1970s-1980s to achieve better corrosion resistance while maintaining the strength and dimensional stability. This alloy currently serves in the majority of the PWRs [6]. Lower Sn content can result in better corrosion performance [18], so with the aim of retaining the favourable performances of ZIRLO alloy while increasing the corrosion resistance, the Sn content was reduced from 1 wt% to 0.67 wt% in Optimized ZIRLOTM alloy [19]. Some variant alloys were also developed based on the suggestion that other elements have the potential to contribute to extra corrosion resistance, including Cu in the HANA-6 alloy [20], and V and Mo (provided the formation of ZrV₂/ZrMo₂ SPPs) [17, 21, 22]. M5 (Framatome) became another popular alloy choice in the early 1990s [23], and AXIOM[®] alloys (X1, X2, X4 and X5, Westinghouse) were developed more recently as the next generation cladding alloy aiming for very high fuel duties, with improvements in corrosion resistance, hydrogen ingress, and structural stability [24, 25]. AXIOM[®] alloys show substantial improvements in both corrosion resistance and structural stability under irradiation in comparison with ZIRLO alloy as shown in **Figure 2-2**. The nominal composition of the common Zr alloys is

shown in **Table 2-1**. ZIRLO alloy, X2 and two variants of alloys with Cu and V additions were studied in this thesis, details are in **Section 0**

Baseline samples.

Table 2-1. Nominal composition of Zr alloys (wt%)							
Alloys	Sn	Nb	Fe	Cr	Cu	V	Ni
Zircaloy-2	1.5	-	0.14	0.1	-	-	0.05
Zircaloy-4	1.5	-	0.14	0.1	-	-	-
E110	-	1.0		-	-	-	-
E635	1.2	1.0	0.35	-	-	-	-
ZIRLO	1.0	1.0	0.1	-	-	-	-
Low-Tin ZIRLO™	0.67	1.0	0.1	-	-	-	-
M5	-	1.0	-	-		-	-
X1	0.3	0.7-1	0.05	-	0.12	0.2	-
X2	-	1.0	0.06	-	-	-	-
X4	-	1.0	0.06	0.25	0.08	-	-
X5	0.45	0.7	0.35	0.25	-	-	0.05

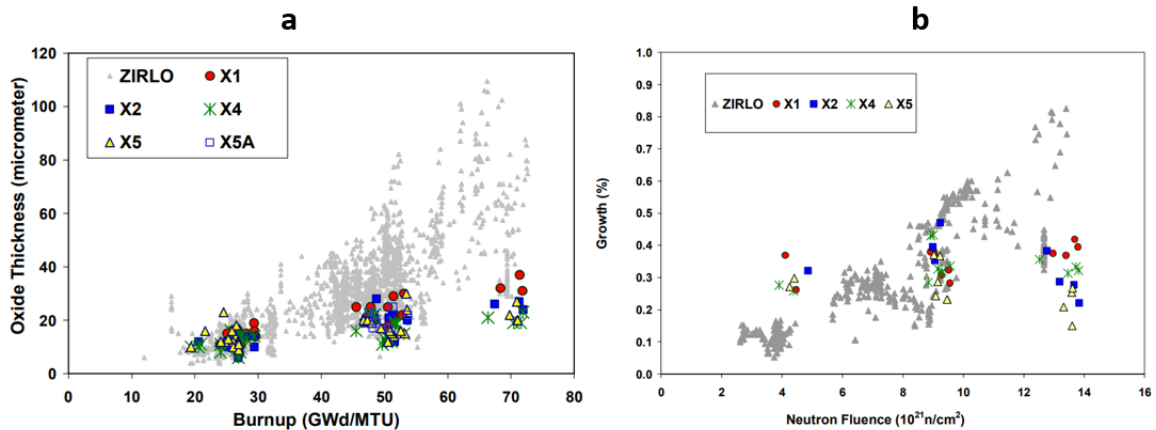


Figure 2-2. Degradation of AXIOM alloys in comparison with ZIRLO alloy. (a) Oxide thickness during the in-pile corrosion as a function of burnup. (b) Irradiation induced growth as a function of neutron fluence [25].

Processing

Common steps for processing Zr alloy tubes can be summarised as: 1. **Melting of Ingot**. 2. **Forging** to billets for hot extrusion. 3. **Hot extrusion** to form the tube-shell shape. 4. **Homogenization** at β phase temperature close to 1050 °C to allow all alloying elements dissolve into the β matrix. 5. **β quenching** in water. 6. **Cold work** to reduce grain size

(rolling for sheets, and pilgering for tubes). 7. **Final annealing** to determine the grain morphology and the SPP size. A stress-relieve annealing (SRA) at 450-500 °C (Zr-Sn alloys require higher temperature than Zr-Nb alloys) can only release part of the internal stress induced by deformation, leaving the material strong but brittle, while recrystallized annealing (RXA) at above 560 °C eliminates all the cold work and allows grains recrystallize into an equiaxed morphology, resulting in ductile material with strength lower than that for SRA condition [4]. **Figure 2-3** shows the final microstructure of elongated grains after SRA and more equiaxed grains after RXA.

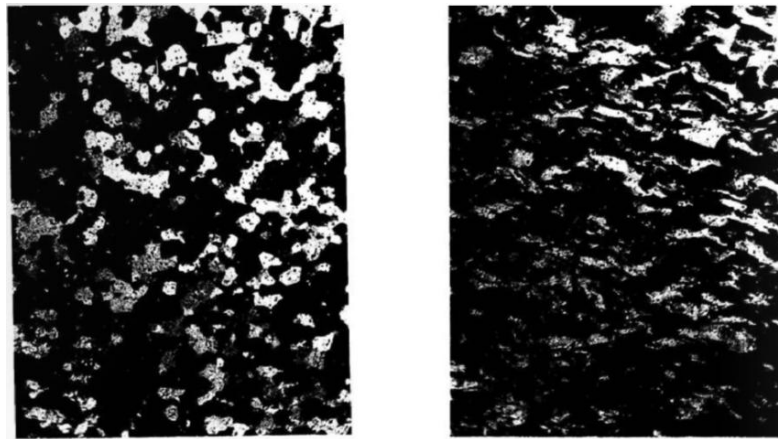


Figure 2-3. Optical images of microstructure of Zircaloy tube annealed for 2 hours at 580 °C (RXA, left) and 480 °C (SRA, right) [4].

Second Phase Precipitates

Only limited concentrations of solute atoms can be retained in solid solution in the α -Zr matrix, and any supersaturation of solutes results in segregation to grain boundaries (GBs) and dislocations [26], but mostly the formation of precipitates of different phases (SPPs), which will behave differently with α -Zr matrix when subjected to corrosion and irradiation. Sabol et al [17] suggest that longer annealing times allow the supersaturation of solutes in the matrix formed during the β quenching to reach equilibrium concentrations, and that this improve the corrosion resistance, **Figure 2-4**. However, longer annealing coarsens the SPPs and deteriorates the corrosion performance [17]. Therefore, the annealing process should

aim for the balance of equilibrium matrix concentrations and moderate-size SPPs, and thus the best corrosion resistance, as shown by the intersection of curves in **Figure 2-4**.

Proff et al [21] summarised the SPP types and crystal structure seen in common Zr alloys. The Zircaloy-4 alloy only has Zr(Fe,Cr)_2 Laves phase SPPs (C14 structure). ZIRLO[®] and X2 alloys have Zr(Fe,Nb)_2 Laves phase (C14 structure) and $\beta\text{-Nb}$ (BCC) SPPs. Normally the Laves phase SPPs are larger than $\beta\text{-Nb}$, but $\beta\text{-Nb}$ has a larger number density [27]. Not surprisingly, the Zr-0.5 wt% Nb (denoted as Zr-xNb hereon) alloy contains much less $\beta\text{-Nb}$ SPPs than Zr-1Nb, but still shows much improved corrosion resistance compared to Zr-4 (no Nb), indicating that the Nb in solid solution, rather than Nb in SPPs, plays the major role in corrosion resistance [17]. Indeed, the SPPs only account for limited volume fraction of the materials (less than 3%), and the corrosion process is mostly the consumption of the $\alpha\text{-Zr}$ matrix.

The clear importance of the distribution of solute and SPPs in Zr alloys means that it is important to be able to analyse these microstructural features, and this will be a major focus of the work reported in this thesis.

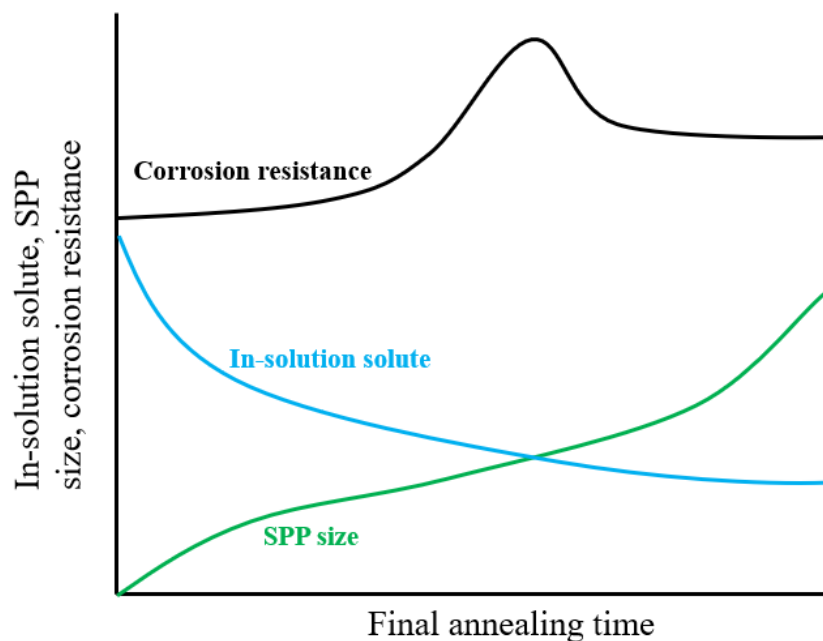


Figure 2-4. Schematic of in-solution solute concentrations, SPP size, and corrosion resistance as a function of annealing time. Reproduced from [17].

2.2 Irradiation

In service as fuel cladding materials, very high fluxes of fast neutrons released during the fission reaction collide with the Zr metal lattice, causing cumulative irradiation damage. This introduces a substantial number of microstructural defects and alters the microchemistry of the metal matrix. There is a considerable literature on these effects in commercial cladding alloys.

2.2.1 Microstructural defects

As shown in **Figure 2-5**, primary collisions happen when the incident neutron collides with and knocks out an atom. This primary knock-on atom (PKA) inherits high kinetic energy from the incident neutron and continues to collide and knock out the surrounding atoms, causing damage cascades. This process continues until the cascade fades out when the energy of each displaced atom is lower than displacement threshold so they are unable to generate further knock-outs [28]. The knocked-out atoms then come to rest as self-interstitial atoms leaving a vacancy at its original lattice position. As numerous such displacement events occur simultaneously, these point defects agglomerate together forming nm-scale defects like voids [29], solute clusters [30] and dislocations [31], causing macroscopic changes like irradiation-induced growth (IIG) [32] and embrittlement [33] that undermine the cladding integrity.

The lower migration energy of interstitials than the vacancies in Zr alloys during irradiation suppresses the formation of voids but enables the migration of interstitials forming dislocation loops [34, 35]. Two types of dislocations are normally observed in irradiated Zr alloys, known as $\langle a \rangle$ and $\langle c \rangle$ type dislocation loops depending on whether they lie on prismatic or basal planes, as shown in **Figure 2-6**. $\langle a \rangle$ type dislocation loops (~5 nm in diameter [36]) form nearly at the beginning of irradiation [37], and gradually grow and line

up on the basal plane as $\langle a \rangle$ loop rafts [30] (**Figure 2-7(a-c)**). Much larger $\langle c \rangle$ loops (50-200 nm) start to form after ~ 5 dpa (displacements per atom) [36] (depending on different alloys, irradiation condition, etc), which grow both in size and density at higher dose [38] (**Figure 2-7(d-e)**). The initiation of $\langle c \rangle$ loops normally correlates with the onset of the accelerated irradiation-induced growth (breakaway growth) [39].

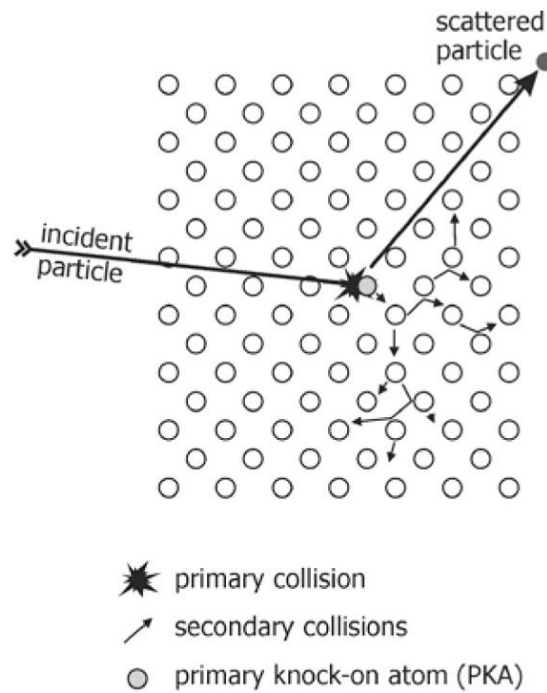


Figure 2-5. Schematic illustration of interactions between incident particle and crystal materials [28].

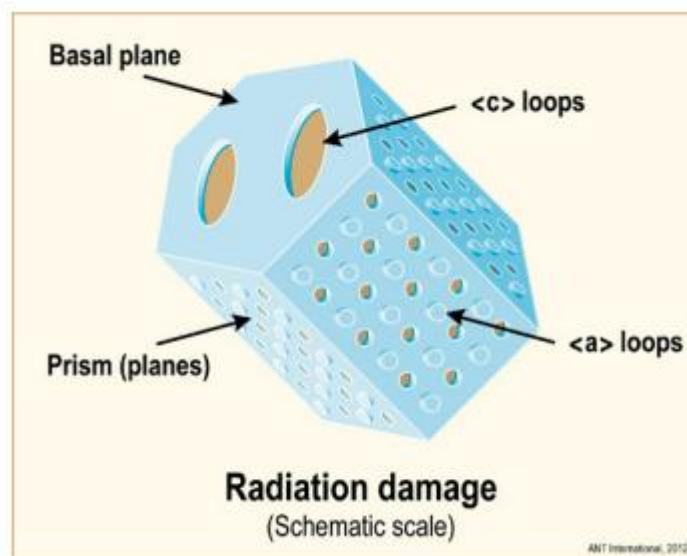


Figure 2-6. Schematic diagram of $\langle a \rangle$ and $\langle c \rangle$ dislocation loops in HCP structure.

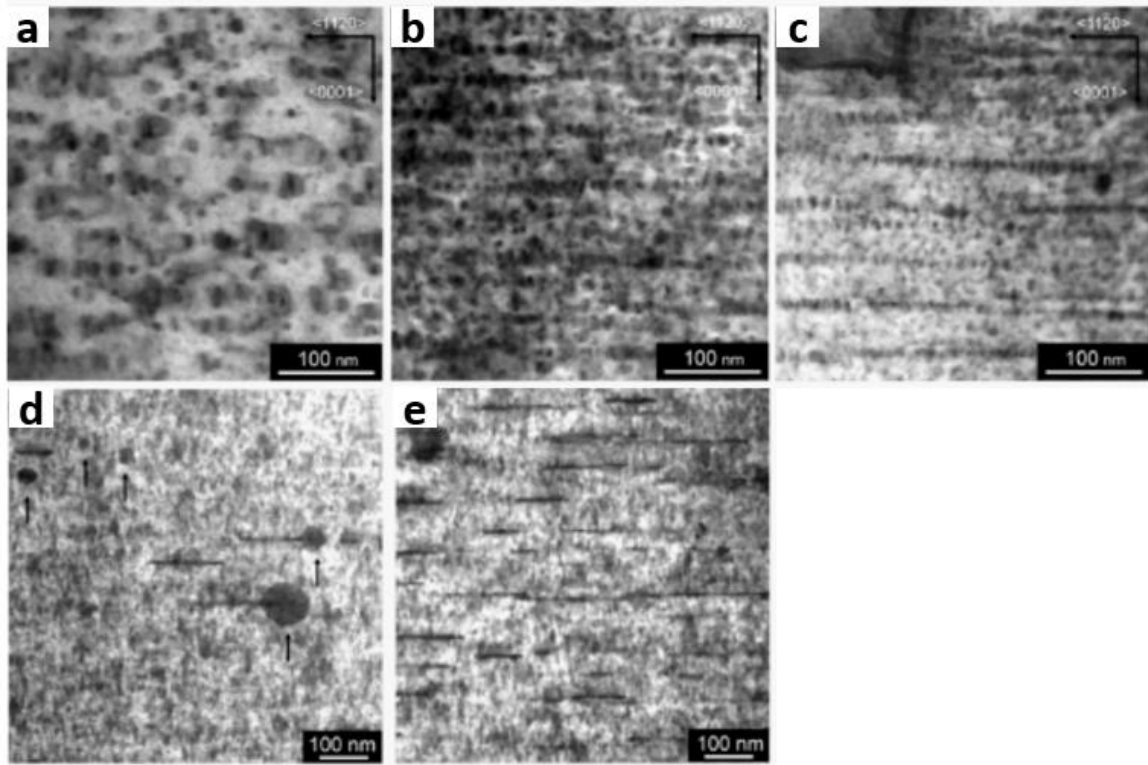


Figure 2-7. Transmission electron microscope (TEM) bright-field images of dislocations on Zr-2 alloy after proton irradiation. (a-c) $\langle a \rangle$ loops at 2.3, 4.7 and 1.0 dpa. (d and e) $\langle c \rangle$ loops at 4.7 and 7.0 dpa [40].

2.2.2 Microchemistry changes

Before irradiation, most of the Sn, and some of the Fe, Nb and other trace elements are in solution in the matrix, with the rest enriched in sinks including SPPs, GBs, etc. Solutes knocked-out from their original positions during irradiation need to redistribute to new energy-favourable sites in the irradiated metal matrix where a large number of lattice defects have been created.

SPPs

STEM images from Harte et al [30] in **Figure 2-8** show that Fe and Cr are released from a Zr(Fe,Cr)_2 SPP in Zr-2 alloy to the surrounding matrix after neutron irradiation, and the SPP gradually becomes amorphous. He et al [32] showed that, in Zr-Nb type alloys, instead of losing Nb into the matrix, β -Nb SPPs are intermixed with Zr and coarsen during irradiation,

and the BCC crystal structure can be maintained to 40 dpa [38, 41, 42]. These indicate that β -Nb SPPs are more stable under irradiation.

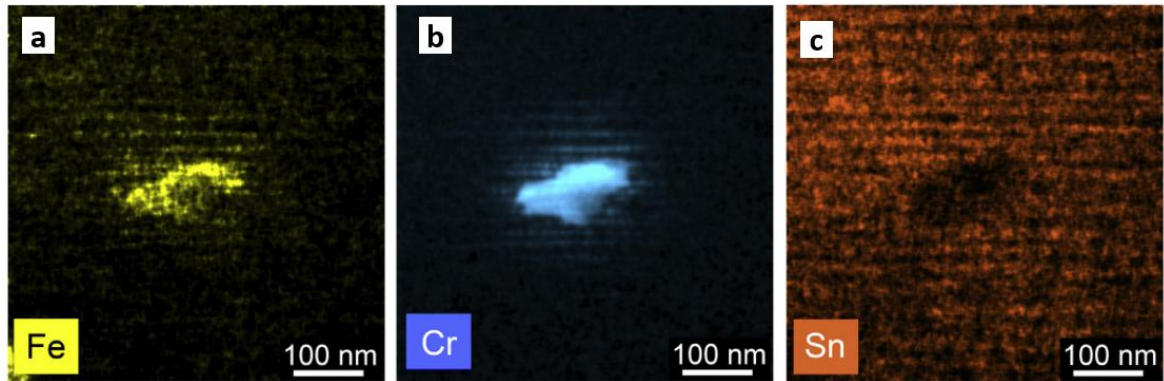


Figure 2-8. STEM-EDS images of a $\text{Zr}(\text{Fe,Cr})_2$ SPP in Zr-2 alloy after 15.8 dpa neutron irradiation [30].

Solute clusters and bands

Many atom probe tomography (APT) [43, 44] and TEM studies [43] have shown the formation of nm-scale solute clusters after irradiation, possibly due to the anisotropic diffusivity of solutes along the $\langle a \rangle$ and $\langle c \rangle$ directions in the α -Zr matrix [45]. Nb and Fe clusters formed in a Zr-2.5Nb alloy at 1.9 dpa are shown in **Figure 2-9**. These clusters have two compositions that are similar to those of the β -Nb and Laves $\text{Zr}(\text{Nb,Fe})_2$ SPPs in this alloy, suggesting similar thermodynamics of the formation of clusters and SPPs [46]. **Figure 2-10(b)** clearly shows Fe segregation on $\langle a \rangle$ loops, and similar observations of solute segregation on $\langle a \rangle$ loops have been reported [47, 48]. It is likely solute clusters are also related with $\langle a \rangle$ loops or the strain field around the loops. These clusters are relatively small and randomly distributed at lower doses, and grow larger and align on the basal plane at higher doses to give the characteristic solute bands, as shown in **Figure 2-10**.

Solute bands are observed in irradiated Zr-2 [29] (**Figure 2-8** and **Figure 2-10**) and ZIRLO alloys [49]. In **Figure 2-8**, it is evident that Fe and Cr released from the Laves phase SPP and the in-solution Sn are forming this banding. Interestingly, Sn banding is usually out of

phase with the banding of other solutes (Fe, Cr, etc) [30, 49]. These bands are spatially correlated with $\langle a \rangle$ loop rafts at lower dose, and $\langle c \rangle$ loops at higher dose on the basal planes [30, 44, 49]. It is thus reasonable to consider that these irradiation defects are the sinks for solutes to form bands. Full understanding of the redistribution behaviour of these elements during irradiation is essential to study the mechanisms of the formation of these bandings.

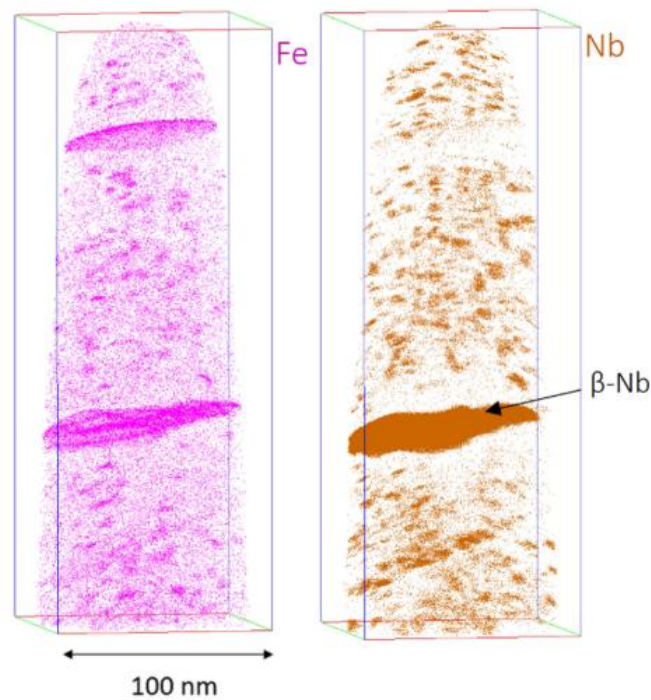


Figure 2-9. APT images of Nb and Fe clusters in Zr-2.5Nb irradiated to 1.9 dpa [46].

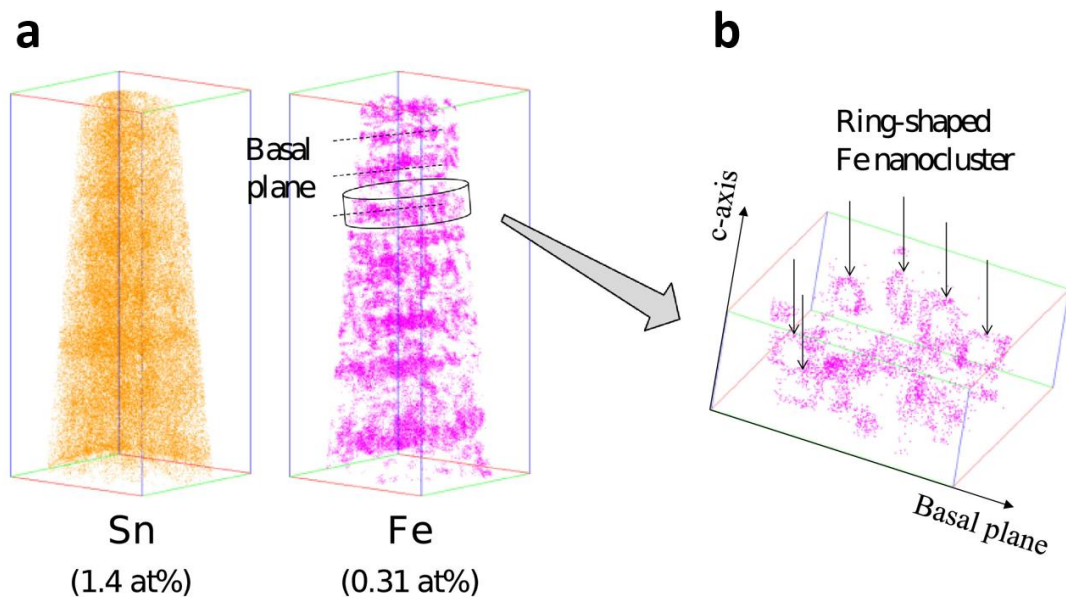


Figure 2-10. APT result showing (a) Sn and Fe bands on the basal plane, and (b) the observation of one specific Fe band, consisting of several Fe ring segregations in a modified Zr-2 alloy irradiated to ~ 30 dpa [48].

2.2.3 Irradiation conditions

Due to the rarity of neutron-irradiation materials and the significant costs for handling them, proton and ion irradiated samples were often studied as a proxy for in-service irradiated conditions. They have the advantages of shorter radioactive period and higher flux rate, enabling access to samples with variable irradiation doses and conditions in days. The irradiation damage profile with depth is normally created and transformed into dpa using Stopping and Range of Ions in Materials (SRIM) programme [50, 51].

However, during irradiation, there is a competing mechanism between irradiation-induced displacements and temperature-dependent back diffusion to the original position of atoms (recovery) [52]. The lower dose rate of neutron irradiation ($10^{-8} - 10^{-7}$ dpa/s comparing with 10^{-3} dpa/s for ion irradiation [53]) means there would be a much longer recovery time under real in-reactor conditions [38]. So the chemistry of SPPs and the matrix may be more stable in-service and the formation of microstructural defects may be slower than suggested by proxy irradiation experiments at same irradiation doses. There is currently no agreement on the accurate conversion between neutron and proton/ion irradiation damage, and different irradiation species and conditions cause disparate results [28], therefore, it is essential to study materials that have been subjected to neutron irradiation. This thesis has detailedly studied in-reactor neutron irradiated W13, X2 and ZIRLO alloys in **Chapter 5 Irradiation damage in Zr alloys**.

2.3 Corrosion

The outer surface of the cladding tube reacts with coolant water at $\sim 300-350$ °C forming an oxide layer that can reach a thickness of many tens of microns after one year in the reactor core [6]. Such oxide layers are normally porous, so provide degraded mechanical support and heat dissipation and cause severe safety concerns for the nuclear plant. Oxide layers

formed by autoclave corrosion have been widely used as proxies to study in-service corrosion mechanisms [20], whereby the difficulties and costs of dealing with active ex-reactor samples can be avoided.

2.3.1 Cyclic corrosion

Like most of the reactive metals, a protective oxide film forms first on Zr to limit further corrosion, but it cannot provide outstanding long-term protectiveness like alumina [54]. Alloying elements can significantly improve the corrosion resistance, and **Table 2-2** summarizes three common types of corrosion kinetics of Zr and its alloys, in corresponding with the purple, blue and red lines in **Figure 2-11**.

Table 2-2. Three types of Zr alloy corrosion kinetics.			
	Name	Compositions	Description
1	Direct breakaway	Pure Zr	Nonprotective, rapid growth
2	One transition + breakaway	Zr-0.5Fe, Zr-0.5Cr, etc	Limited protectiveness followed by breakaway
3	Cyclic transitions	Advanced Zr alloys (ZIRLO alloy, M5, X2, etc)	Multiple cycles of transition

The difference between the 2nd and 3rd types lies in the post-transition kinetics. For the 2nd type of oxidation process, breakaway happens right after the only transition, while for the 3rd, similar new cycles repeat after the first transition. This thesis focuses only on more advanced alloys that show the 3rd kind of corrosion kinetics. Bouineau et al [55] have shown that, **Figure 2-12**, for Zr-4 alloy, the oxide growth within each cycle is a reproduction of the initial cycle, with roughly equal spacing between transition layers, indicating the same kinetics for all cycles, and such cyclic corrosion can repeat to more than 13 cycles. This spacing is inversely proportional to the corrosion rate [56].

Corrosion kinetics are very sensitive to temperature, where with 10 °C higher temperature, the first transition occurs earlier with a higher growth rate, and all the following cycles

accelerated equally [55]. The alloy composition can be another major factor, where the first transitions for Zr-1Nb and Zr-2.5 Nb alloys are between 360-540 and 600-1040 days, respectively [57]. The time to the onset of the first transition is important in controlling the oxide thickness and hydrogen pickup (HPU) for longer service times [37]. Therefore, the obvious focus of alloy development programmes is how to delay the first transition and limit the corrosion rate within the first cycle.

Several theories have been proposed for the cyclic kinetics of oxidation, including the accumulation and release of stress [58], the creation of cracks in the oxide, and the change in grain size with oxide growth [59]. In order to understand this, it is essential to investigate the connection between oxidation kinetics and microstructure evolution within one transition cycle. From careful observation of the oxidation kinetics, each transition cycle can be divided into three key stages as indicated in **Figure 2-11**.

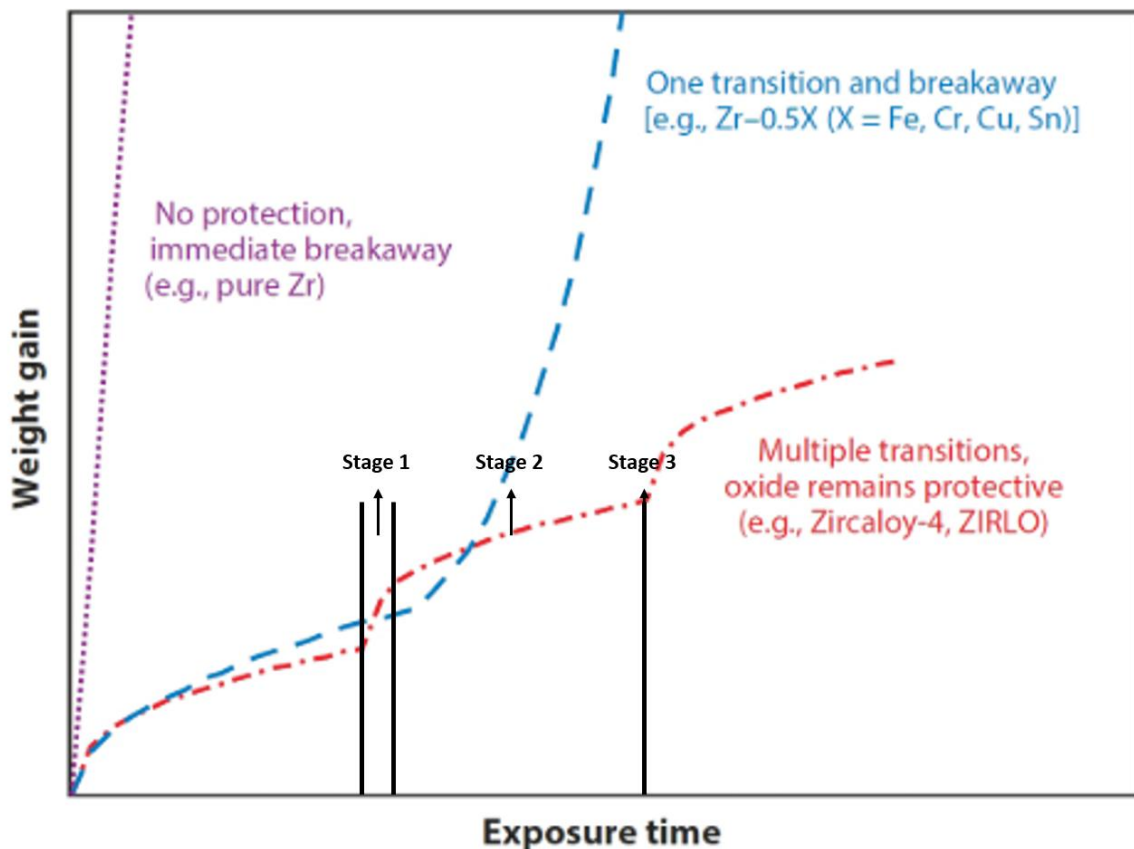


Figure 2-11. Weight gain versus corrosion time curves for pure Zr and Zr alloys, reproduced from [1]. Oxide growth within one transition is divided into three stages.

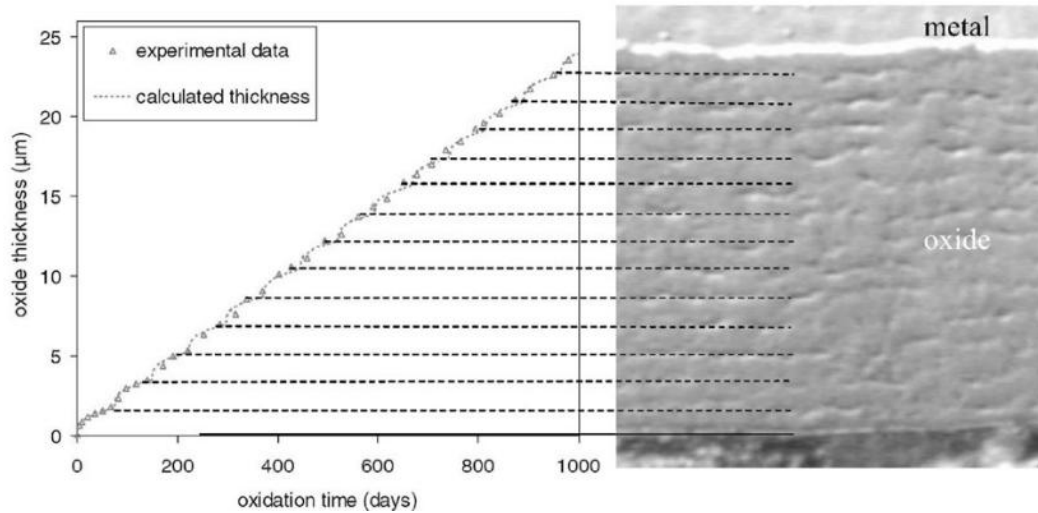


Figure 2-12. Long-term autoclave corrosion of Zr-4 in 3.5 ppm LiOH and 1000 ppm H₃PO₃ water [55].

Stage 1. Fast growth

At the beginning of oxidation or of a new transition cycle, the coolant water directly contacts and intensively interacts with the Zr metal, by the overall reaction: $\text{Zr} + \text{H}_2\text{O} \rightarrow \text{ZrO}_2 + 2\text{H}_2$.

Stage 2. Protective period

Stage 2 accounts for most of the time within one cycle and defines the protectiveness of the oxide layer. The oxidation rate gradually reduces and plateaus due to the formation of an oxide layer during stage 1 separating the metal and corroding water. The subsequent oxidation within the current cycle will require the diffusion of corrosion species (O, H, etc) from the water/oxide (W/O) interface through the existing protective oxide layer. The parabolic kinetics imply that the oxide growth is diffusion-controlled [60-62], and the gradually decreasing corrosion rate in stage 2 [63] can be explained by the increasingly difficult transport of oxygen ions becoming as the protective oxide layer becomes thicker.

Figure 2-13 shows a schematic of oxidation mechanisms on a protective oxide layer using coupled current charge compensation (C4) model proposed by Couet et. al. [62]. This model is based on Fromhold's oxidation theory of a zero net current through the oxide [64] and

assumes that the motion of charged species, driven by both concentration gradients (Fick's law) and electric field, is the rate-limiting factor [62]. Water molecules dissociate into O^{2-} and H^+ species, the O^{2-} ions are adsorbed onto the oxide layer where they react with oxygen vacancies forming mobile oxygen anions, which migrate through the oxide layer to the oxide/metal (O/M) interface and react with metal to form a new oxide layer. This process is accompanied with electrons migrating to the oxide/water interface or protons diffusing from the oxide surface into the metal matrix to balance the charge of the oxide. The validity of the C4 model may be doubted because it regards the oxide layer as ideal semi-conductor and calculates electrochemical properties and the diffusion of O and H through this perfect layer, whereas the oxide actually contains a high density of defects, such as nanopores [57], cracks [57], SPPs [65] and GBs [57]. The oxide thickness (w) versus time (t) within the first transition cycle can be fitted by a power law:

$$w = At^n$$

where A and n are constants, with n denoting the corrosion kinetics of a certain alloy, which is mainly determined by the alloying elements [66]. The power-law fit aligns with the C4 model prediction in **Figure 2-14**, so the errors caused by defects is within an acceptable range.

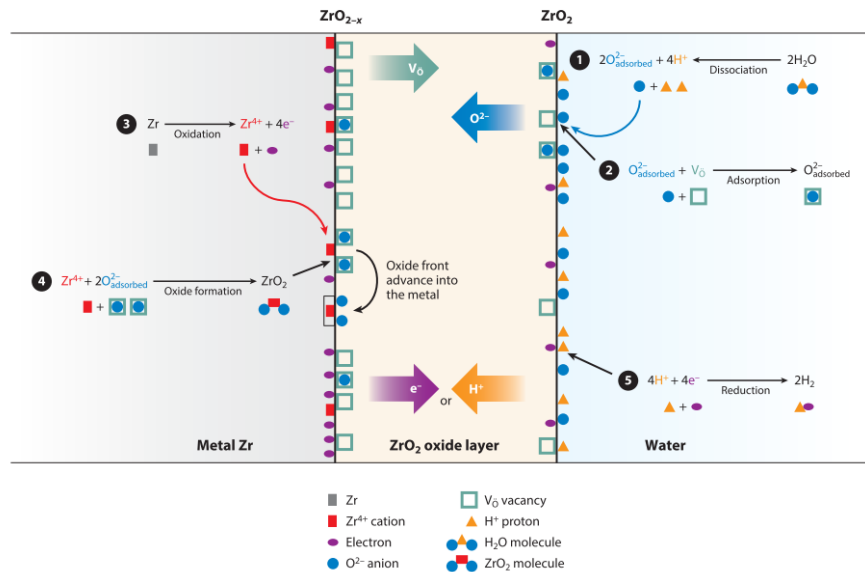


Figure 2-13. Schematic diagram showing the oxidation mechanisms of Zr alloys [1].

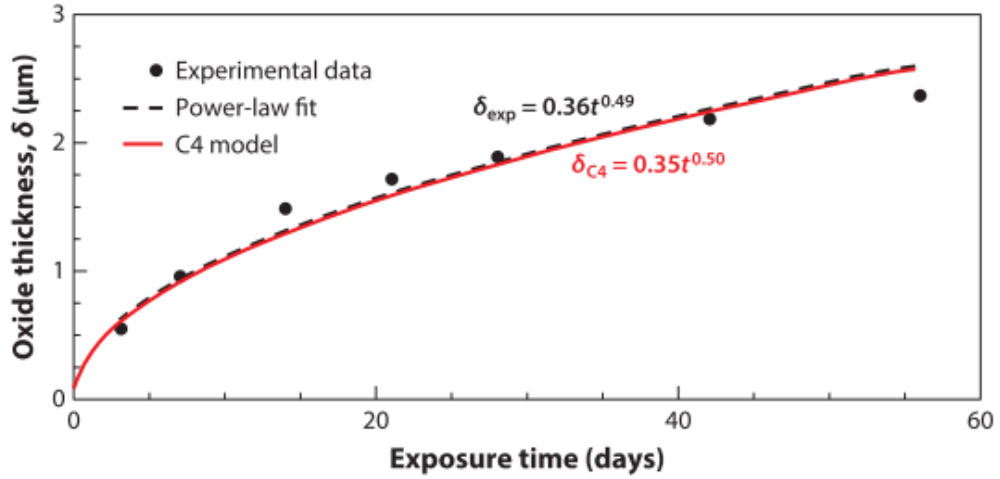


Figure 2-14. Oxide thickness of Zr-0.4Nb alloy during oxidation. Overlaid experiment data, power-law fit, and C4 model results [1].

Stage 3. Transition

The volume expands as a factor of ~ 1.56 during the transformation from Zr to ZrO_2 (the Pilling-Bedworth ratio [67]), and so the metal and oxide adjacent with the O/M interface are under tension and compression, respectively.

During stage 1, due to the fast growth rate, equiaxed grains, which are mostly tetragonal ZrO_2 , form with random orientation at the W/O interface [57, 68]. In stage 2, with the protection of the existing oxide layer, ZrO_2 nucleation and grain growth occur more slowly, allowing self-selection of columnar monoclinic grains [57]. These columnar grains have a preferred texture with the $(200)_m$ parallel to the O/M interface and grow along the corrosion direction in order to minimise the stress accumulation during oxide growth [27, 57]. They have a characteristic morphology of 30-40 nm in diameter and 100-200 nm in length [69]. Stress accumulates as oxide grows, and vacancies form preferentially on oxide GBs, **Figure 2-15**, due to their amorphous structure [70] and lower tensile strength [71]. These vacancies agglomerate into nanopores, nano-pipes and micro cracks along the GBs [72, 73], thereafter, intergranular microcracks tend to form and gradually become interconnected networks [74]. Once an interconnected pathway is built, the oxide layer loses any protective character as

the coolant water is in direct contact with the metal substrate again, so Stage 1 of a new cycle restarts. Therefore, limiting the formation of nanovoids and the build-up of crack networks could prolong Stage 2, and delay the start of the next transition cycle.

Hu et al [75] have shown the correlation of periodic equiaxed-columnar transition in oxide grain morphology with transition cycles, **Figure 2-16**. A similar oxide morphology has also been reported in other studies [27, 76]. The equiaxed regions are about 150 nm thick and only appear at the start of each transition (stage 1), accompanied with higher density of nanovoids and lateral cracks [20, 27], because that the self-selection of grain orientation and morphology to minimise stress buildup is restricted by the high corrosion rate and that the formation of nanovoids is easier on the equiaxed tetragonal GBs due to their lower cohesion than columnar GBs [57].

Quite a few studies attribute the equiaxed oxide grain structure as the **cause** of the accelerated corrosion [56, 74, 77], probably because there are more preferential diffusion pathways for corrosion species during further corrosion. However, The grain size of equiaxed grains is similar to the width of columnar grains (around 30 nm) [78], and it is unclear how a smaller grain size in the direction normal to the O/M interface will have any effect on the overall rate of transport in this orthogonal direction. Other research suggests more reasonably that the columnar to equiaxed transition is a **result** of the accelerated oxidation kinetics at the O/M interface [79-81].

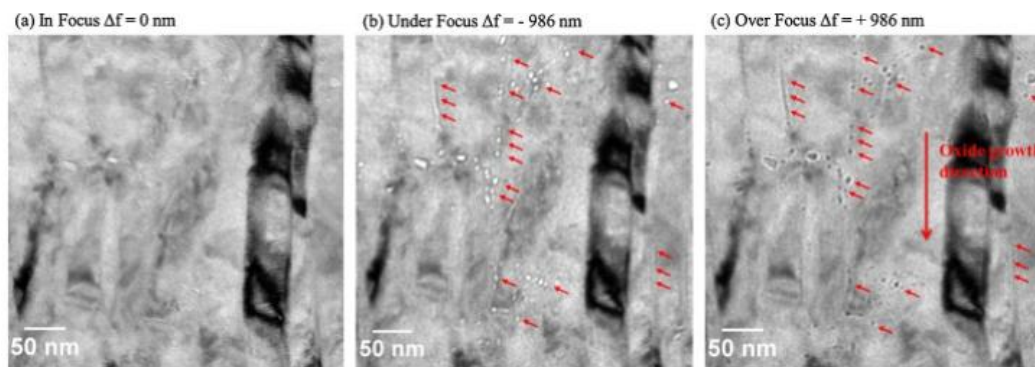


Figure 2-15. Fresnel contrast images showing nanovoids present on oxide GBs in corroded Zr-1Nb alloy [57].

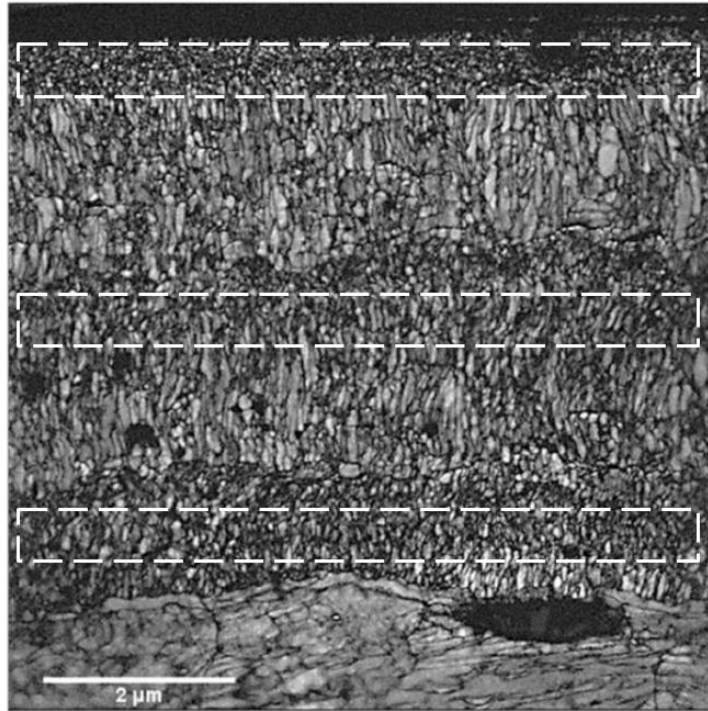


Figure 2-16. TKD band contrast image of Zr-1Nb oxide after 585-day corrosion. White dashed boxes indicate the equiaxed regions. Reproduced from [75].

2.3.2 Corrosion of SPPs

SPPs in Zr alloys can significantly improve the corrosion resistance due to anodic protection [17, 21, 82], and some types of SPPs present delayed oxidation kinetics compared to the matrix. Proff et al [21] summarised SPP types in Zr alloys, and concluded that the SPP size, crystal structure, solute to Zr ratio, and the thermodynamics of the corrosion of the SPP are the main factors to determine if a SPP type can contribute to delayed oxidation, and that β -Nb and most of the Laves phase SPPs will be effective. This delayed oxidation means that SPPs remain metallic as they are absorbed into the growing oxide, and as shown in **Figure 2-17**, both types of SPPs in ZIRLO alloy show delayed oxidation than the matrix.

The oxidation of SPPs is normally accompanied with amorphization or formation of small crystallites, and reduction of solute concentrations [74]. $\text{Zr}(\text{Nb,Fe})_2$ Laves phase SPPs in ZIRLO alloy can stay crystalline longer in the oxide than β -Nb SPPs, suggesting a more stable character [27], however both become fully amorphous after longer time incorporated

in the oxide [27]. Laves phase Zr(Fe,Cr)_2 SPPs in Zr-4, and Zr(Nb,Fe)_2 in ZIRLO alloy show similar delayed oxidation behaviour, eventually becoming amorphous, fully oxidised and depleted of most of the solutes [27, 74]. The available evidence suggests that the same kind of SPPs behave similarly under corrosion and irradiation in different alloys, despite the slightly different compositions of both matrix and within the SPP.

This delayed oxidation of SPPs often induces tensile stress at the interface because of the larger volume expansion of the surrounding matrix during corrosion [74]. Crescent-shape cracks form at the opposite side of the SPP to the O/M interface once this stress exceeds the maximum that the interface can bear [21, 27].

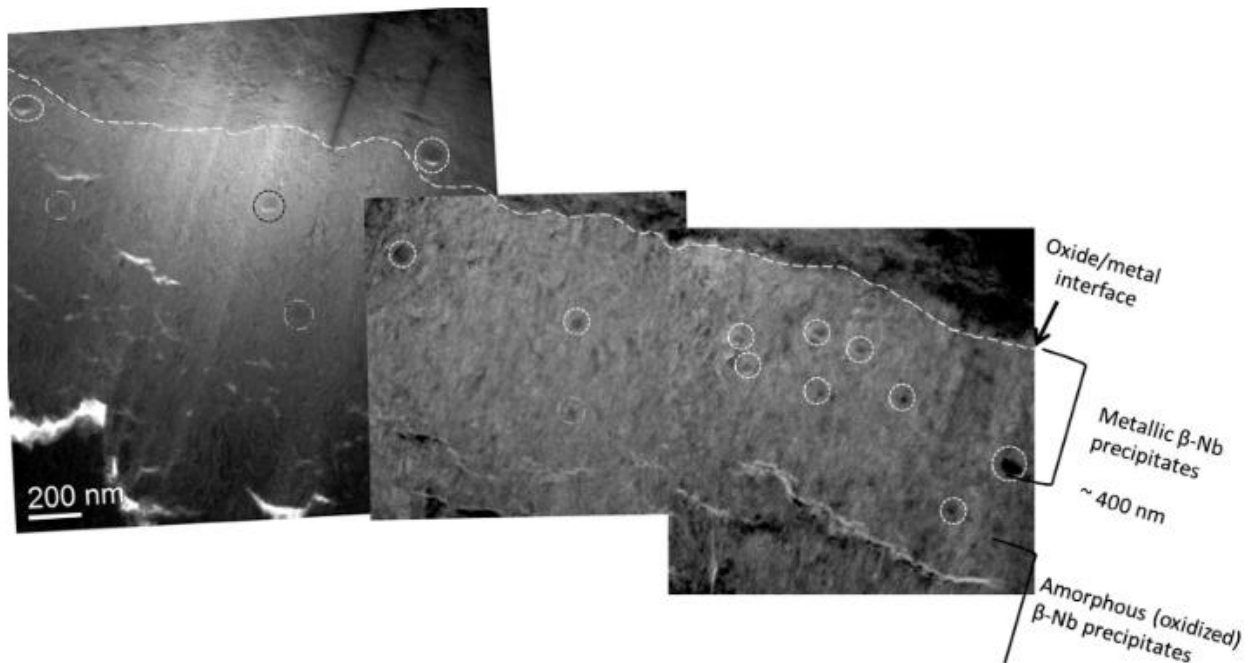


Figure 2-17. TEM results showing SPPs found in autoclaved ZIRLO alloy around the O/M interface with delayed oxidation [27]. β -Nb and Zr(Nb,Fe)_2 Laves phase SPPs are indicated in black and white circles, respectively.

2.3.3 Diffusion of corrosion species

Corrosion species including O and H ions need to be transported from the W/O interface to the O/M interface to continue the oxidation process. The oxide layer normally consists of an inner protective layer (oxide within 100-200 nm of the O/M interface) and an outer porous

layer (the rest of the oxide). The coolant water can easily penetrate through the outer oxide via the interconnected crack networks [65, 83] and make direct contact with the outer rim of the inner protective layer. Despite the presence of a dispersed distribution of nanopores, the inner oxide is generally denser and is known to form an effective electrochemical barrier that is protective against further corrosion [66]. Hence, the permeation of O and H through the inner oxide is considered to be the rate-limiting mechanism of the overall corrosion process [65, 84].

O diffusion

The transport of O from the water to the O/M interface contributes to the $\text{Zr}^{4+} + 2\text{O}^{2-} \rightarrow \text{ZrO}_2$ reaction, so directly determines the corrosion rate. Nanoscale secondary ion mass spectrometry (NanoSIMS) has previously been used to study Zr oxide layers formed in water isotopically spiked with ^{18}O [84, 85]. The results show ^{18}O segregation to sub- μm features, suggesting preferential trapping and diffusion behaviour, however, no definitive mechanistic conclusions could be drawn from these NanoSIMS results due to the limited spatial resolution of the data, complex defects, and the very fine grain structure shown in **Figure 2-15**. O is known to diffuse faster through amorphous zirconia than the crystalline phases [70]. Oxide GBs have similar arrangement of atoms with that of amorphous zirconia, thus oxide GBs are considered to act as preferential diffusion pathways for corrosion species [27]. APT can generate chemical information on the distribution of all elements at near atomic scale and with near ppm-level chemical sensitivity [86]. Further APT analysis on ^{18}O -spiked oxide to study this hypothesis is given in **Section 6.2 ^{18}O -spiking**.

H ingress

H is ubiquitous in the environment and can be introduced into metals and alloys easily during fabrication processes and in service, causing serious detrimental effects on the mechanical

properties. This phenomenon is known as hydrogen embrittlement [87, 88], and has been widely reported on steels [89, 90], aluminium alloys [91, 92] and titanium alloys [93, 94]. Hydrogen ingress is also of particular concern for the zirconium alloys during corrosion in PWRs. H is produced as a by-product of electrochemical corrosion, and permeates towards the metal matrix through oxide layer to maintain the charge balance [62] (also electrons moving along the opposite direction). Once the H content exceeds the solubility in α -Zr (a few ppm at room temperature [95]), the supersaturated H can form Zr hydride precipitates [96, 97], which are very brittle and degrade the ductility and toughness of the cladding. These hydrides are normally found in the metal matrix near the O/M interface, which have an acicular shape aligned 30-45° (**Figure 2-18**) to the O/M interface and are mostly identified as δ -hydrides by electron diffraction. Cubic δ -hydrides have an orientation relationship with the α -Zr matrix of $(0002)\alpha \parallel (111)\text{ZrH}_2$ and $[11-20]\alpha \parallel [202]\text{ZrH}_2$ [27].

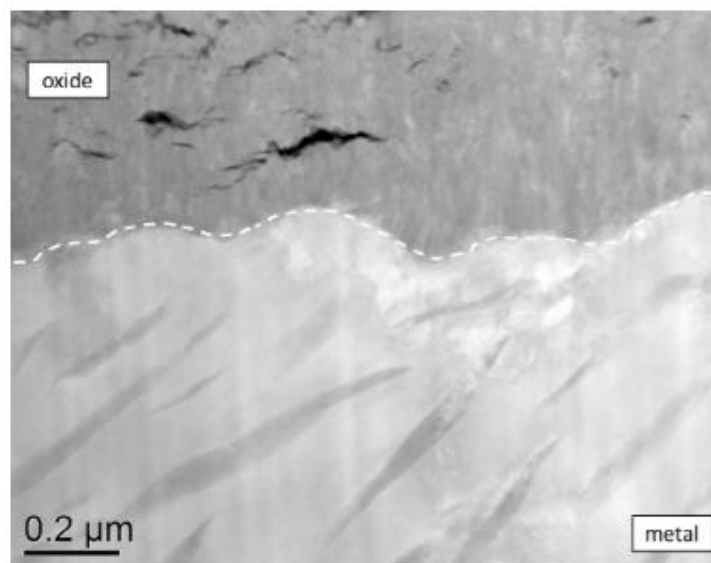


Figure 2-18. Hydrides observed in metal near the O/M interface of a 75-day autoclaved Zircaloy-4 sample [27].

Thus, H ingress significantly compromises the integrity of the cladding [98], causing severe safety hazards to the operation of a nuclear plant. To avoid this, it is important to understand the mechanisms of permeation and to develop ways to avoid excess concentrations of H

reaching the Zr metal matrix. Like the diffusion of O, the permeation of H through the inner oxide is considered to be the rate-limiting process for H ingress [65, 84]. The intragranular diffusion coefficients of H in the oxide matrix are extremely low ($\sim 10^{-24}$ m²/s in the monoclinic and $\sim 10^{-18}$ m²/s in the tetragonal ZrO₂ phase at 600 K [99]), and hence it has previously been proposed that H preferentially diffuses through interconnected porosity [73, 83, 100] and grain boundaries (GBs) in the inner oxide layers [101-103].

Deuterium can be used effectively as a proxy to investigate the local behaviour of H in the microstructure. Interconnected D hotspot can be found by NanoSIMS analysis in D-spiked oxide [65, 84, 104], but because of the limited spatial resolution, these hotspots cannot be unambiguously linked to any specific microstructural defects. Previous APT studies have successfully imaged deuterium (D) distributions in steels [105, 106], Al alloys [91], Ti alloys [107] and Zr alloys [108]. However, APT analysis of D distributions in oxides has proved much more difficult [109, 110]. The fine grained structures, and complex defects such as cracks and nanovoids [57], make the APT tip specimens very vulnerable to failure under the stresses imposed by the high electrostatic fields that are necessary for APT analysis [111], significantly reducing the chance of acquiring statistically significant results on D distribution in the oxide. Furthermore, due to the insulating and fragile character of the oxide, the field evaporation process must be carried out in the laser-pulsed mode of operation [111], which enhances the formation of complex molecular ions, complicating the resulting mass spectra and making data interpretation very difficult [111, 112].

Two good examples of APT results showing that D segregate at oxide GBs are shown in **Figure 2-19** and **Figure 2-20**. **Figure 2-19** shows a comparison of H and D distribution in oxides formed in (a) 100% H₂O water (H oxide) and (b) 100% D₂O water (D oxide), where the 17 Da OH⁺ signal segregates at H oxide GBs and the 18 Da OD⁺ signal segregates at D oxide GBs. 1 Da H⁺ and 2 Da D⁺ signals are randomly distributed. Thus it can be inferred

that both H and D are segregating and preferentially diffusing along the oxide GBs, possibly in the form of hydroxyl groups. Similarly, **Figure 2-20** shows D segregation on GBs and nanovoids identified by the localised higher atom density due to APT trajectory aberrations (details in section 3.4.5). The 2 Da D^+ signal shows the same segregation behaviour as the 18 Da OD^+ signal, which could be the dissociation of OD^+ into O^+ and D^+ during flight, giving the impression of D^+ segregation at GBs.

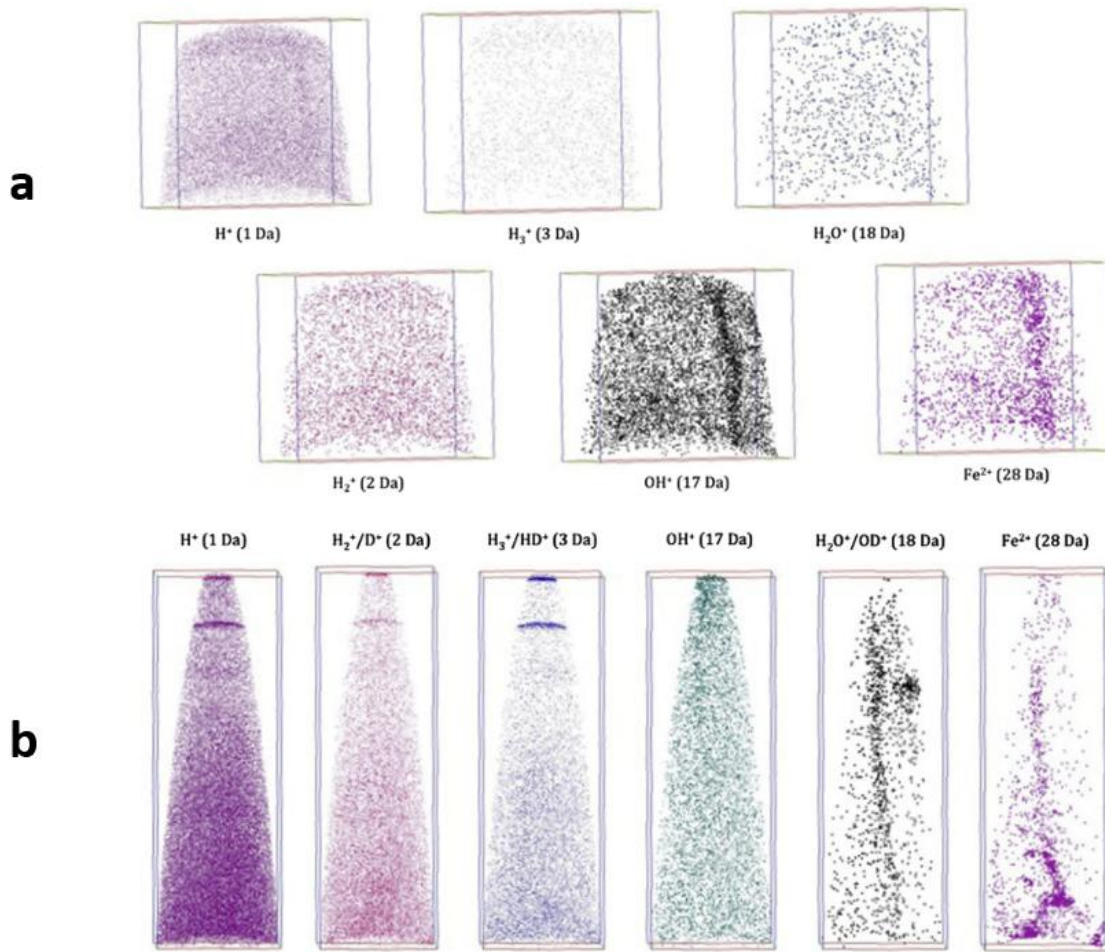


Figure 2-19. APT datasets showing the ZrO₂ oxide near the O/M interface in Zr-2.5Nb samples that were corroded in (a) H₂O water and (b) D₂O water [103].

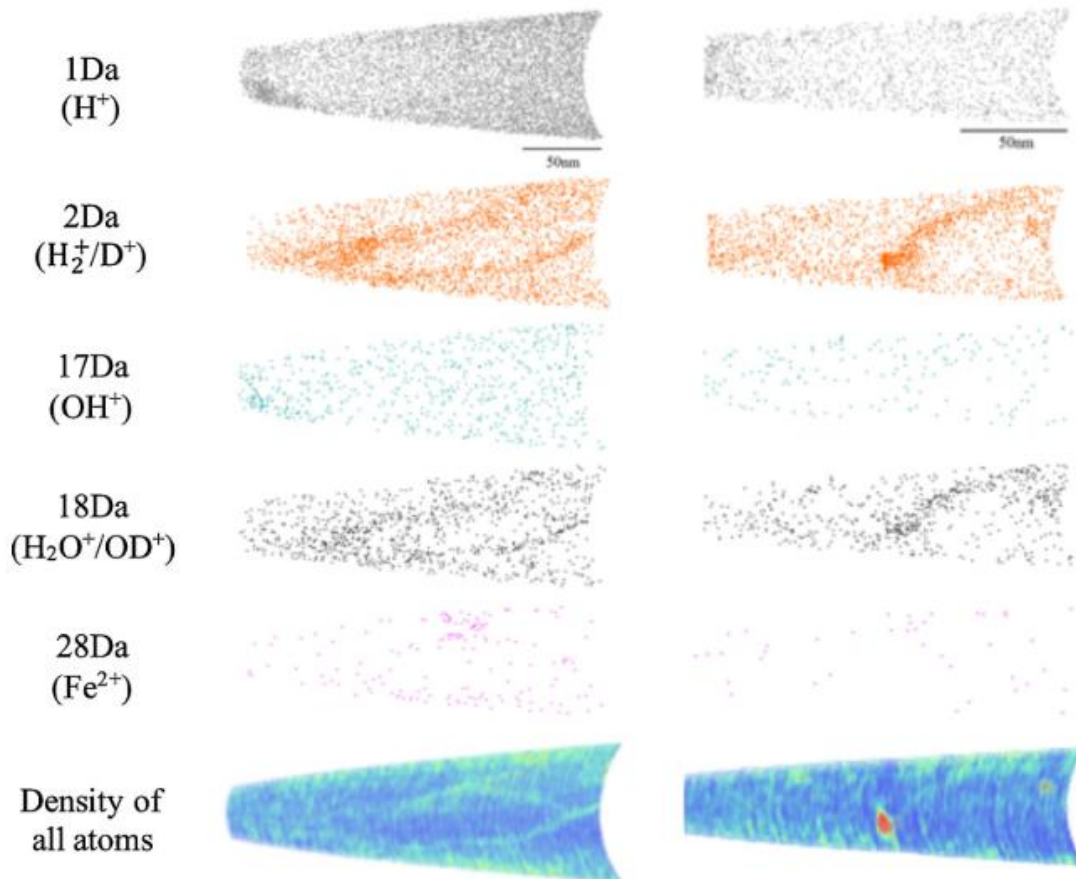


Figure 2-20. APT dataset on Zr-2.5Nb sample near the O/M interface. Samples were corroded in Canada Deuterium Uranium (CANDU) reactors with D₂O water [57].

2.3.4 Li accelerated corrosion

Boric acid (¹⁰B) is normally added to the primary water in PWRs as a neutron poison to control the reactivity [113]. An additional 2-5 wtppm LiOH is added to achieve a pH between 6.9 and 7.4 at ~300 °C to minimise corrosion of the primary circuit materials (mainly stainless steels and nickel-based alloys) [114]. The addition of LiOH to the coolant can significantly accelerate the corrosion kinetics of Zr cladding alloys, as previously reported from both modelling [115] and experimental results [116-119]. Jeong et al [120] showed that the corrosion rate is approximately the same in NaOH, KOH, RbOH and CsOH solutions, but increases significantly in LiOH solutions, indicating that the accelerated corrosion is induced primarily by Li rather than the pH of the environment, similar results

can be found in [121]. Hulme et al [116] concluded that the onset of this Li-accelerated corrosion depends on three key factors, Li concentration, temperature and stress. Although there is less evidence to validate the effect of stress, it has been reported that the critical concentration of Li required to activate the acceleration is lower at higher temperatures [114]. At a typical cooling water temperature of 310 °C, ~1000 wtppm Li is needed, which is far beyond the normal Li concentration in the coolant water. However, the critical Li concentration required for accelerated corrosion at 360 °C decreases dramatically to less than 100 wtppm. Due to the poor thermal conductivity of ZrO₂ [122], the temperature increases from the W/O interface to the O/M interface [121], and so any accumulation of Li at the inner oxide near the O/M interface can encourage Li-accelerated corrosion as the oxide layer thickens.

Low content of the Li in the PWR water chemistry (~3 wtppm) makes the detection of Li very difficult in the oxide layer, so previous studies often investigate Zr oxides that formed in Li-doped water (100-200 wtppm Li) to better understand Li diffusion within the oxide layers. The emitted X-ray signal intensity from Li is too low for energy dispersive (EDS) analysis [123], but SIMS has been proved useful to detect Li content and diffusivity in Li electrodes [124] and geomaterials [125]. Pêcheur et al [119] and Liu et al [126] have also shown the possibility of using SIMS to measure the local Li content in ZrO₂ oxides formed on Zr cladding alloys during corrosion. It was noticed that the Li-accelerated corrosion is normally accompanied by the columnar to equiaxed transition of the oxide grain morphology [119], similar to the change at the start of a new transition cycle during the cyclic corrosion process [37, 79, 81, 126]. SIMS results from Xie et al [127] showed,

Figure 2-21, that Li concentration peaks within the oxide at probably the interface of inner and outer oxide, and gradually decreases within the inner oxide towards the O/M interface due to the protective nature of the inner oxide layer, and finally becomes undetectable in the

underlying metal substrate. Thus the O/M interface is not acting as a barrier for Li diffusion, and the low concentration in the metal could be because (i) no Li gets to the metal, (ii) any limited Li reaching the metal is immediately dispersed due to higher diffusivity in α -Zr than in the ZrO₂. There are currently no such results to confirm which of these is more likely.

The spatial resolution of SIMS results is limited to ~ 20 nm [128], so it is unable to map precisely the Li distribution in the nanosized grain structures in corrosion scale, or to study the interaction with defects like nanovoids [57] or cracks [65]. More recently, APT has been used to analyse the distribution of Li in Al₂O₃ nuclear coatings [129], carbon fibre [130] and lithium-ion battery materials [131], and it is well suited to map the very low concentrations of Li in nano-structured Zr oxides. Garner et al [114] investigated ZrO₂ oxides formed during autoclave corrosion in Li-doped water (**Figure 2-22**), and the results showed Li atoms are spatially correlated with oxide GBs that are also decorated with Fe and OH signals, suggesting that Li segregates to and preferentially diffuse along the oxide GBs. Similar segregation of Li and Fe at oxide GBs were also reported by Xie et al [127]. This is not surprising because Li is almost insoluble in both ZrO₂ and metallic Zr [132, 133]. A modelling study of the interaction between Li and oxide GBs, using amorphous ZrO₂ as an analogue for GB structure [70], has reported that Li stabilises ZrO₂ GBs [134] and that Li segregation promotes the formation of oxygen defects on GBs. An excess of oxygen vacancies at GBs could accelerate the diffusion of O [135], leading to faster O transport to the O/M interface and a higher overall corrosion rate. What is missing is precise mapping of the Li distribution around the O/M interface and in the metal after exposure to real in-service conditions. New results showing Li penetration throughout the oxide layer into the metal substrate are shown in section **7.1 Li ingress**.

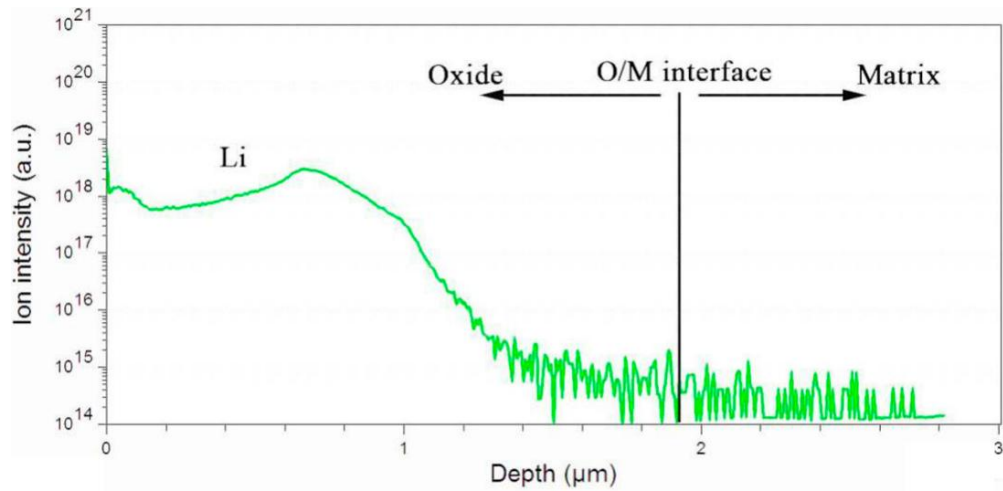


Figure 2-21. SIMS profile of ${}^6\text{Li}^+$ signals around the O/M interface in a Zr-4 sample corroded in Li-doped water [127].

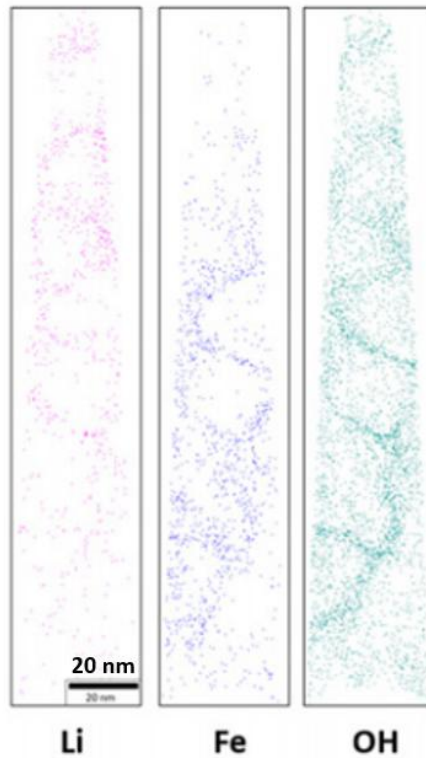


Figure 2-22. APT dataset on Zr-4 oxide near the O/M interface corroded with Li-doped H_2O at $350\text{ }^\circ\text{C}$ [114].

2.3.5 The O/M interface

Once oxygen reaches the O/M interface, metal below the O/M interface is continuously consumed to form a new oxide layer, accompanied with local phase transformations and solute redistribution. Since the 2010s, this region of the microstructure has received a great

deal of attention and investigation with some of the more modern analytical tools unavailable to earlier researchers.

Phase transformation

As measured by APT [13] (**Figure 2-23**) and EELS [141] the chemistry of the O/M interface is transformed from metallic α -Zr matrix to ZrO_2 over a distance of about 100-300 nm. There are complicated phase transformations and a characteristic variation in Zr:O ratio across this region, which can be summarised as

1. **Stable ZrO_2 oxide**, mostly monoclinic phase, small fraction of tetragonal phase. Zr:O = 1:2 [74].
2. **ZrO suboxide**, Zr:O = 1:1. Hexagonal phase, $a=5.31 \text{ \AA}$ and $c=3.20 \text{ \AA}$ [136, 137].
3. Oxygen saturated region, **Zr(O_{sat})**, 30-35% of O in solid solution in the α -Zr matrix [78]. O occupies the octahedral interstitial positions [138] and the Zr unit cell retains similar dimensions [139].
4. Oxygen enriched region, **Zr(O)**, the O content decreases towards the metal substrate, from $\sim 30 \text{ at\%}$ to $<1 \text{ at\%}$.
5. **α -Zr**, unoxidized Zr metal, O concentration $<1 \text{ at\%}$, HCP structure with $a=3.23 \text{ \AA}$, $c=5.15 \text{ \AA}$ [140] .

Regions 2, 3, 4 compose the O/M interface, and are a gradual transition from metal to the fully oxidised Zr (ZrO_2). It has been reported that oxides with slower growth rate normally have thicker interface, up to 200-300 nm [14, 77, 141, 142], because the interface is consumed at a slower rate. Regions 3 and 4 show distorted α -Zr diffraction patterns due to the high O content in the solid solution [27].

The corrosion process involves the formation of new oxide. This might take place by the nucleation of small crystallites with random orientation, but after self-selection only those

with preferred orientation ((001)m parallel with the corrosion direction) then grow to alleviate the accumulated mismatch stress at the O/M interface. As a result, the oxide will have columnar grain structure with strong crystallographic texture [143]. At higher growth rate conditions, this self-selection process is restrained, and as a result, equiaxed grains with random orientations dominate, which are normally observed at the beginning of each transition cycle as summarised in **Section 2.3.1 Cyclic corrosion**.

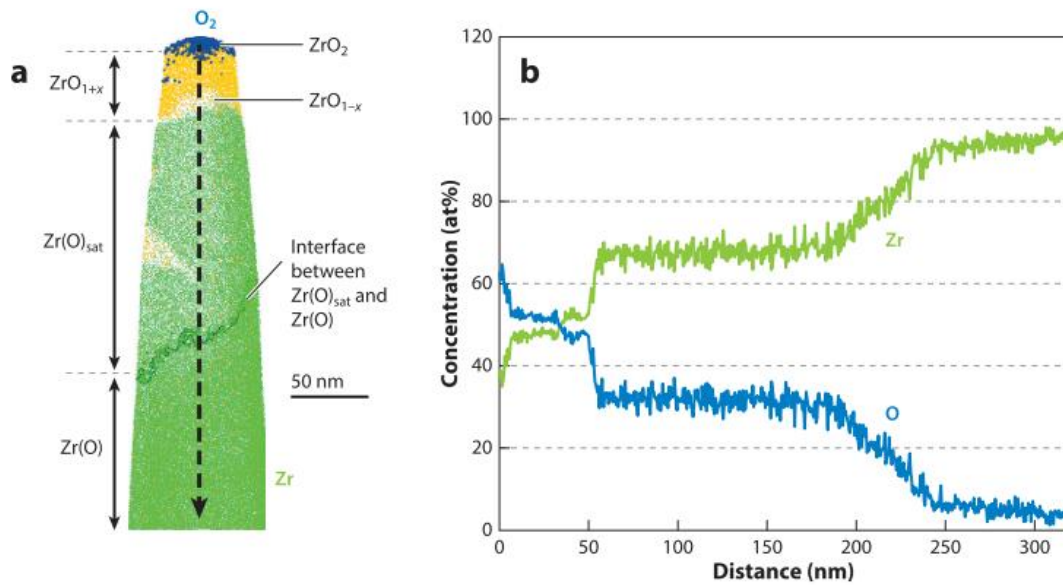


Figure 2-23. (a) APT dataset containing O/M interface from a corroded Zircaloy-4 alloy. (b) Line profile of O and Zr across the interface [14].

Solute redistribution

The oxidation process occurs at the O/M interface, so the localised solute distribution and thus the electrochemical properties are of particular interest. Setiadinata [144] and Hudson [145] reported complex Fe redistribution in the underlying metal immediately below the O/M interface. Dong et al [14] reported that the Sn content reduces from 0.8 at% in $Zr(O_{sat})$ to 0.3 at% in ZrO_2 , indicating rejection of Sn during the oxide growth. This trend was also reported by Hudson [145], where the Sn and Nb content in $Zr(O_{sat})$ is much higher than that in the ZrO_2 , and Sn also shows a pile-up at the $Zr(O_{sat})$ side of the interface. However, Sundell et al [142] have reported no evident solute rejection at the O/M interface. The reason

for these disagreements may be that APT cannot calculate accurate solute contents in the oxide due to the worse quality of the data obtained from the oxide [111] (thermal tails and peak overlaps, as discussed in **Section 3.4 APT data analysis**), and that it may be more reasonable to use solute/Zr ratio rather than the solute/all elements concentration to consider the solute redistribution.

2.3.6 In-pile corrosion

Much of the work reported in this thesis is on the APT analysis of the local chemistry of in-reactor samples with long exposures. Although many corrosion studies have been carried out on proxy autoclave samples, in-pile corrosion is the actual degradation process that the cladding materials undergo in the reactor core. It is an in-situ irradiation and corrosion process, which normally has a much higher corrosion rate compared with autoclave corrosion at an equivalent temperature and water chemistry, by a factor of up to more than 10 [55, 74, 146]. In-pile corrosion is a very complicated degradation process, and there are several aspects to consider for the accelerated corrosion kinetics.

Irradiation of the Zr metal

Section 2.2 Irradiation reviews the microstructural defects and microchemical changes in the metal matrix induced by neutron irradiation. Corrosion of this irradiated metal substrate occurs much faster than the pristine metal, as shown by corrosion tests on post-irradiation materials [147]. Gebhardt et al [148] have reported a similar corrosion rate of Zr-4 samples during post-irradiation corrosion and in-pile corrosion, suggesting that irradiation-induced displacement damage in the metal is the major factor for the accelerated kinetics, and other in-situ irradiation effects (like irradiation on the diffusion of corrosion species, oxide, interface, water, etc) are less significant. Bouineau et al [55] have shown an increasing accelerated factor (in-pile corrosion rate/autoclave corrosion rate) with longer in-pile times,

indicating that the accumulated irradiation damage is having a progressively stronger effect on accelerating the corrosion rate. Such acceleration seems to be more prominent on Zr-Sn alloys than Zr-Nb alloy [37]. Although some study has shown that after 0.5-1 dpa proton irradiation the corrosion resistance of Zr-0.5Nb alloy becomes better [149], the very low-dose irradiation can hardly change the matrix chemistry and the recorded corrosion time (38 days) is too short to draw a conclusion.

Schematics summarising the oxidation mechanisms in pristine and irradiated metal were published by Hu et al [37], **Figure 2-24**. This shows that the oxide layers formed on post-irradiation metal become more porous, and grains are more equiaxed but less textured. The combined effect of the following factors contributes to these oxide morphologies and enables faster transport of corrosion species, inducing earlier transitions:

1. If one SPP has already become depleted and amorphous due to irradiation by the time the oxide front reaches it, it can no longer provide protectiveness to the surrounding materials. Alloys containing irradiation-stable SPPs have a better in-pile corrosion resistance [150].
2. Depleted solutes like Fe and Cr from SPPs and formation of irradiation-induced solute clusters alter the localised solute contents [74, 151], which may reduce the matrix corrosion resistance by changing the electrochemical properties. There is currently little evidence on this, and new results will be given in **Chapter 7 In-pile corrosion**.
3. All the defects induced by irradiation would embrittle the oxide, undermining the ability to accommodate stress from expansion during metal to oxide transformation and resulting easier formation of new voids and cracks [152].

4. The existing irradiation-induced defects readily interact with new corrosion-induced ones [74], making the build-up from isolated vacancies to interconnected crack networks much easier.

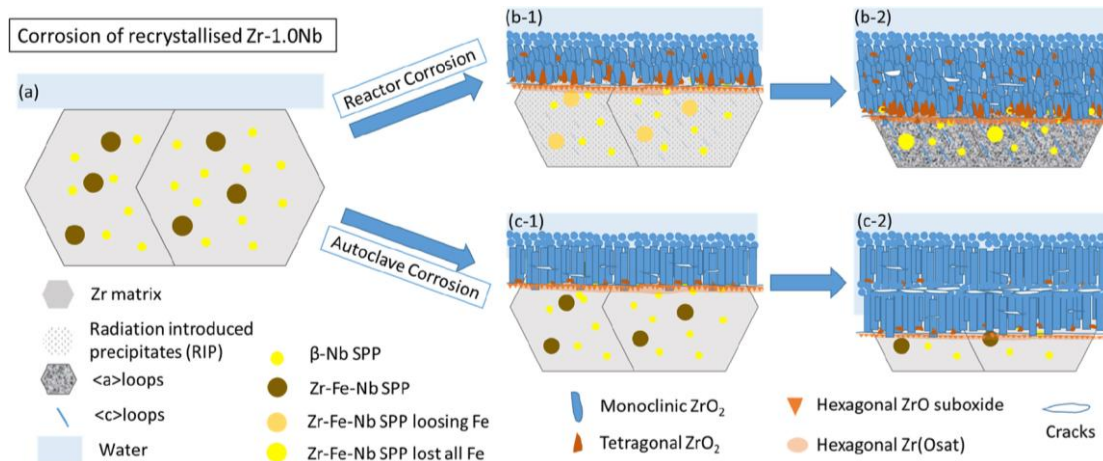


Figure 2-24. Schematic of Zr-1Nb alloy microstructures in (a) as-received state, and after (b) in-pile corrosion and (c) autoclave corrosion [37].

Irradiation of the oxide

Liu et al [53] have reported a transformation from m-ZrO₂ to the higher symmetry c-ZrO₂ with the relationship orientation of (110)_m || (110)_c and [001]_m || [001]_c at 1 dpa, followed by the growth of the c-ZrO₂ grains at higher dose, as shown in the in-situ ion irradiated TKD map in **Figure 2-25**. This phase transformation is possibly promoted by the adsorption of point defects from the collision cascades [153] and stabilised by lattice strains [53]. Formation and growth of nanovoids condensed from vacancies were also observed in the oxide matrix [53]. Therefore, it is expected that the diffusion of O²⁻ through the oxide layer is accelerated due to the presence of extra defects [154]. Similar observations on the formation of c-ZrO₂ under irradiation were also reported by Pêcheur et al [155].

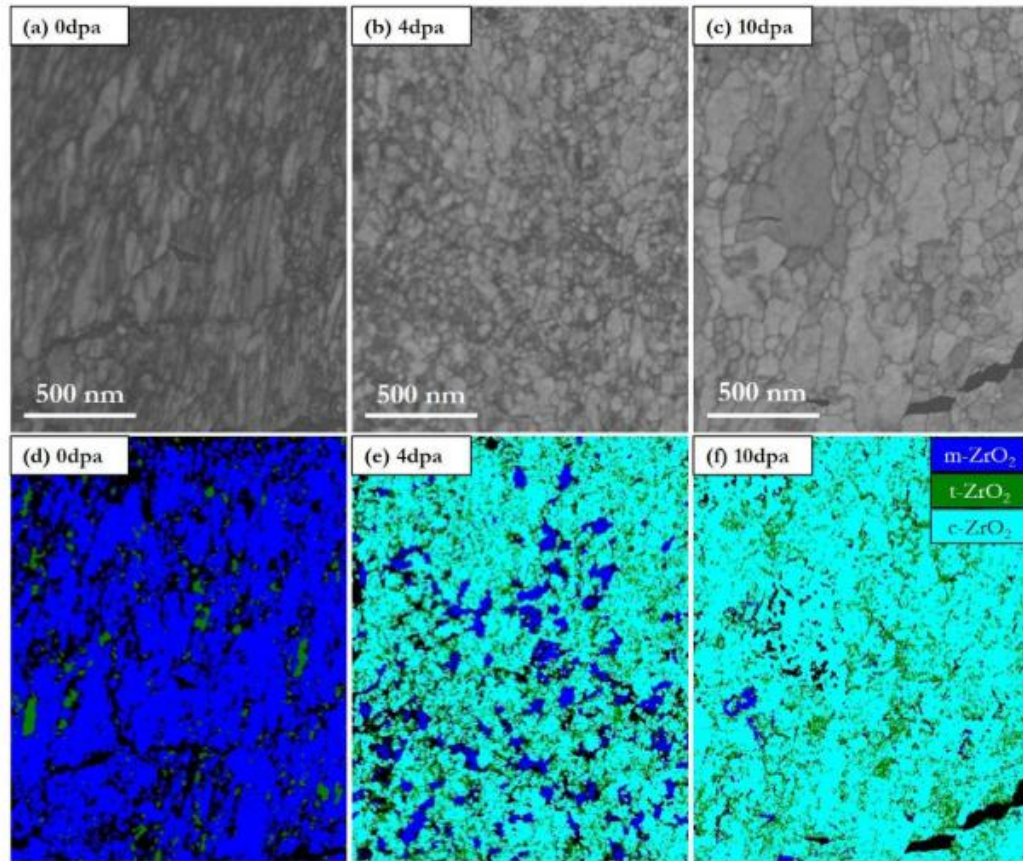


Figure 2-25. TKD map on the similar region of a Zr-0.5Nb oxide sample after 0-10 dpa Kr^{2+} ion irradiation. (a-c) band contrast, (d-e) phase map [53].

Irradiation at the O/M interface

Liu et al [156] have reported that the h-ZrO suboxide becomes amorphous, while α -Zr(O) region becomes partially amorphous and ZrO_2 is still crystalline during in-situ ion irradiation TEM analysis, **Figure 2-26(d)**. The h-ZrO phase is more prone to irradiation damage compared to the surrounding phases, possibly because the ordered interstitial O arrangement is less stable, similar to the observations that the ordered interstitial arrangement of Fe [157] is more easily destroyed [156] during the amorphization of $\text{Zr}(\text{Nb},\text{Fe})_2$ SPP under irradiation. This indicates that in-service irradiation would continuously disrupt the nucleation and growth of new ZrO_2 grains at the interface, compared with oxides formed in autoclaves reviewed in section **2.3.5 The O/M interface**. This will presumably lead to significantly different oxide grain structures, including a higher density of cracks and porosity, more

random texture, smaller grain size, and reduced cohesion of grains, through which the corrosion species are expected to have accelerated diffusion kinetics.

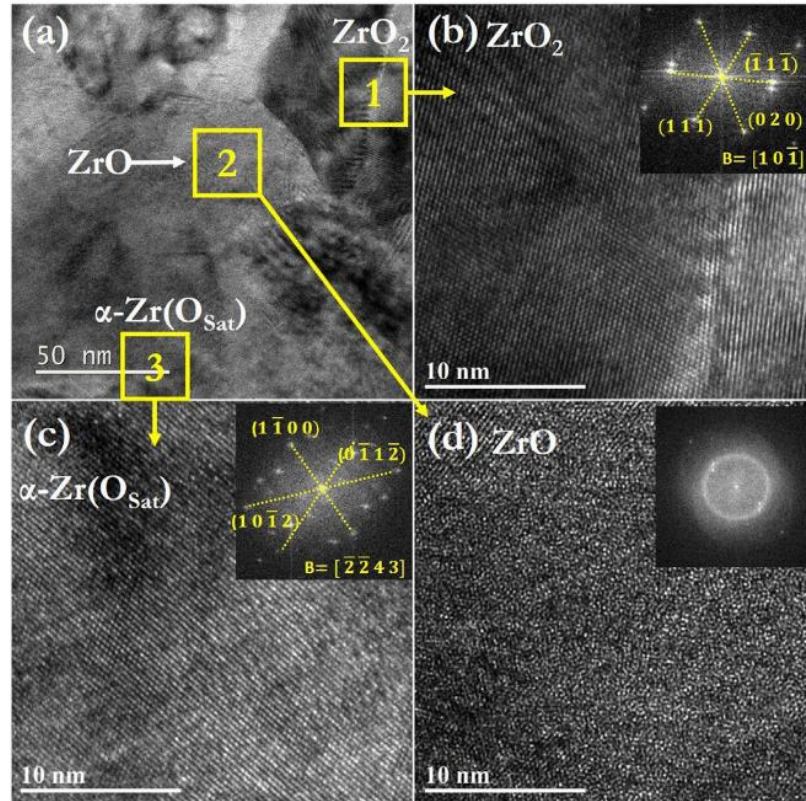


Figure 2-26. (a) BF-TEM image, (b-d) HRTEM image with diffraction pattern in ZrO_2 , and $\alpha-Zr(O_{sat})$ and ZrO regions on an Kr^{2+} ion irradiated Zr-0.5Nb alloy around the O/M interface [156].

Irradiation and water chemistry

The ^{10}B addition in the primary water can transmute into 7Li under neutron irradiation ($^{10}B + ^1_0n \rightarrow ^4_2He + ^7_3Li + 2.79 \text{ MeV}$ [158]). Therefore, the corrosion resistance provided by boric acid will diminish once the boron in the coolant water is depleted at the end of reactor cycles [66]. The cladding may actually be exposed to water chemistry with a higher Li concentration than the nominal value, and more Li can diffuse into the inner oxide making Li-accelerated corrosion more likely. There can also be more active O and hydroxyl species in the in-reactor primary water than autoclave water due to the radiolysis of H_2O under irradiation [146, 159], and these can be faster transported to the O/M interface under hypothesis that hydroxyl groups are the corrosion species [160-162].

3. Experimental Methods

This thesis focuses on the degradation mechanisms of a set of Zr alloys. These samples were provided by the industrial partners in the Mechanistic Understanding of Zirconium Corrosion (MUZIC) Programme grant from the Engineering and Physical Science Research Council and the Mechanistic understanding of Irradiation Damage in fuel Assemblies (MIDAS) Programme involving universities and industrial partners. These materials have been exposed to different corrosion and irradiation environments, and the microstructure was studied at the micron to atomic scale mainly with the use of APT, in support of analysis by other methods carried out by PhD students and postdoctoral researchers in Oxford and partner institutions.

This chapter introduces all the samples (section 3.1) and characterisation methods used in this thesis. Sections 3.2, 3.3 and 3.4 illustrate the working principle, specimen preparation procedures and the data analysis of APT, respectively. An introduction to other complementary characterisation techniques is given in section 3.5.

3.1 Materials

The ultimate goal of this thesis is to understand the in-reactor degradation of Vogtle ex-reactor samples provided by Westinghouse, which undergo very complicated degradation processes involving corrosion, irradiation and other in-situ effects simultaneously. The mechanisms of corrosion and irradiation are first studied individually, and then this understanding is combined to interpret the accelerated kinetics and complex degradation processes of in-pile corrosion. The samples are categorised into four groups depending on the different conditions, **Table 3-1**. Sections 3.1.1 to 3.1.4 introduce the samples in baseline,

autoclave-corroded, irradiated-only and in-pile corroded states, corresponding to the results presented in **Chapters 4 to 7**, respectively.

Table 3-1. Sample summary				
Chapters	Method sections	Names	Conditions	Alloys
4	3.1.1	Baseline	Baseline	ZIRLO, X2, W13, W10
5	3.1.2	Irradiation	Irradiated-only	ZIRLO, X2, W13
6	3.1.3	Autoclave	Autoclave-corroded	ZIRLO, X2, Zr-4
7	3.1.4	In-pile corrosion	In-situ irradiation and corrosion	ZIRLO, X2

3.1.1 Baseline samples

The nominal compositions of the four cladding Zr alloys provided by Westinghouse are listed in **Table 3-2** [163]. The key differences between the W13 and ZIRLO alloys are the addition of 0.24% Cu (concentrations are given in atomic %, if not otherwise stated), and the Sn and Fe are decreased to 0.22% and 0.08% from 0.52% and 0.18%, respectively. In the W10 alloy, the Cu addition is replaced by 0.32% V. The ZIRLO alloy is stress-relieved at 460 °C, and X2, W10 and W13 are full recrystallised at 580 °C for 4 hours. The final heat treatment resulted in α -Zr matrix in four alloys. ZIRLO, X2 and W10 alloys have β -Nb and Laves phase SPPs, W13 alloy has additional Zr_2Cu SPPs. The mechanical properties and processing history of the X2 alloy have been reported [25]. Due to the reduced Sn content and recrystallised condition, X2 has a 63% of the tensile strength and 200% of the elongation of ZIRLO alloy at room temperature [25]. Only elements given in the nominal composition are considered as **solutes**, and all the other elements detected in the APT analysis are defined as trace **impurities** (including Al, Cr, W, Mn, Si and Ni).

Table 3-2. Nominal composition of W13, W10, ZIRLO and X2 alloys								
Element	Weight Percent (wt.%)				Atomic percent (at.%)			
	W13	W10	ZIRLO	X2	W13	W10	ZIRLO	X2
Nb	0.99	0.97	1.00	1.00	0.97	0.95	0.98	0.98
Sn	0.29	0.29	1.00	-	0.22	0.22	0.77	-
Cu	0.17	-	-	-	0.22	-	-	-
Fe	0.05	0.05	0.10	0.06	0.08	0.08	0.16	0.10
V	-	0.18	-	-	-	0.32	-	-
O	900-1500 wppm				3600-5000 appm			

3.1.2 Irradiated-only samples

Samples from the BOR-60 reactor

The W13 alloy samples were neutron irradiated in the BOR-60 reactor to up to 33.5 dpa (displacement per atom) at 320 ± 10 °C, and were stored at the UK Atomic Energy Authority (UKAEA) Materials Research Facility (MRF). The baseline (0 dpa), 4.1, 17.5 and 33.5 dpa samples were selected for analysis (dpa level converted from neutron flux of $F=2 \times 10^{25} \text{ m}^{-2}$, $8.6 \times 10^{25} \text{ m}^{-2}$ and $16.4 \times 10^{25} \text{ m}^{-2}$ [164]), **Table 3-3**. These three irradiation doses were achieved in times of 4 months, 11 months and 16 months, respectively [164].

Table 3-3. BOR-60 W13 sample information.			
Sample code	Fluence/m^{-2}	Dose/dpa	Time/months
W13-0	0	0	0
W13-11	2×10^{25}	4.1	4
W13-9	8.6×10^{25}	17.5	11
W13-7	16.4×10^{25}	33.5	16

Samples from Vogtle reactor

APT tips were made from the metal matrix at least 50 μm away from the O/M interface on the Vogtle ex-reactor samples to study the effect of irradiation separately. Details are given in **Section 3.1.4**. Samples in BOR-60 and Vogtle have both been irradiated to ~ 32 dpa, but

in 16 and 64 months, so the BOR-60 samples have a flux rate four times that of Vogtle samples. Effect of the different dose rates will be compared in **Chapter 5**.

3.1.3 Autoclave corroded Samples

Normal water

The baseline X2 and ZIRLO tube samples were corroded in a Cormet C215 1.6 L static autoclave at the University of Manchester, as part of the MIDAS programme. The autoclave was set at 310 °C and 10 MPa with water containing 1000 ppm B and 2 ppm Li to mimic the in-service corrosion environment in PWR reactors. Five sets of X2 and ZIRLO samples (with the dimension of 4mm×8mm×0.6mm, ten in total) were cut from the baseline cladding tubes and loaded into the autoclave for corrosion testing. Oxide thickness was measured every ~30 days. Three sets of samples corroded to 30, 60 and 90 days were selected for analysis in **Section 6.1 H₂O water corrosion**. Corrosion testing for the other two sets of samples is still ongoing, with the aim of reaching the 1-cycle time (~470 days) in the Vogtle reactor to compare the oxide thickness with Vogtle ex-reactor samples. At the time of writing, the corrosion tests have reached 276 days, and the oxide growth measured up to date is shown in **Figure 3-1**.

The oxide layers on ZIRLO and X2 samples grow to 1.4 and 1.6 μm, respectively, and determining from the growth rate, both alloys have gone through the first transition between 150 to 215 days. The power law fits are applied on the oxide thickness measured in the first cycle, which can well describe the growth curves, with $n=0.39$ for both, and $A=0.18$ for X2 and 0.17 for ZIRLO, respectively. This oxide growth rate is much less significant comparing with other Zr alloys under similar autoclave conditions, like Zr-0.4Nb [1], Zr-4 [165]. X2 has been reported to have a better corrosion resistance than ZIRLO [24], but opposite trend is seen here, possibly because this is only a short-term measurement.

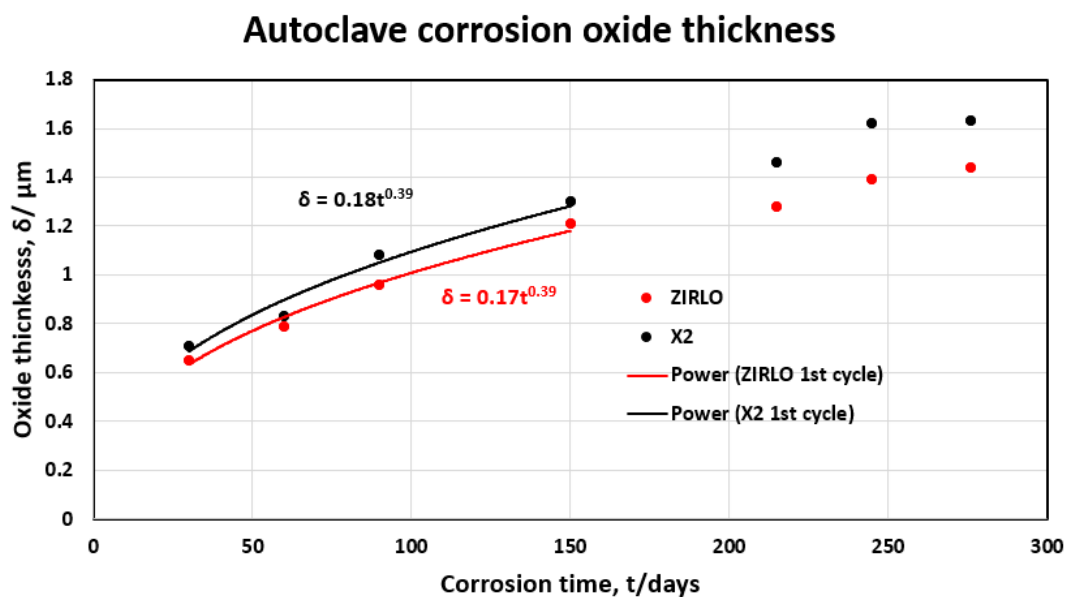


Figure 3-1. Oxide thickness diagram in the function of corrosion time for X2 (black) and ZIRLO (red) alloys, and the overlaid power law fits.

Spiked water

As summarised in **2.3.3 Diffusion of corrosion species**, the addition of stable isotopes to the corroding water can be used to trace the distribution of corrosion species in the oxide and so study the oxidation mechanisms. This thesis studies samples exposed to ^{18}O and D enriched water in spiking corrosion tests in the autoclave at the University of Manchester to explore the O and H in-diffusion process, **Table 3-4**. A Zr-4 sample was corroded at 320 °C and 12 MPa in pure deionized water for 150 days, followed by 60 days in 15% ^{18}O water. The oxide is 1.5 μm thick. A ZIRLO alloy was exposed for 10 days to H_2O and 20 days to 50% D_2O at 10 MPa and 310 °C, giving a 600 nm thickness oxide. Both spiked oxide layers are considered to be in the pre-transition regime [166]. Characterization results are presented in **Section 6.2** and **6.3**.

Table 3-4. Spiked corrosion tests.					
Spiking isotopes	Alloys	Temperature	Water chemistry	Stage 1	Stage 2
^{18}O	Zr-4	320 °C	1000 ppm B + 2 ppm Li	150 days 100% H_2O	20 days 50% D_2O
D	ZIRLO	310 °C		10 days 100% H_2O	20 days 15% H_2^{18}O

3.1.4 In-pile corroded samples

The ex-reactor samples were in-pile corroded in the Vogtle reactor for 1 to 4 cycles at $\sim 302^\circ\text{C}$ [167], with 1 cycle for ~ 1.3 years. The measured fast fluences ($E > 1\text{ MeV}$) are $3.88 \times 10^{25}\text{ n/m}^2$ for 1 cycle and $16.5 \times 10^{25}\text{ n/m}^2$ for 4 cycles, with estimated damage levels of 8 and 32 dpa. The active samples were shipped from the Studsvik hot laboratory (Sweden) to prepare bulk samples for characterisation at the UKAEA MRF. SEM images on the oxide cross section are shown in **Figure 3-2** for observation of the oxide thickness. At 1 cycle, X2 and ZIRLO alloy have similar oxide thicknesses of 2.15 and 2.27 μm . At 4 cycles, X2 oxide grows to 4.63 μm , while ZIRLO oxide significantly grows to 13.45 μm . Observation on X2 oxide thicknesses are slightly lower than the Fourier-transform infrared spectroscopy (FTIR) measurements of 2.7 and 5.1 μm thick [168]. The much higher corrosion rate of ZIRLO alloy after longer exposure in the reactor is discussed in **Chapter 7**.

The bulk metal matrix of the tube materials is free of corrosion and can be used to study the irradiated-only state. Therefore, each of the six tubes are cut into two parts and mounted on SEM stubs with the axial direction or radial direction facing up, termed as **axial cross section** and **radial cross section** samples, as shown in **Figure 3-3**(a and b). Information on twelve cross section samples is given in **Table 3-5**, and these samples codes will be used in the rest of the thesis. APT tips are made from the metal matrix of axial cross section samples at least 50 μm away from the O/M interface to study the effect of irradiation effect alone, **Figure 3-3**(c), and made vertically at the O/M interface from the radial cross section samples to study the combined effect of irradiation and corrosion (in-pile corrosion), **Figure 3-3**(d).

Table 3-5. Vogtle ex-reactor sample information.				
Sample code	Materials	Dose / dpa	Direction	Study purpose
1cXA*	1-cycle X2	8	Axial	Irra only
1cXR			Radial	Irra & corrosion
4cXA	4-cycle X2	32	Axial	Irra only
4cXR			Radial	Irra & corrosion
1cZA	1-cycle ZIRLO	8	Axial	Irra only
1cZR			Radial	Irra & corrosion
2cZA	2-cycle ZIRLO	16	Axial	Irra only
2cZR			Radial	Irra & corrosion
3cZA	3-cycle ZIRLO	24	Axial	Irra only
3cZR			Radial	Irra & corrosion
4cZA	4-cycle ZIRLO	32	Axial	Irra only
4cZR			Radial	Irra & corrosion

* A and R denotes the mounting direction of the bulk half-tube sample: A – axial direction facing up, R – radial direction facing up. 1cXA denotes 1-cycle X2 alloy axial cross section sample.

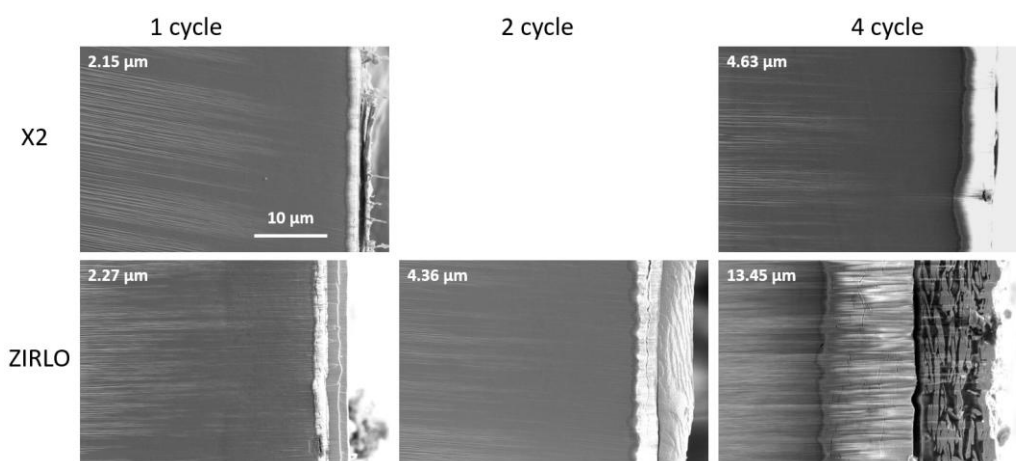


Figure 3-2. Oxide thicknesses measured by SEM images on the pFIB milled axial cross section ex-reactor Vogtle bulk samples.

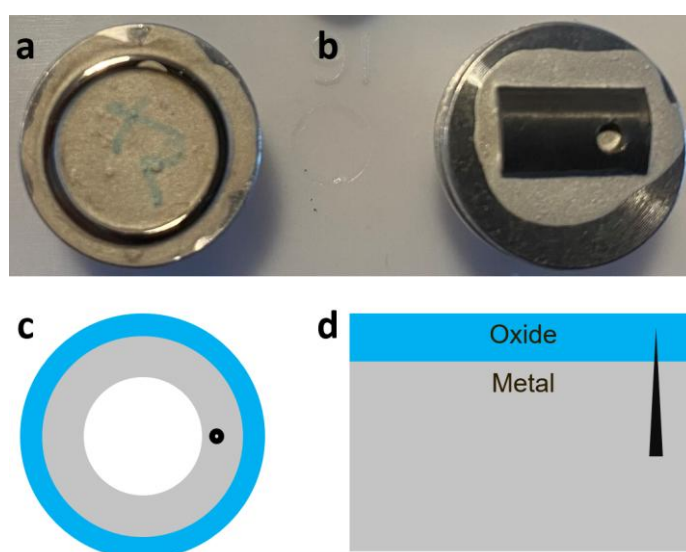


Figure 3-3. Schematics of the APT preparation from Vogtle ex-reactor tube samples. (a) axial cross section sample, and (b) radial cross section sample. (c) APT tip made from the metal matrix from (a) to study the irradiation effect alone. (d) APT tip made vertically at the O/M interface from (b) to study the combined effect of irradiation and corrosion at the O/M interface.

3.2 Atom Probe Tomography

The history of atom probe tomography (APT) can be traced back to 1935 when Muller developed the field electron emission microscope, followed by the progression to the field ion microscope (FIM) in 1955 [169]. A key development was field evaporation, where surface atoms are ionised and removed from a sharp specimen under high electric field, enabling atomic-scale analysis [169]. Based on this, the first one-dimensional (1D) atom probe combining FIM and a time-of-flight mass spectrometer was developed in 1973 [170, 171], followed with the design of three-dimensional atom probe (3DAP) by Cerezo et al in 1988 [172], which initiated the kind of analysis that is now known as APT. APT provides three-dimensional compositional mapping with sub-nm resolution and parts-per-million (ppm) sensitivity for all elements, and complements electron-based or X-ray-based microscopies and spectroscopies in the analysis of complex material systems, **Figure 3-4** [86]. The fundamentals of APT have been thoroughly illustrated in textbooks [169, 173, 174].

As summarised in **Figure 3-5 (a)**, APT analysis is carried out in the analysis chamber with ultra-high vacuum around 10^{-9} Pa (equivalent as 10^{-11} Tor). The APT specimen is normally a conical-shaped tip made from the analysed bulk sample, less than 100 nm in diameter and several hundred nm in length (details in Section 3.3.1). The sequential processes of ionisation and ejection of atoms from the tip surface are termed **field evaporation**. The evaporated ions will follow a flight pathway determined by the local electric field profile and hit a 2D detector where both the hit position and time of flight will be recorded. This process is known as **ion detection**. This information of millions of ions will be converted back to the original position and chemical identity on the tip specimen during the process of **reconstruction**.

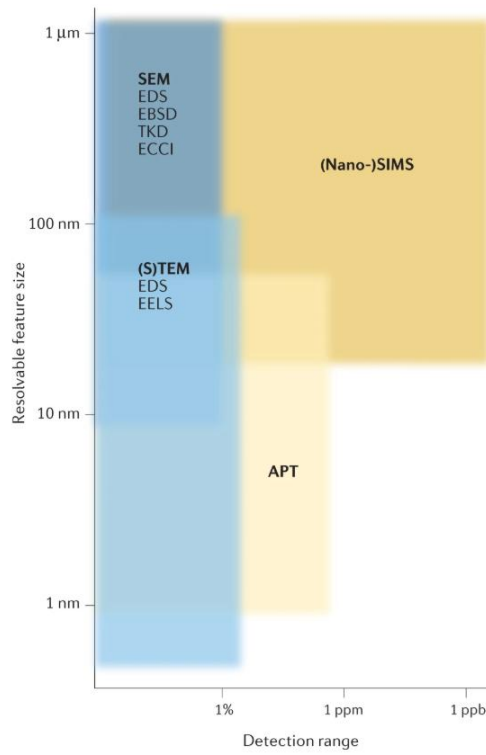


Figure 3-4. Diagram of chemical sensitivity and spatial resolution of characterisation techniques [86].

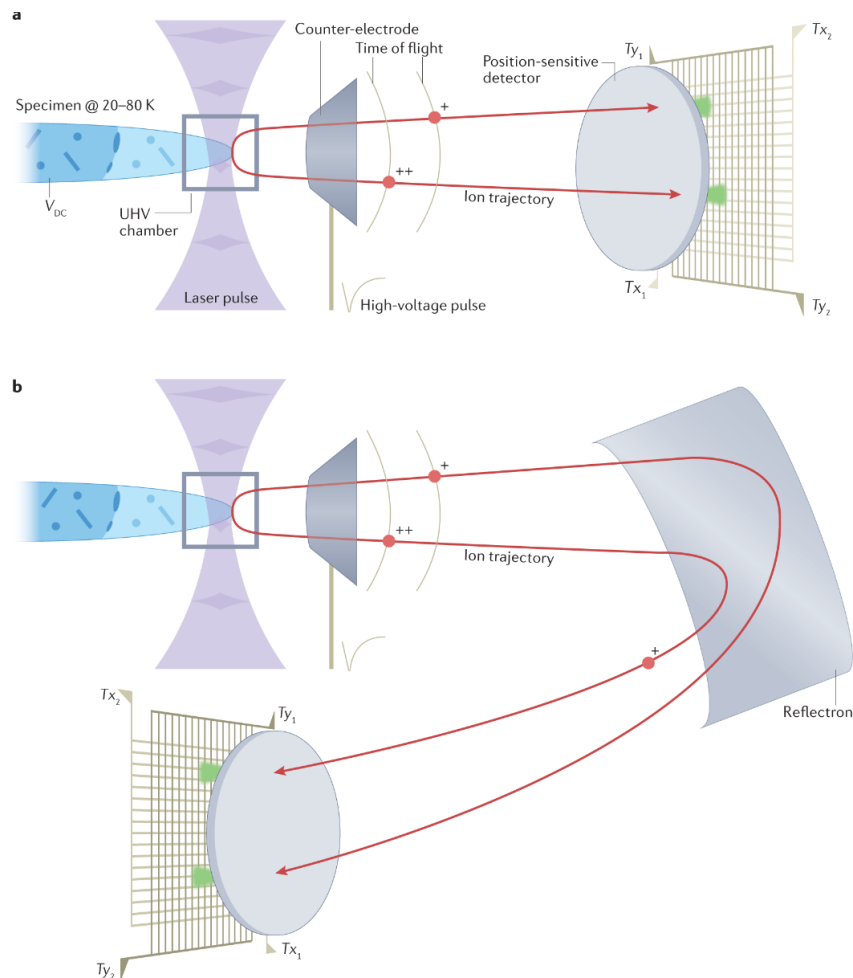


Figure 3-5. Schematic diagram of APT with (a) a straight flight pathway and (b) a reflectron [86].

3.2.1 Field evaporation

The specimen is held at a cryogenic temperature of 20-80 K by contacting to a helium-based cryogenic cooler, and a base voltage of up to 10 kV, as shown in **Figure 3-5(a)**. The electric field F applied by the voltage on the tip surface can be estimated as

$$F = \frac{V}{k_f R},$$

where V is the applied voltage, k_f is the field factor constant describing the tip shape and electrostatic environment, and R is the radius of the tip at the apex. The electric field must exceed the evaporation field of the surface atoms to trigger the evaporation event. In the currently most common APT instrument, the local electrode atom probe (LEAP), the tip is aligned with an electrode. As shown in **Figure 3-6**, the base temperature and voltage on the tip are kept below the evaporation field, and an extra voltage increase (applied to electrode to increase the electric field, vertical arrow) or laser pulse (to increase the temperature, horizontal arrow) is applied to the tip to trigger field evaporation of atoms on the tip apex at a controlled rate. These field evaporated ions are accelerated by the electric field around the tip surface, and fly towards the detector.

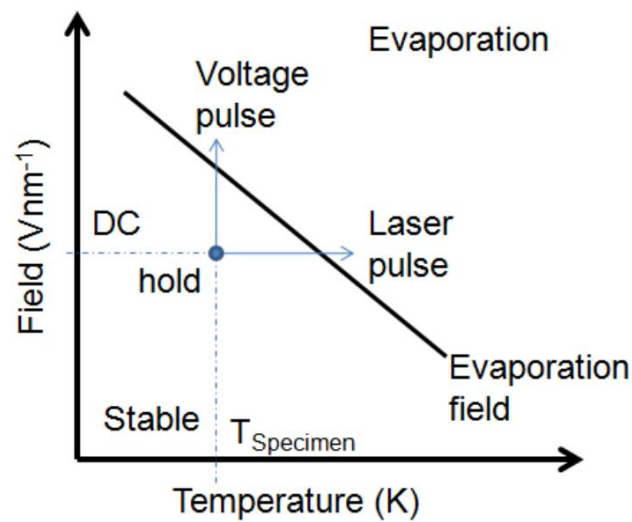


Figure 3-6. Schematic showing the APT field evaporation of a surface atom. The blue dot indicates the specimen under base voltage and temperature. The two arrows mark the effect of voltage pulsing (vertical, increase field) and laser pulsing (horizontal, increase temperature) to trigger field evaporation [174].

During the early stage of flight, singly charged ions can be further ionised to 2+ or 3+ states, **Figure 3-5(c)**, depending on the ionization energy and the magnitude of the electric field [173]. Thus the ratio of the same ions detected at different charge state can be used to estimate the applied electric field during APT analysis [175], e.g., the required evaporation field for Zr^{3+} and Zr^{2+} are approximately 35 V/nm and 28 V/nm, respectively, so a higher Zr^{3+}/Zr^{2+} ratio indicates a more intense electric field during analysis.

3.2.2 Ion detection

The APT ion detector consists of microchannel plates and three polarised conductive lines (delay lines) behind, **Figure 3-5(a)**. The APT detector records the timing and the position of the arriving evaporated ion. The impact of a single ion on the microchannel plates produces an electron cascade [176], which is then conducted to the two ends of two delay lines. The times reaching the four ends are convert to lateral coordinates of the ion impacting position [86]. The third delay line is used to process multiple hit events (more than two ions hit the detector simultaneously) to help improve the accuracy of the positional information [86, 177].

The evaporated ion has potential energy E_p equal to the kinetic energy E_c gained from the electric field. The time of flight of ions, t_f , defined as the time between the application of the voltage/laser pulse that triggers the filed evaporation and the time when an ion arrives at the detector [173]. t_f relates directly to the ion kinetic energy, E_c and the velocity, v , acquired from the electric field,

$$E_p = neV,$$

$$E_c = \frac{1}{2}mv^2,$$

$$v = \frac{L}{t_f},$$

and therefore,

$$\frac{m}{n} = M \approx 2eV \left(\frac{t_f}{L} \right)^2,$$

where ne is the charge of the ion, V is the applied voltage, m is the ion mass, L is the flight distance, and $\frac{m}{n} = M$ is the mass-to-charge-state ratio (mass ratio) of the ion. So ions with larger mass ratio require longer flight time to arrive at the detector.

The design with a reflectron in the flight pathway is shown in **Figure 3-5 (b)**. A reflectron acts as an electric mirror that bends the ion trajectory and extends the distance of the flight pathway. Thus, it prolongs the time of flight of all ions and increases the mass resolution [178]. The APT instrument CAMECA LEAP 5000XR, used in this thesis to acquire APT data, adopts this design.

3.2.3 Reconstruction

APT raw data consists of a sequence of xy coordinates and the corresponding times of flight. The z coordinate of an ion is determined by the sequence of its evaporation during the analysis, assuming a layer-by-layer evaporation process. The **reconstruction** process assigns spatial coordinates and chemical identities to each detected ion, ultimately constructing a 3D tip dataset that approximates the original dimension of the tip specimen using all the detected ions.

The time of flight is converted to the mass-to-charge-state ratio in Daltons (Da), and the distribution of the mass ratios of all ions detected in one analysis is represented as a histogram, termed a mass-to-charge-state spectrum (**mass spectrum**). The accumulation of detected ions induces many mass peaks in a mass spectrum. Each peak normally is composed of the same kind of ions and needs to be assigned with a chemical identity, known as **mass peak ranging**. Normally all isotopes of an element are expected to follow their natural abundance, e.g., the isotopes of Zr, ^{90}Zr , ^{91}Zr , ^{92}Zr , ^{94}Zr and ^{96}Zr , follow the abundance of 51.45%, 11.22%, 17.15%, 17.38% and 2.8%, with exceptions found for elements that undergo biotic fractionation or nuclear **transmutation** (**Chapter 5**) [86]. Such

isotope fingerprints can be referred to when ranging the peaks, and when deconvoluting peaks that contain more than one types of ions (details in Section **3.4 APT data analysis**).

Finally, millions of these ions can be transformed into the reconstruction of the real-space APT tip, using the known chemical identity and 3D coordinates of each detected ion. The reconstructed dataset enables atom-by-atom analysis of local compositions and the distribution of nanoscale features like grain boundaries and precipitates. The optimal data analysis method depends on the specific purpose, the quality of the data, the nature of the materials, etc. This thesis focuses on the APT data on Zr metal and oxide, and details are given in Section **3.4 APT data analysis**.

3.2.4 Laser-pulsed APT

The APT technique was originally designed for metal specimens, but can also be applied to semi-conducting or insulating materials thanks to the incorporation of a pulsed laser system [179, 180]. During laser-pulsing mode analysis, the laser illumination increases the local temperature of the tip apex so that the electric evaporation can be triggered at a relatively lower electric field (the lateral arrow in **Figure 3-6**). Atoms in oxide are more likely to be evaporated in the form of complex molecular ions, which can dissociate during flight, inducing loss of neutral species or multiple hits on the detector [181]. Also, due to the limited thermal conductivity, although the laser is only applied to the tip apex for femtosecond, the tip stays at the elevated temperature for a significant time, leading to delayed evaporation [182, 183] and increased surface diffusion [184, 185]. All these effects can degrade the composition accuracy and the spatial resolution, and thus the data quality of insulating materials is inevitably worse than metallic materials.

3.3 APT data acquisition

APT specimens with better quality can better withstand the stress during field evaporation and thus have the potential to output larger datasets with better data quality. The considerations for APT **specimen preparation** and **experiment design** are illustrated below in sections 3.3.1 and 3.3.2, respectively.

3.3.1 Specimen preparation

The preparation of APT specimen requires milling the bulk material into a sharp, thin tip, this was achieved previously by a two-step electropolishing [186, 187], and more recently by focussed ion beam (FIB) milling [188]. FIB enables the preparation of specimens from more complex sample types (like oxides on metals), and allows tips to be prepared from site-specific regions from the bulk materials [189].

This thesis only employed the FIB methods. FIB sample preparation requires a flat and smooth surface of the bulk sample. This was conducted mostly using traditional mechanical grinding and polishing method. For axial cross section Vogtle samples, Section 3.1.4, to avoid dealing with the active bulk samples and minimise the active wastes, a pFIB (plasma-FIB) polishing method was used to give a small region with a relatively smooth surface for subsequent APT sample preparation. **Figure 3-7** shows the secondary electron microscopy (SEM) view along the axial direction on the tube wall, the initial cut left a rough surface, and pFIB polishing was conducted using a TESCAN AMBER X PFIB at the MRF with ion beam vertical to the tube wall to give a smooth surface.

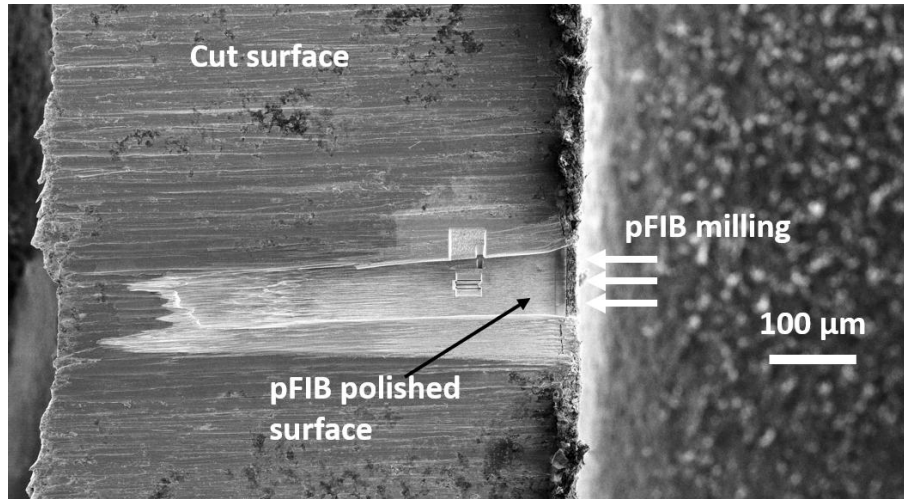


Figure 3-7. pFIB polished surface for APT sample preparation.

Focussed ion beam sample preparation

FIB employs a finely focused beam of high-energy ions (normally Ga^+ or Xe^+) to sputter and remove material from a bulk sample surface. By controlling the voltage, current and milling pattern of the ion beam, materials can be selectively removed at targeted positions, enabling the creation of complex structures with high precision. FIB is widely used to prepare thin TEM lamella and sharp APT tips. Advanced FIB systems are normally equipped with SEM and other characterisation tools like energy dispersive X-ray spectroscopy (EDS), electron backscattered diffraction (EBSD) and secondary ion mass spectrometry (SIMS).

The APT tip specimens in this thesis were prepared using several FIB systems, including a Zeiss Crossbeam 540 and a Thermo-Fisher Helios G4-CXe Plasma FIB (pFIB) at the David Cockayne Centre for Electron Microscopy (DCCEM) at the University of Oxford, a Helios 600i at UKAEA MRF (for radioactive bulk materials), a ThermoFisher Helios pFIB instrument at the University of Manchester. Detailed comparison of the use of Ga FIB and pFIB has been published by Koc et al [190].

If not otherwise stated, APT tip specimens were prepared following a previously published preparation procedure, including trenching, liftout, welding to post, annular milling and

cleaning [191]. FIB parameters of the full process are displayed in **Table 3-6**. The annular milling defines the final tip shape and is thus the most important step. This needs to remove any protruding parts other than the tip in the top 10 μm , to avoid extra evaporation from protrusions during APT analysis. Tips are sharpened only at the top 1 μm of the liftout section, and by controlling the depth of the milling pattern, the lower part of the tip is left wider, **Figure 3-8**. This is to leave a strong base to withstand the stress generated by the applied voltage during evaporation and better dissipate heat from the laser pulses. Tips made by this strategy are more likely to produce substantial datasets in the APT.

Table 3-6. FIB parameters for making APT tip samples.					
Parameters	Trenching	Welding	Annular milling 1	Annular milling 2	Cleaning
Voltage (kV)	30	30	30	30	2
Current (nA)	15	0.05	1.5	0.1	0.2
Depth (μm)	10	1	1.5	1	0.2

Because of the limited analysed volume of an individual APT dataset (an approximately conical volume 100 nm in diameter and several hundreds of nm in height), it is difficult to obtain data from interesting regions in the overall microstructure if the APT tips are made from random regions of the bulk material. Sometimes FIB work needs to be delicately carried out at height- or site-specific regions in order to analyse specific regions of the bulk material.

Height-controlled sample preparation

Height-controlled tip preparation can be achieved by observing the different contrast of phases or measuring the depth in SEM view during milling, leaving the interesting region ~ 200 nm below the final tip apex. In this thesis, the solute distribution at the O/M interface is a key to understanding oxidation mechanisms, so annular milling steps were delicately controlled so that the final APT tips are milled vertically with the O/M interface to a

controlled height, containing oxide, O/M interface and metal substrate, as described in [111].

An example of the milling process aiming for the interface is shown in **Figure 3-8**.

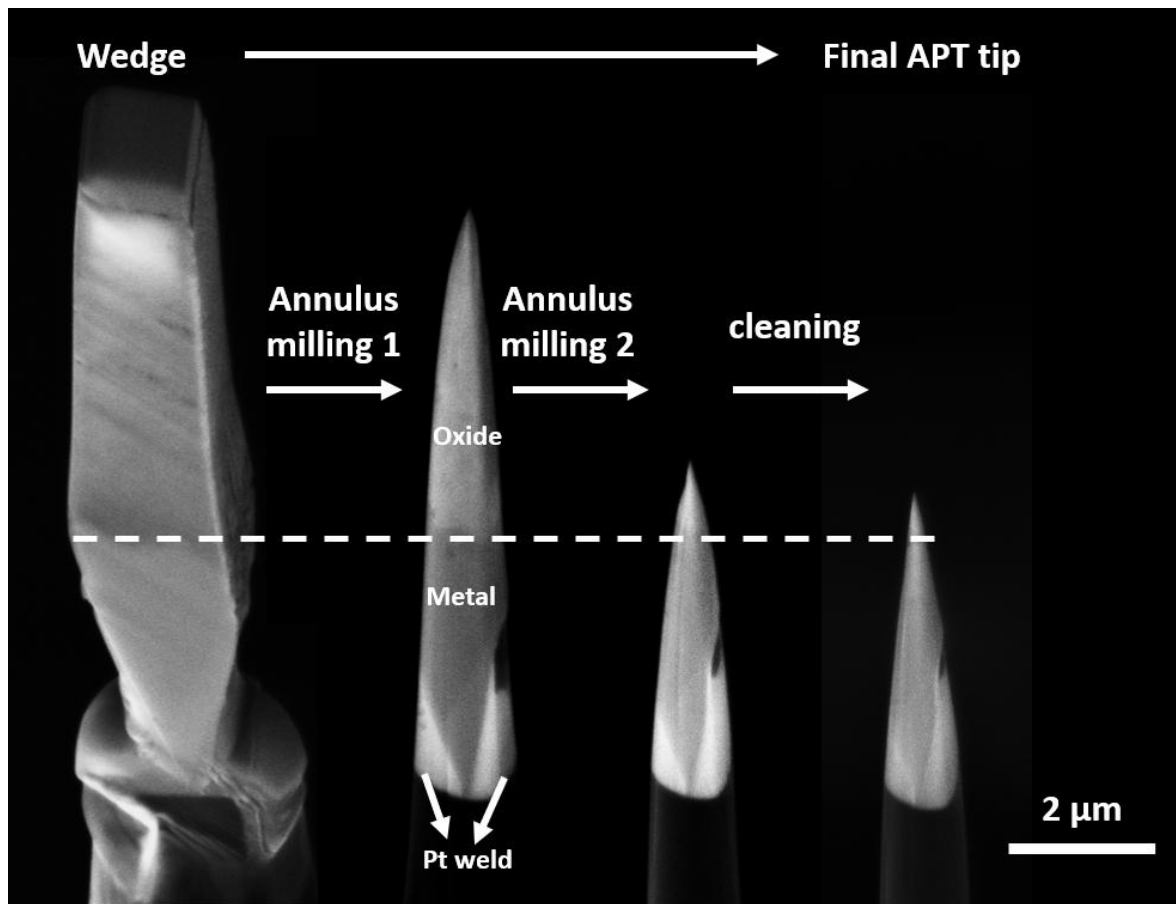


Figure 3-8. SEM view of the annular milling workflow from the wedge to final APT tip to produce a height-controlled APT tip at the O/M interface. The dashed line indicates the position of the O/M interface. Oxide shows brighter contrast than the metal substrate.

Site-specific sample preparation

The behaviour of Zr_2Cu SPPs before and after irradiation is a core focus for the W13 alloy, but they are well-dispersed in the α -Zr matrix. Hence, an EDS-FIB correlated site-specific lift-out method was used in order to make APT specimens containing Zr_2Cu SPPs. The Zr_2Cu SPPs were first identified using EDS on a TESCAN AMBER X PFIB at UKAEA MRF as shown in **Figure 3-9(a)**. Pt dots were deposited on the Zr_2Cu SPPs as markers (**Figure 3-9(b)**), with FIB pattern parameters of 0.5 μm in diameter and 1 μm in thickness. Then, after the bulk samples were moved to the FEI Helios Nanolab 600i system, a protective Pt bar was deposited on the top of these dots, followed with the normal process

of trenching, liftout and welding the liftout onto the premade Si posts [191]. The annular milling pattern was carefully placed on the dots so that the sharpened tip comes from the centre of the dot. The height of the tips was then controlled during annular milling so that no material below the Pt cap was removed, giving a good chance that the Zr_2Cu SPPs are located at the top of the tip specimen. This method has worked successfully to produce APT tip with Zr_2Cu SPP on the top, **Figure 5-5**.

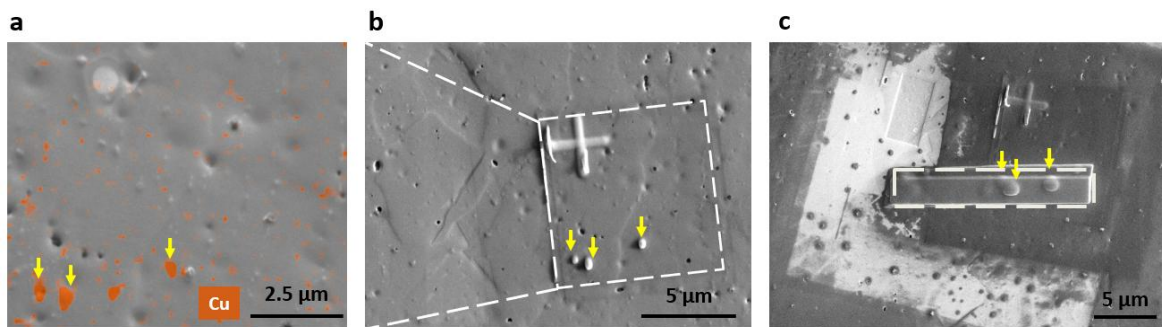


Figure 3-9. EDS-FIB correlated site-specific liftout method for making APT tip specimens containing Zr_2Cu SPPs. (a) Cu SEM-EDS map overlaid on SEM image, yellow arrows indicate the three Zr_2Cu SPPs. (b) Pt dot depositions made on the top of Zr_2Cu SPPs. The dashed white box indicates the region of the EDS map in (a). A cross was made to help locate these marked SPPs after moving the bulk sample to the second FIB. (c) Protective Pt bar deposition (dashed box) over Zr_2Cu SPPs.

CryoFIB

The FIB ion beam sputters the sample causing a localised temperature increase [192], which promotes the attachment of contamination gases from the FIB chamber during milling, mostly H, C, N, etc. This effect is considered insignificant at the bulk milling stage (trenching) as the heat can be readily conducted away into the bulk sample, but becomes significant at the final milling stage of APT and TEM specimens due to the limited volume of materials, thus the poor heat extraction. The elevated temperature promotes the adsorption of H and the formation of hydrides, which significantly affect the composition and structure analysis, especially when H analysis is the interest. Milling the specimen at cryogenic temperatures can minimise the H ingress and formation of hydrides [193, 194]. In this thesis,

cryoFIB was applied at the annular milling and cleaning stages at -90 to -120 °C whenever possible. The cryoFIB systems were set up with liquid nitrogen in a dewar, and conductive Cu bands to a cryogenic sample stage on the Thermo-Fisher Helios G4-CXe pFIB at the University of Oxford, the Helios 600i at UKAEA MRF and the ThermoFisher Helios pFIB at University of Manchester.

Figure 3-12(a and b) compare mass spectra from APT tips made by FIB at cryogenic and room temperatures. The 1 and 2 Da and ZrH_x^{2+} peaks are much higher in the room temperature APT dataset, indicating that the use of cryoFIB significantly reduces spurious H in the APT data, making the analysis of actual H or D distributions in the material possible (**Section 6.3 D-spiking**). It also helps with the analysis of Zr-Nb alloys in this thesis, as there are lower ZrH^{2+} signals and the peak overlap between $^{92}\text{Zr}^1\text{H}^{2+}$ and $^{93}\text{Nb}^{2+}$ at 46.5 Da is much improved. More benefits of the APT analysis on tips made by cryoFIB can be found in [190, 195].

3.3.2 Experiment design

APT datasets analysed in voltage-pulsing mode are normally simpler to analyse and have a better data quality than those analysed in the laser-pulsing mode because there are fewer complex molecular ions, smaller of thermal tails, less content of contamination species and better spatial resolution [184, 196] due to the higher evaporation field, lower temperature, less surface diffusion [197, 198] and less gas adsorption. However, voltage pulses apply extra stress, so tips are more likely to fracture early, while the laser-pulsing mode normally enables larger volume of materials to be analysed, so better statistics. Especially, as is well-known, the viability of Zr APT tips is extremely low under the voltage-pulsing mode [111], compared to other material systems like steels and Al alloys. Therefore, a balance must be made between data quality and dataset size when designing the experiment. In this thesis,

APT analyses are mostly designated in laser mode to get larger volume of materials analysed with acceptable data quality before specimen fracture.

The corrosion process introduces nanovoids and cracks into the oxide layer [57, 199], and APT tips made of such materials must also contain them, **Figure 3-10**. These defects will make the APT tips vulnerable to fracture under the stress required for field evaporation. The metal Zr matrix, despite the nanovoids induced by irradiation, are relatively denser. It has been reported that the effect of base temperature on the solute composition is negligible [200], and running conditions of higher laser energy and higher base temperature, lower detection rate and pulse frequency can reduce the electric field applied to the specimen, and are more likely to result in larger datasets [186, 201].

With these considerations, different parameters are applied for the analysis of metal and oxide tips, **Table 3-7**. All the APT analyses, unless otherwise stated, were carried out on a CAMECA LEAP 5000XR at the APT group at University of Oxford. It has a micrometre-size laser spot with 10-ps laser pulses at 355 nm wavelength, and a 52% detection efficiency (percentage of the evaporated ions that are eventually detected) [86]. Metal tips were analysed under parameters of 50-65 K, 0.3-0.6% detection rate (detection of 0.3-0.6 ions in every 100 pulses on average), 40-100 pJ laser pulse energy, 125-250 kHz pulse frequency. Oxide tips were analysed with base temperature of 65-75 K, 60-120 pJ laser pulse energy, 125-200 kHz pulse frequency, and 0.2-0.4% detection rate. The auto-control of the base voltage was turned on, so that the base voltage will increase as the tip getting blunter to maintain the input detection rate.

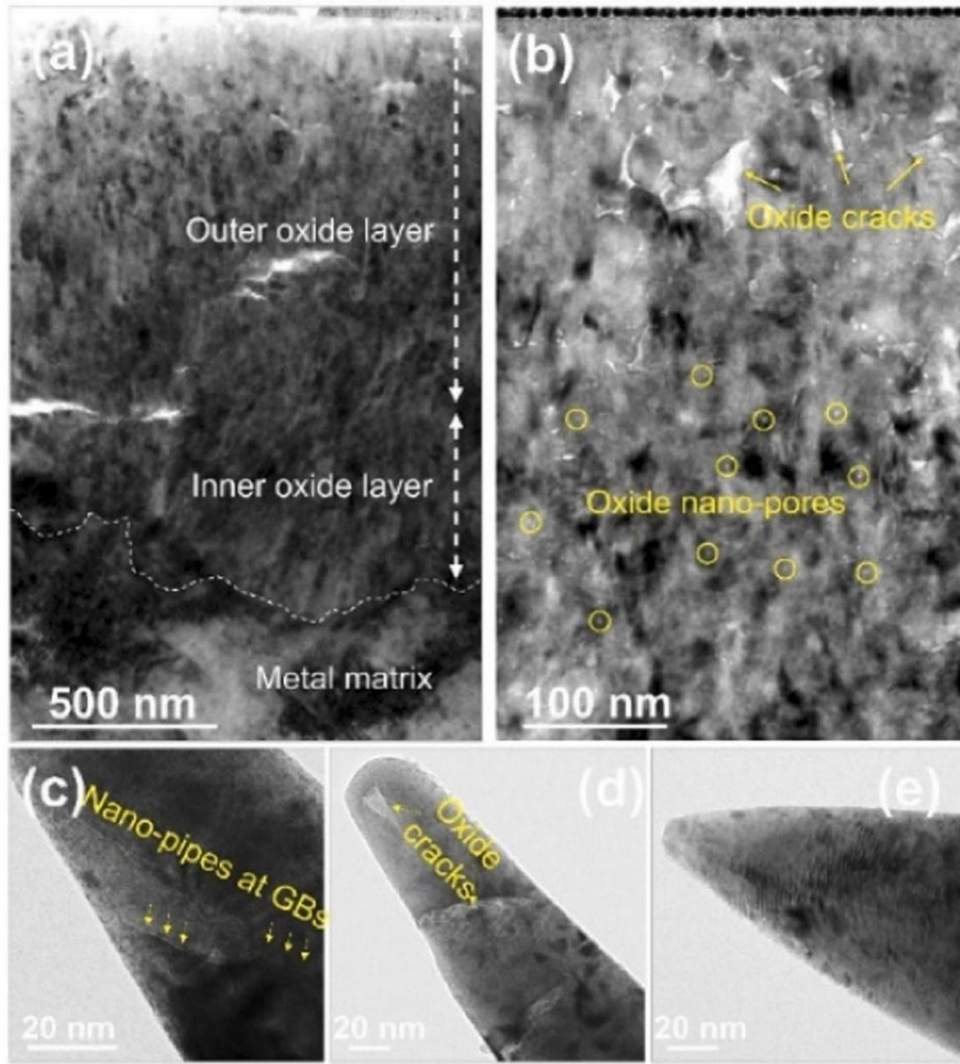


Figure 3-10. (a) Bright-field TEM images showing an overview of the O/M interface (dashed line) on Zircaloy-4. (b) A TEM image showing the distribution of oxide cracks and nanopores in the oxide layer; (c-e) TEM images of APT tips prepared from the inner oxide, containing a high density of nm-scale voids and cracks. (Courtesy of Junliang Liu, University of Oxford)

Table 3-7. APT experiment parameters for Zr metal and oxide APT tips.				
Regions	Base temperature / K	Detection rate	Laser energy / pJ	Pulse frequency / kHz
Metal	50-65	0.3-0.6%	40-100	125-250
Oxide	65-70	0.2-0.4%	60-120	125-200

3.4 APT data analysis

APT data analysis can be very user-dependent and requires careful interpretation of the data to output accurate results. This section introduces the key APT data processing methods used in this thesis.

3.4.1 Voltage-based reconstruction

The evolving radius of the APT tip, R , during the analysis determines the electric field and thus the base voltage required to evaporate the surface atoms. R can be acquired according to

$$F = \frac{V}{k_f R},$$

where F can be estimated from the evaporation field of the most abundant elements in the tip, V is recorded during the analysis. Crystallographic poles are normally used to determine the image compression factor (ICF) and field factor k_f [202, 203]. However, this method is mostly not applicable in this thesis, because crystallographic poles are normally not clear in most of the APT metal datasets due to the HCP crystal structure of α -Zr matrix and ion surface diffusion induced by laser pulsing, and does not exist at all in oxide datasets. k_f was determined in the range of 3.0 – 3.8, inversely proportional to the laser pulse energy, consistent with [144].

The diagram of voltage curve in the function of detected ion number during the APT analysis containing firstly oxide, then the O/M interface and the underlying metal (**Figure 7-16**) is shown in **Figure 3-11**. If the specimen consists of a single phase, the evaporation field for the surface atoms is constant and thus the required voltage only depends on the progressing radius on the tip apex which should increase monotonically throughout the analysis, as shown by the red curve. An abrupt voltage increase is observed when the analysis passes the O/M interface. FIB beam mills the specimen with constant shank angle so the actual radius of the specimen should not have such sudden increase. This indicates a sudden increase of the evaporation field from the oxide into the metal, suggesting that atoms in the metal requires larger electric field to evaporate than those in the oxide. This is important in

understanding the detection of different ion types in two phases, e.g., it is less likely to have complex ions in the metal where the evaporation field is higher.

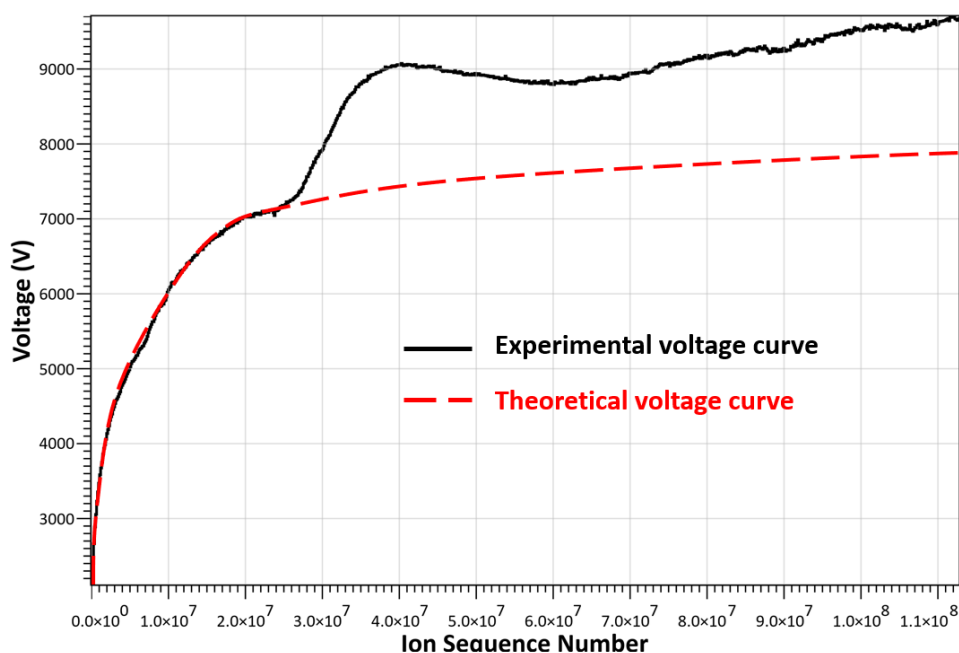


Figure 3-11. Voltage curve in the function of detected ion number during the analysis of APT dataset in **Figure 7-16** (black), and a theoretical voltage curve (red) for a specimen with uniform shank angle and same evaporation field.

3.4.2 Mass spectrum analysis

Reconstruction and data analysis were performed in the commercial software **AP Suite 6.3.1** developed by CAMECA. One of the most important steps of processing APT data is to assign chemical identity to peaks in the mass spectrum. Due to very different material properties and analysis parameters, datasets from Zr metal and ZrO₂ oxide show significantly different mass spectra and are thus processed differently. An overall view of the mass spectrum extracted from typical metal dataset made by cryo-FIB, metal dataset made by room temperature FIB, and oxide dataset is shown in **Figure 3-12(a-c)**. Some detailed mass spectra will be shown in the results chapters for tip-specific analysis.

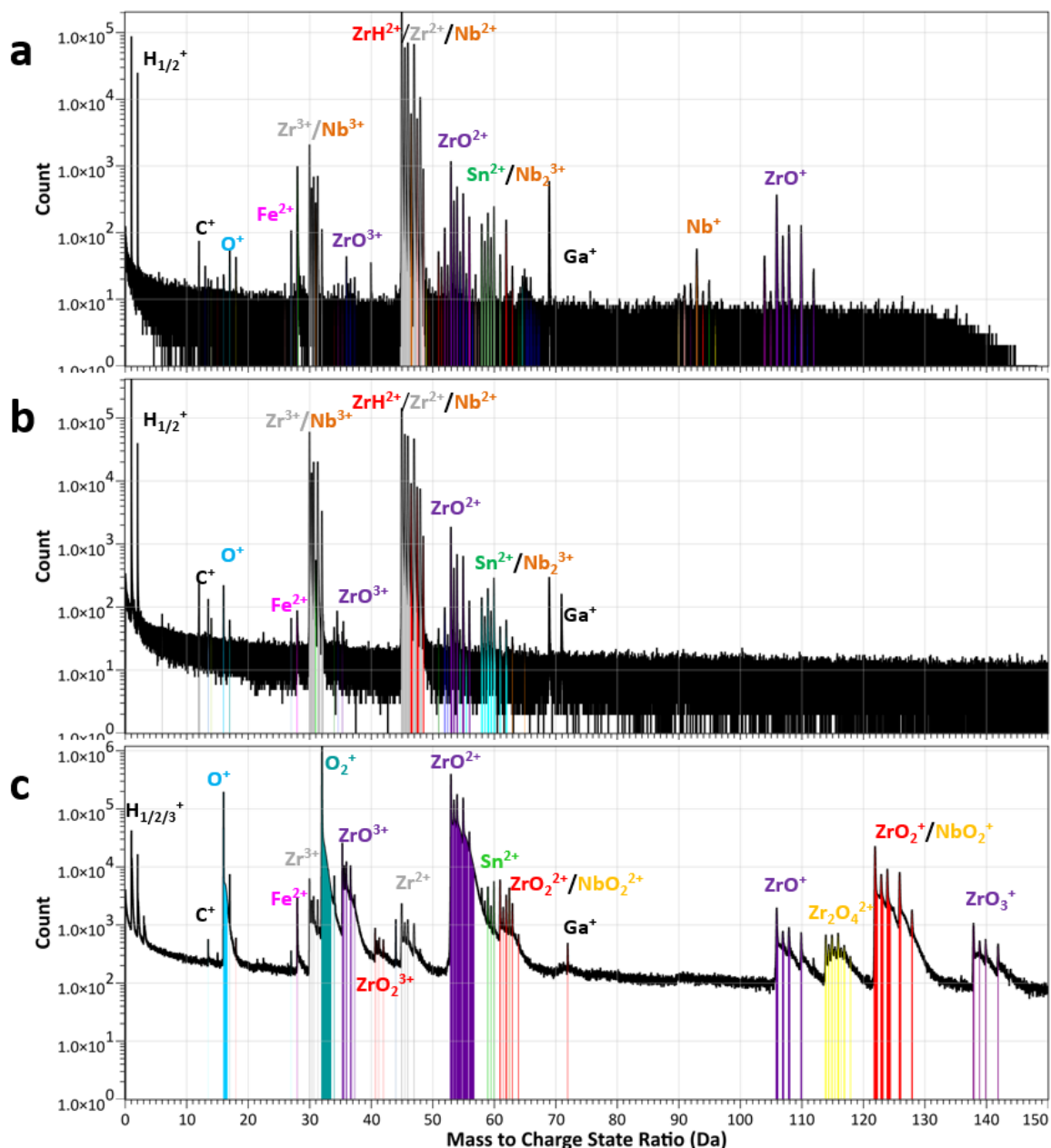


Figure 3-12. Typical mass spectra of APT datasets from (a) metal tip made by cryoFIB, (b) metal tip made by room temperature FIB, and (c) oxide tip made by cryoFIB. Note, the y axis is in log scale to include all the peaks with huge count differences in the same figure.

Metallic dataset

In Zr metal dataset, Zr ions account for more than 98% of the material, with Zr^{2+} ions as the main peaks. The background noise level is generally low, so a background-to-background ranging method was used to assign chemical identity to ion peaks.

Oxide dataset

After oxidation, the α -Zr matrix transforms into insulating ZrO₂ with more than 60% O. The significant changes in composition, material properties, and analysis parameters lead to distinct evaporation behaviours and mass spectra. Complex molecular ions are frequently seen in the mass spectrum and the background noise is significantly higher, making ranging more difficult. Additionally, due to the warmer parameters used to run the oxide specimens and the poorer thermal conductivity of the oxide, the tips stay at elevated temperature for longer times, so the time window for evaporation after a laser pulse is prolonged. The later evaporated ions are detected with a longer time of flight, presented as a tail on each peak in the mass spectra, known as **thermal tails**, as shown by the evident contrast between **Figure 3-12(c)** and **Figure 3-12(a)**. Most of these thermal tails behind the initial sharp peaks should also be ranged to get the actual composition. However, small peaks positioned closely behind the thermal tails will be buried, and the contributions to the overall composition of these small peaks will be significantly affected. Thermal tails are unavoidable and deteriorate the quality of the data.

Another major difference is that in APT tips made by cryoFIB that and that do not contain additional D within the bulk material, the 3 Da H₃⁺ peaks are not seen in metal dataset, but are seen in all oxide datasets. This suggests that attached H from the analysis chamber is likely to be evaporated as H₃⁺ from an oxide tip, probably due to the strong affinity of H to oxide surface or the lower evaporation field of oxide so H₃⁺ is less likely to decompose during the flight stage.

Peak overlap

The Zr alloys studied in this thesis contain deliberately added elements of Zr, Nb, Sn, Fe, Cu, V and O, and trace impurities incorporated from processing histories or service environment of Li, Al, Cr, Ni, Ti, Si, Mn W, Hf and Mo. APT analysis detects all these elements in all their isotopic states, so it is unavoidable that there are more than two kinds

of ions with very similar mass ratios. When this difference is close to the mass resolution of APT, these peaks are partially or completely overlapping in the mass spectrum, as indicated in **Figure 3-13**(b and c). Peak overlap makes precise assignment of the chemical identity of each ion very difficult, affecting the accuracy of the analysis.

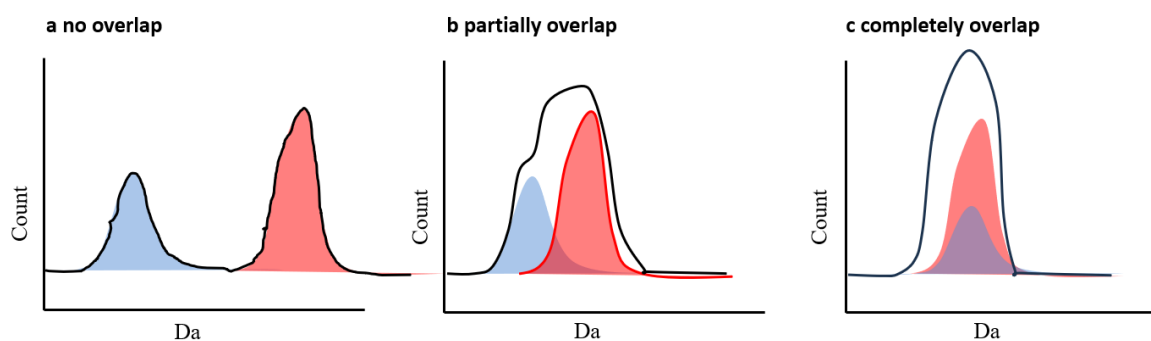


Figure 3-13. Schematics of APT mass spectra showing two peaks that are (a) not overlapped, (b) partially overlapped, (c) completely overlapped. Red and blue shows the peaks of two ions with adjacent mass ratios, black lines indicate the overall counts.

The overlapped peaks can normally be decomposed for the contribution to the compositions of the two species, based on the estimate of isotope signals from the known isotope abundance, and this process is known as **deconvolution**. In this thesis, peak overlap solving was carried out using the APLab MATLAB code developed by London et al [204]. For example, both $^{56}\text{Fe}^+$ and $^{96}\text{Zr}^{16}\text{O}^{2+}$ ions contribute to the 56 Da peak, and the fraction of $^{96}\text{Zr}^{16}\text{O}^{2+}$ can be calculated from its ratio to the $^{94}\text{Zr}^{16}\text{O}^{2+}$ peak at 55 Da, and the rest of the 56 Da peak is from $^{56}\text{Fe}^+$. However, when the overlapping ions do not have isotopes, or when one signal is dominating the peak, deconvolution becomes very difficult. The overlaps that most affect the solute composition are summaries in **Table 3-8**.

Deconvolution for the spatial distribution of completely overlapped ions is not possible, like $^{93}\text{Nb}^{2+}$ and $^{92}\text{Zr}^1\text{H}^{2+}$ at 46.5 Da. When partially overlapped, **Figure 3-13**(b), the distribution of the two ions can be addressed by a separate ranging strategy. In **Figure 3-14**, a partially overlapped double peak can be seen at ~28 Da, between $^{56}\text{Fe}^{2+}$ (left) and $^{12}\text{C}^{18}\text{O}^+$ (or N_2^+ ,

right). Fe shows strong segregation at the oxide GBs, while CO, stemming from the gas in the analysis chamber shows a random distribution. Consensus on the efficiency of this ranging method for Fe has been previously reported in [144, 205]. The middle part of the composite peak should not be ranged because it is a combination of both signals, and only the most left side and the most right side of the peak consist definitely of signals from one of the ions, as shown in the schematic in **Figure 3-13(b)**.

Table 3-8. Peak overlap table	
Mass ratio/Da	Overlapping ions
28	$^{56}\text{Fe}^{2+}$, $^{12}\text{C}^{16}\text{O}^{2+}$
46.5	$^{93}\text{Nb}^{2+}$, $^{92}\text{Zr}^1\text{H}^+$
56	$^{56}\text{Fe}^+$, $^{96}\text{Zr}^{16}\text{O}^{2+}$
62	$^{124}\text{Sn}^{2+}$, $^{93}\text{Nb}_2^{3+}$
93	$^{93}\text{Nb}^+$, $^{92}\text{ZrH}^+$, $^{91}\text{ZrH}_2^{2+}$

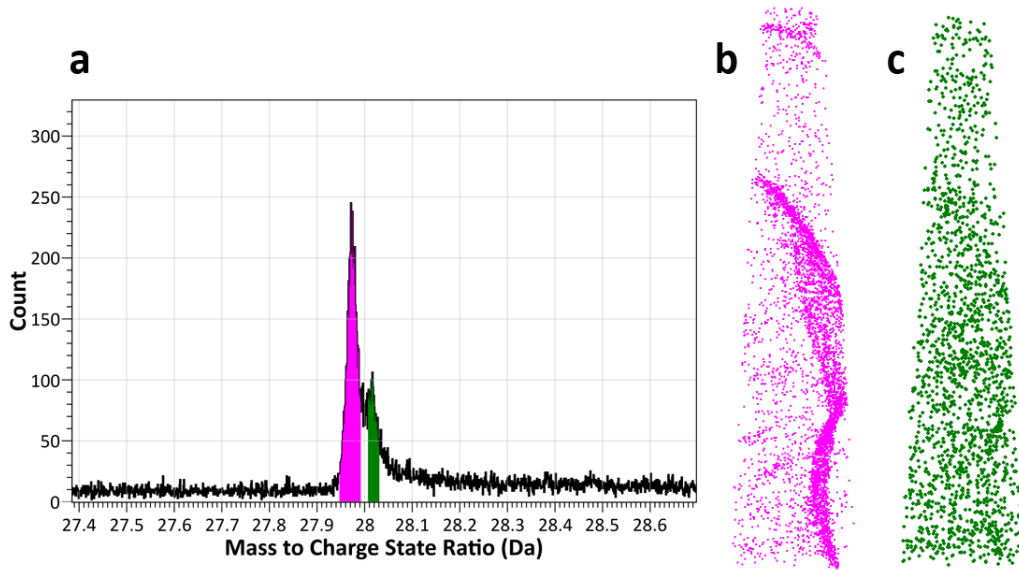


Figure 3-14. APT dataset ‘PZ08_M4’ from ZIRLO oxide formed in 60-day autoclave corrosion. (a) Mass spectra in the range of 27.5-28.5 Da. Spatial distribution of (b) $^{56}\text{Fe}^{2+}$, and (c) $^{12}\text{C}^{16}\text{O}^+$.

Dataset-specific analysis

The composition of different phases in the microstructure can be very different, resulting in completely different mass spectra. Sometimes the quality of the data (surface diffusion, thermal tails, background noise, multiple hits, etc) is significantly different, so dataset-specific analysis is required to extract the most accurate data. Most of these considerations

are described in result chapters, and here are some examples. If the one dataset contains two different regions, they require different ranging strategies, depending on the analysis purpose. The same peak in the same dataset might be ranged differently to suit two analysis purposes. For example,

1. when the background noise is high, if the distribution of a species is the primary interest, only a thin peak should be ranged to avoid background obscuring the distribution; if composition is the focus, the peak should be ranged background-to-background and then subtracting the background to ensure all ions from the interested species contributing to the peak are included.
2. $^{56}\text{Fe}^+$ ions completely overlap with $^{96}\text{Zr}^{16}\text{O}^{2+}$ at 56 Da, if the distribution of Fe is the primary interest, this peak should be ranged as Fe, but it should be ranged as ZrO if the O concentration is the interest.

3.4.3 Composition calculation

During APT experiments, gas molecules from the analysis chamber adsorbed onto the APT sample surface can be evaporated, leading to detection of adventitious H, C, N, etc. It is impossible to separate these contaminations from ions really arising from the bulk sample material, and thus these elements are excluded when calculating compositions.

Bulk compositions

Bulk compositions can be calculated from all the ranged ions within the entire dataset or from selected regions in ionic or ion-decomposed forms. The difference is that the former calculates Zr^{2+} , ZrO^{2+} and ZrO_2^{2+} as separate ions, whereas the latter breaks these ions down into their constituent elements and sums the amounts of Zr and O individually. Any errors in the composition data may rise from factors such as mass range selection, data scattering

and peak deconvolution. The specific values of error will be omitted under circumstances when they are below 0.01% or when a reliable value cannot be determined.

Concentration profiles

Compositional changes between two different regions, or at the interfaces, are often of interest in this thesis, including grain boundaries and interfaces between oxide and metal, SPPs and matrix, and clusters and matrix. Most of these are measured by putting a cylindrical region of interest (ROI) with appropriate diameter (xy) and length (z) directly across the interface. A 1D composition profile can be calculated along the z direction with a selected bin size, where the cylinder is divided into a series of adjacent slices with equal thickness along z direction. Atoms within the same bin are grouped to calculate the composition for that specific slice. This process is repeated for all bins along z, creating a composition profile. Choosing the appropriate bin size is a balance between spatial resolution and statistical reliability of the composition profile. Smaller bin sizes (<1 nm) offer higher resolution and can resolve smaller features but may contain too few atoms per bin, leading to noisy data. Larger bin sizes (>1 nm) provide smoother profiles by including more atoms per bin but can blur small features. The optimal bin size depends on the feature size and localised density of the ions of interest.

For the irradiation-induced solute clusters, due to nm-scale size, the ROI method incorporates too few atoms, so instead the **proxigram** method (details in **Section 3.3.4**) is used. Composition profile and proxigram mainly aim to visualise the variation of the solute concentrations at interfaces, and peak deconvolution is omitted due to the computational complexity.

3.4.4 Cluster analysis

During irradiation, solutes (Fe, Nb, Sn and Cu) and impurities (Al, Cr, etc) are knocked out from the equilibrium positions and can redistribute as solute clusters. Analysis of the trends of size, density and composition of clusters helps understand the mechanisms of microchemistry changes during irradiation, which can be related to the accumulation of irradiation structural damage and the accelerated kinetics of in-pile corrosion. These clusters have a diameter of ~5-10 nm [206] and the interesting chemistry change in clusters and matrix can be down to tens of ppm, so it is difficult to acquire precise measurements using EDS, electron energy loss spectroscopy (EELS) or NanoSIMS. The near-ppm chemical sensitivity and sub-nm spatial resolution make APT the optimal technique for this analysis. APT has been extensively used to analyse irradiation-induced clusters in reactor pressure vessel (RPV) steels since the 2000s [207-210]. However, there are currently limited studies on solute clusters in irradiated Zr alloys [46], possibly because the well-reported cluster analysis methods on RPV steels may not readily suffice in Zr alloys. The warmer conditions required to acquire successful Zr APT datasets [83] and lower concentration of solutes makes it more difficult to define the boundaries between cluster and matrix, and distinguish between clusters and artificial composition fluctuations in the matrix [111].

For the Zr alloys in this thesis, there are only low concentrations of solutes and impurities (Cu, Cr, Al, W, etc), and the quantification their clustering behaviours are considered less significant. Sn, due to rapid surface diffusion during evaporation, strongly segregates to crystal poles, and so accurate distribution of Sn requires very strict analysing conditions, i.e., low base temperature, and low laser energy, which would highly increase the fracture rate during the analysis. The accurate Sn redistribution during irradiation is beyond the scope of this thesis. Nb and Fe clustering in W13, X2 and ZIRLO alloys are studied in detail in **Chapter 5**.

Results of cluster analysis can be highly user-dependent [211], due to differences in defining the physical extent of the cluster. Take a Nb cluster for example, in **Figure 3-15(b)**, the composition inside a cluster is not uniform at the nm scale, and includes a cluster core with a saturated peak Nb concentration, and a periphery where the solute content gradually decreases to the matrix level. At an earlier irradiation stage, the Nb content may not reach saturation, and it can increase all the way from the matrix to the cluster core, **Figure 3-15(a)**. The boundary of clusters should be determined differently depending specifically on the purpose of the analysis. As in **Figure 3-15(b)**, for matrix composition, the boundary should be the black circle so to remove all the solute-enriched regions; for cluster statistics, the boundary should be the yellow circle, which is at the centre of the interface; for the core composition of clusters, the red circle should be the boundary so that only the Nb saturation core is included.

Research using both iso-concentration surface (**isosurface**) method and maximum separation method (**MSM**) to study cluster in steel have been reported [212], showing that although the two methods use different indexes to define clusters, if the parameters are set correctly, the results should be similar. Both two methods are used in this thesis to minimise user-dependent errors and to ensure the selection of parameters for cluster analysis is reasonable and repeatable. More details are reported in [213].

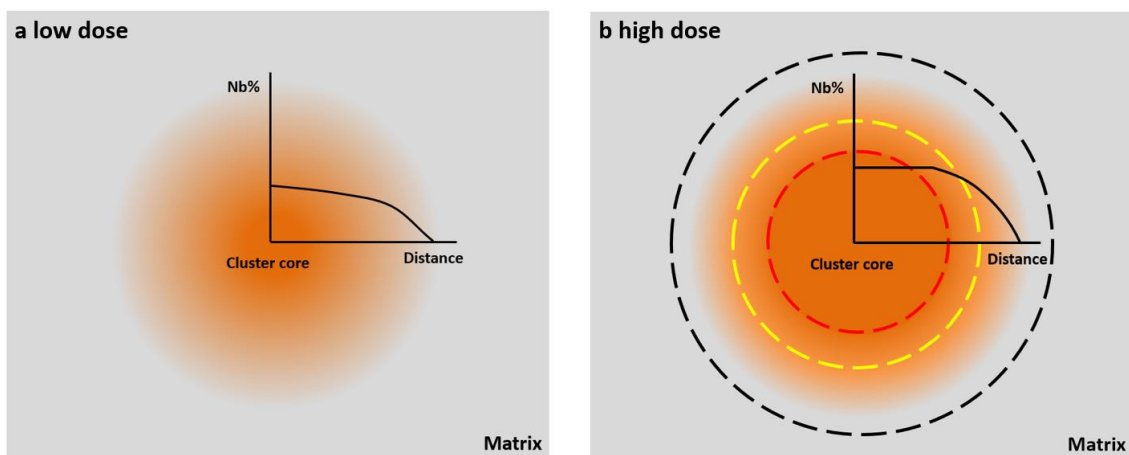


Figure 3-15. Schematic diagram of one Nb cluster in (a) early and (b) late stage of irradiation, the intensity of colour indicates the Nb concentration within the Nb cluster. Red, yellow and black dashed circles in (b) indicate the boundaries of cluster depending on specific analysis purposes.

Iso-concentration surfaces

The isosurface methodology is a powerful and frequently-used APT data analysis technique to define particles and clusters using a concentration threshold of selected solutes [214], c_{iso} , assuming that the solute concentration is higher in clusters than in the matrix. The choice of c_{iso} is crucial, as if it is too large, part of the periphery of the cluster is omitted and the cluster size is analysed to be too small. If c_{iso} is defined too small, some matrix may be included and clusters appear larger than they really are. It has been suggested that the optimal c_{iso} should achieve **morphologically-stable results** [212], meaning small changes in c_{iso} do not induce significant changes in the measured cluster size or number density. This method enables the user to select any isosurfaces in the reconstruction with the filter of size, shape and position.

Taking the analysis of Nb clusters as an example, c_{iso} defines the minimum Nb concentration needed to identify a Nb cluster. We must remember that the $^{93}\text{Nb}^{2+}$ signal completely overlaps at 46.5 Da with $^{92}\text{Zr}^1\text{H}^{2+}$, and $^{93}\text{Nb}^{2+}$ accounts for 50% to 90% (depending on the specific electric field) of the overall Nb counts (also detected as $^{93}\text{Nb}^{3+}$, $^{93}\text{Nb}^{+}$ and $^{93}\text{Nb}_2^{3+}$). This overlap cannot be decomposed when applying the isosurface, and in order to include all Nb signals when defining the Nb-enriched isosurfaces (Nb clusters), all the peaks that contain Nb signals in this work were ranged as Nb.

Another key factor in this method is setting the minimum volume v_{iso} to define a cluster. v_{iso} can filter out small composition fluctuations in the matrix that should not be identified as clusters. A value of $v_{iso} = 50 \text{ nm}^3$ is used, based on the TEM observation of ~5 nm diameter Nb clusters [206]. The influence of different choices of c_{iso} and v_{iso} on the identification of Nb clusters is shown in **Figure 3-16** for a typical APT dataset from the W13 alloy irradiated

to 33.5 dpa. **Figure 3-17**(a and b) compare the mass spectra from the whole dataset and from the Nb clusters identified using $c_{\text{iso}}=6\%$ Nb and $v_{\text{iso}}=50 \text{ nm}^3$ isosurfaces. Heights of the red shadow indicates the expected $^{92}\text{Zr}^1\text{H}^{2+}$ contribution to the 46.5 Da peak calculated from the 47.5 Da peak (extracted from the ratio of $^{92}\text{Zr}^1\text{H}^{2+}/^{94}\text{Zr}^1\text{H}^{2+}$). It is clear that in the whole dataset the majority of 46.5 Da peak consists of $^{92}\text{Zr}^1\text{H}^{2+}$, while in the identified Nb clusters the 46.5 Da peak is mostly $^{93}\text{Nb}^{2+}$. This is partly because Nb is mostly enriched in Nb clusters, while ZrH ions are strongly enriched on the laser-incident-side shank. Therefore, the combination of $c_{\text{iso}}=6\%$ Nb and $v_{\text{iso}}=50 \text{ nm}^3$ effectively removes the matrix composition fluctuations and identifies ions that contribute to Nb clusters with little influence from the overlapping $^{92}\text{Zr}^1\text{H}^{2+}$, and thus these values are used for later analysis.

Note that clusters correspond to the enclosed volumes defined by c_{iso} and v_{iso} , while any unbounded isosurfaces are automatically forced to close towards the higher concentrations.

The composition of volumes within these Nb isosurfaces is defined as **Nb cluster composition**, and the solute concentration change from the matrix to the cluster core can be measured using a plot of composition vs proximity to the defined isosurface, called the proximity histogram (**proxigram**) [214]. The proxigram calculates the average compositions as a function of distance from the isosurface, giving 1D averaged composition versus distance to the cluster interface. Proxigram visualises composition change at interfaces, especially when the feature is small or has a complex morphology, and it can be averaged over all the isosurfaces selected. The influence of the choice of c_{iso} and v_{iso} on the Nb proxigram, cluster counts and cluster composition is shown in **Figure 3-18** and **Table 3-9**. These will be compared with the cluster analysis results acquired using the MSM method.

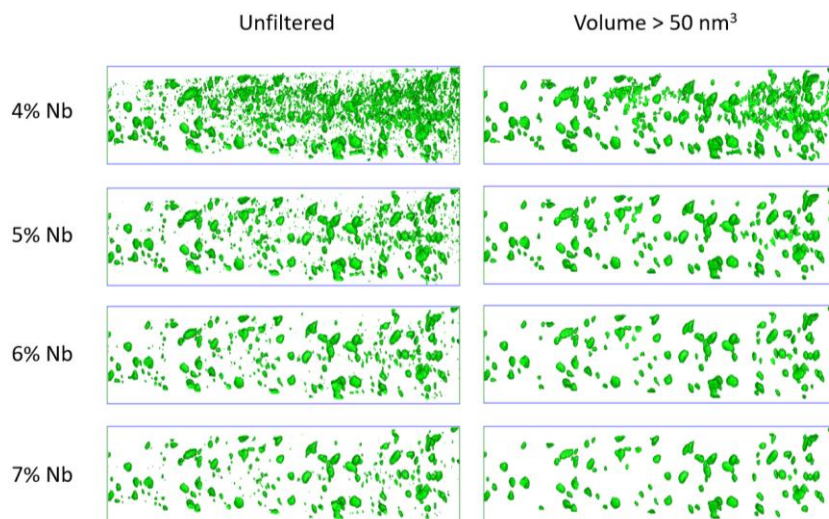


Figure 3-16. Nb clusters defined by isosurfaces with different c_{iso} and v_{iso} . APT dataset ‘PZ02_M8’ from a W13 alloy irradiated to 33.5 dpa.

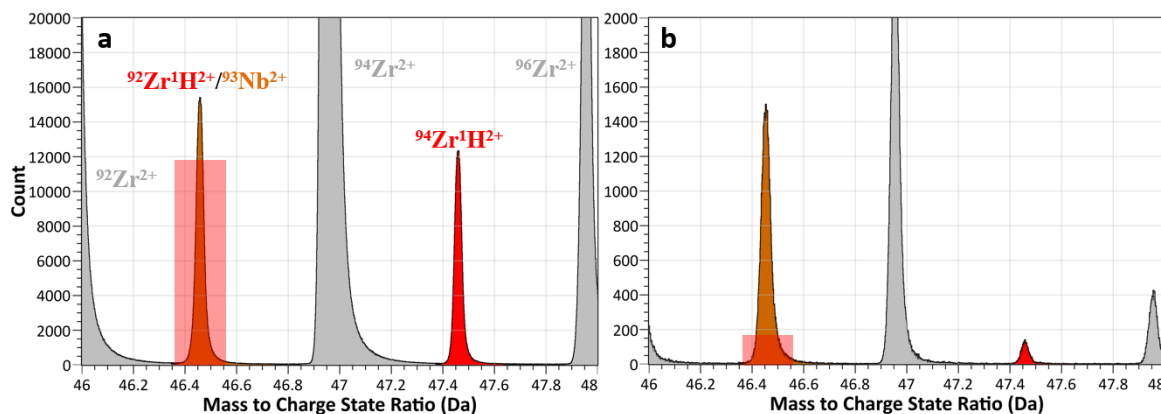


Figure 3-17. 46-48 Da mass spectra of APT dataset ‘PZ02_M8_’ from a W13 alloy irradiated to 33.5 dpa, from (a) the whole dataset, and (b) the Nb clusters identified with combination of $c_{\text{iso}}=6\%$ Nb and $v_{\text{iso}}=50 \text{ nm}^3$. Heights of red shadow indicate the contribution of $^{92}\text{Zr}^1\text{H}^{2+}$ in the 46.5 Da peak.

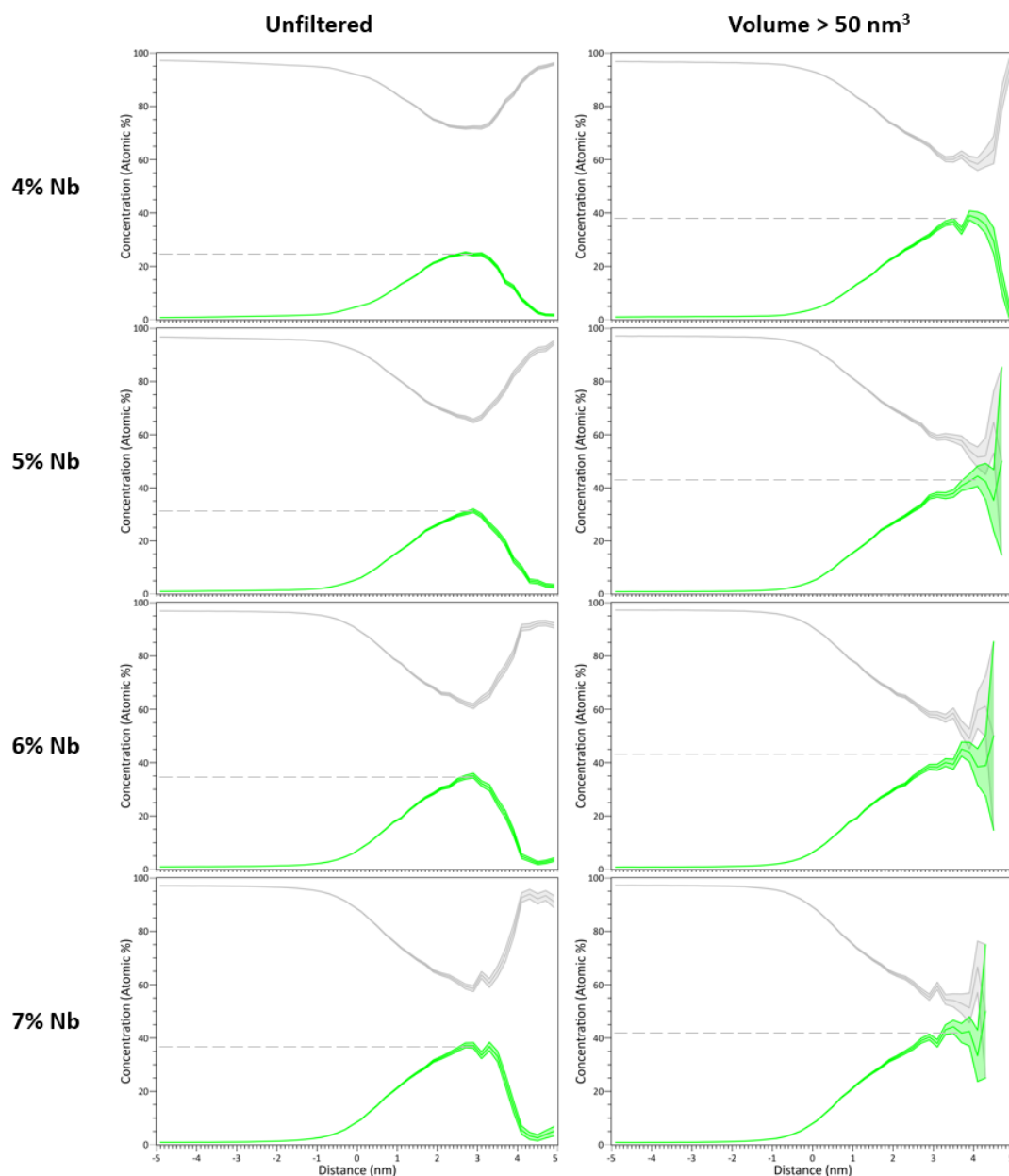


Figure 3-18. 5-nm proxigrams measured using different Nb isosurface parameters on the Nb clusters identified in Figure 3-16.

Table 3-9. Nb cluster counts and in-cluster Nb concentrations measured from the Nb clusters in Figure 3-16.		
c_{iso} (Nb%)	$v_{iso}=0$	$v_{iso}=50$
4	2915 9.47%	218 10.52%
5	1173 12.29%	154 13.10%
6	526 13.35%	134 15.35%
7	365 17.10%	102 17.44%

Maximum separation Method

MSM is another well-known method for cluster analysis and mainly uses four parameters to define clusters [197, 215], as shown in **Figure 3-19**.

$d_{\max}$: solute atoms within this distance are considered to be clustered to the core solute atom. If $d_{\max}$ is too high, several small clusters can be identified as one big cluster. If $d_{\max}$ is too low, some solute atoms that are randomly distributed in the matrix could be mistakenly included.

$N_{\min}$: the minimum number of solute atoms required to identify a cluster. $N_{\min}$ is used to eliminate the identification of random arrangements of solute close together as solute clusters, and is dependent on $d_{\max}$. If $N_{\min}$ is too high, small clusters can be neglected, and if $N_{\min}$ is too low, some composition fluctuations are mistakenly considered as clusters.

$d_{\max}$ and $N_{\min}$ determine the size, number and density of clusters identified, but they only work on the selected solute atoms. The envelop method can be applied for other elements that should also be included within clusters in order to calculate the cluster composition [212], with two parameters: **envelop distance L** and **erosion distance d_e** .

L : includes atoms of other elements within distance L of clustered solute atoms. If $L > d_{\max}$, atoms in the matrix will be mistakenly included in clusters, leading to a reduced solute concentration in the clusters, so normally L is kept equal to or smaller than $d_{\max}$. However, this will unavoidably include a thin shell of matrix atoms on the cluster surface.

d_e : the erosion distance, used to remove enveloped cluster atoms within this distance of a non-cluster matrix atom [216]. d_e can effectively remove the thin matrix shell created by L , but if $d_e > L$, solutes atoms can be mistakenly removed from clusters.

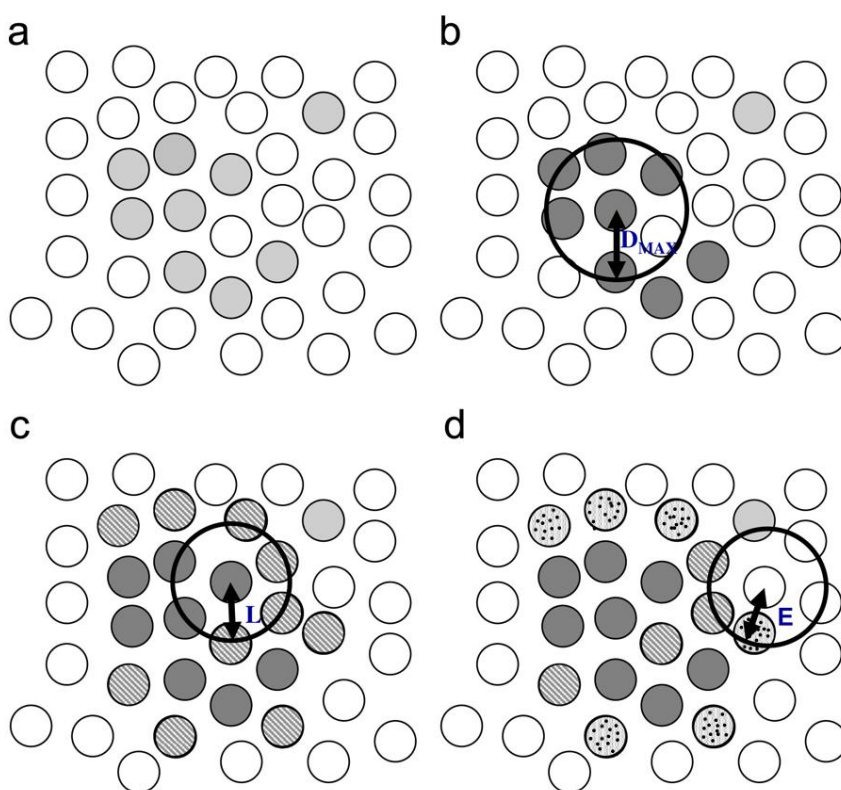


Figure 3-19. Schematic diagram showing the parameters used in the maximum separation method. (a) Solute atoms are in grey. (b) Solute atoms within d_{max} are defined as cluster atoms in dark grey. (c) Searching for clustering atoms of other elements within L (hatched). (d) Erosion of atoms (dotted) within d_e from a non-cluster matrix atom. Reproduced from [215].

Selection of the optimal d_{max} in this thesis was based on the comparison of the output from an experimental dataset and a randomised dataset by plotting the number of clusters as a function of d_{max} [197, 212], called the Cluster Count Distribution function in the AP Suite software. The optimal N_{min} was based on the point where the cluster count in a randomised dataset becomes 0 when increasing N_{min} with the selected d_{max} , called the Cluster Size Distribution function in AP Suite. A combination of $L = d_{max}$, $d_e = 0.5 d_{max}$ was applied for this analysis. Taking Nb cluster from the same 33.5 dpa W13 alloy dataset in **Figure 3-16** for an example. Two ranging strategies were applied using MSM:

(i) only the 31 Da $^{93}\text{Nb}^{3+}$ peak is ranged as Nb, because this is the only Nb peak that is not influenced by peak overlap, and the $^{93}\text{Nb}^{3+}$ signal should have, although a lower number of counts, a distribution representative of all Nb signals.

(ii) similar to the isosurface method, all the Nb-containing peaks are ranged as Nb.

The parameters are selected following the abovementioned criteria, which are $d_{\max}=L=4.2$ nm, $N_{\min}=30$, $d_e=2.1$ nm, and $d_{\max}=L=0.85$ nm, $N_{\min}=30$, $d_e=0.47$ nm, respectively. Comparison of the results is shown in **Figure 3-20**. Strategy (ii) outputs 14.24% Nb and 170 cluster counts, which are not very different from the 15.35% Nb and 134 counts obtained from the one of the isosurface parameter sets, **Table 3-9**. However, for strategy (i), $^{93}\text{Nb}^{3+}$ only accounts for 10-20% overall Nb signals, meaning the counts will be more dispersed than the actual Nb distribution, and a larger $d_{\max}$ is selected. Although most of clustered Nb atoms are identified in clusters, too many matrix atoms are included inducing a much lower Nb concentration in the Nb clusters (4.15%), and many small clusters are mistakenly combined into a bigger cluster, giving a mistakenly smaller cluster count (81). Therefore, all the Nb signals should be ranged when using isosurface and MSM methods, and the two methods using the optimal parameters output identical cluster analysis results. The isosurface method is used to for the cluster analysis in **Chapter 5**.

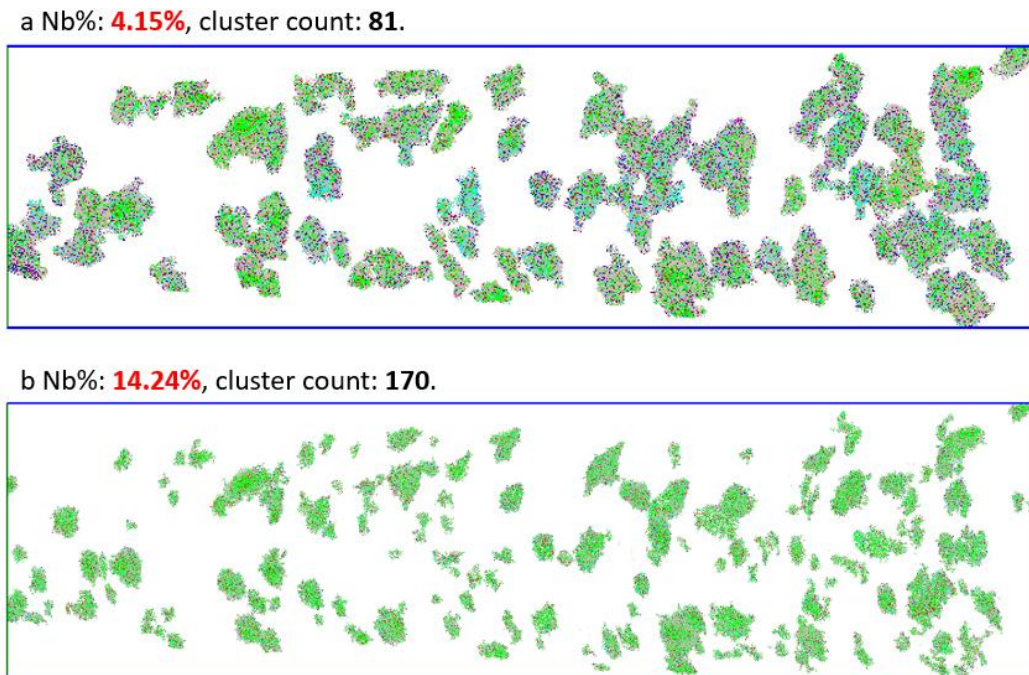


Figure 3-20. Nb clusters in APT dataset ‘PZ02_M8’ from a 33.5 dpa W13 alloy identified by MSM on (a) with $d_{\max}=L=4.2$ nm, $N_{\min}=30$, $d_e=2.1$ nm, (b) all Nb signals with $d_{\max}=L=0.85$ nm, $N_{\min}=30$, $d_e=0.47$ nm. Nb concentration in clusters and cluster count are given in red and black.

3.4.5 Trajectory aberrations

Although there is normally little crystallographic information in the reconstructed APT datasets from highly alloyed materials, nano-scale features in the APT data can be searched for using solute segregation [111] and variations in the localised evaporation behaviour [57]. During the APT evaporation process, nano-scale features that contribute to a reshaping of the specimen apex lead to trajectory aberrations of the evaporated ions that distort the atom positions in the reconstructed data [173]. Clusters rich in atoms with lower evaporation fields, for instance, will evaporate earlier than the surrounding matrix, leading to a local flattening of the surface curvature. This effectively focusses the trajectories of ions evaporated from this region onto the detector, ultimately leading to a region of localised higher ion-density in the reconstructed data. GBs and nanopores require lower electric field to evaporate than the surrounding matrix and thus have a similar effect [29, 57, 217], as shown in **Figure 6-19**, **Figure 7-3**, respectively. For the same reason higher-field features on the evaporating surface will evaporate later than the matrix, and will then be reconstructed as localised lower-density regions. For instance, matrix composed of Nb atoms requires a higher electric field for evaporation (37 V/nm) than Zr matrix (28 V/nm), and a Nb cluster is a mix of both so have an intermediate field and will be spatially correlated with a localised lower density region, **Figure 7-3(b)**.

2D contour map of a slice ROI (**Figure 6-19(b)**), 1D atom count profile of a cylinder ROI (**Figure 6-21(b)**), and iso-density surface (**Figure 7-2**) in AP Suite are widely used in results chapters to visualise the variance in local atom density and thus GBs or nanopores.

3.5 Other characterisation techniques

Although it offers very high precision and accuracy, APT cannot provide crystallographic information or chemical information at larger than the μm scale. This thesis incorporates complementary analyses from several other characterisation techniques that will be briefly introduced here.

3.5.1 Electron Backscatter Diffraction

Electron Backscatter Diffraction (EBSD) is used to analyse the crystallographic structure and orientation of crystalline materials. The incident electron beam interacts with the atoms on the crystal lattice, generating backscattered electrons. Some of these are diffracted by the lattice planes producing diffraction bands [218], known as a Kikuchi pattern, and these patterns can be used to acquire information on grain orientation, phase, crystalline texture, grain morphology, local deformation and the concentration of lattice defects [219].

Both the beam size and interaction volume determines the spatial resolution, which is normally 20-90 nm in conventional EBSD, but can be reduced to the nm scale if the incident electron beam is applied to a TEM thin foil sample [220]. This improved technique is known as Transmission Kikuchi Diffraction (TKD). TKD offers the same crystallographic capabilities as EBSD and is widely used on nanocrystalline materials.

3.5.2 Energy-Dispersive X-ray Spectroscopy

The incident electron interacts with the atoms on the sample surface losing energy and generating X-rays, Auger and secondary electrons. Each element creates a characteristic X-ray signal, and EDS uses these X-ray signals to study the chemistry of the sample surface [221]. Similar to TKD, the spatial resolution can be reduced to the nm scale when doing EDS in the transmission mode, known as STEM-EDS [222].

3.5.3 Transmission Electron Microscopy

Transmission Electron Microscopy (TEM) uses a beam of high-energy electrons to visualise the internal structures of thin samples, achieving atomic-scale resolution [223]. There are a number of different contrasts of the detected imaging modes that can be used to study the crystallography and micro(nano)structure of a wide range of sample types. In this thesis, it is the identification of small pores that is the relevant use of TEM.

Fresnel contrast imaging

Crystal defects like pores, GBs and cracks create variations in the localised effective sample thickness that can be used to create contrast in an image under correct imaging conditions. Nm-scale cavities (pores) should present white contrast in under-focus images and black contrast in over-focus images, known as Fresnel contrast analysis [83]. This is very useful technique to identify nanovoids induced during corrosion and irradiation of the samples in this thesis (**Figure 7-4(c)**), because in APT data the existence of these defects must be inferred from trajectory aberrations.

3.5.4 Secondary Ion Mass Spectrometry

SIMS employs a focused ion beam to bombard the bulk sample surface and generate secondary ions from the surface, which are then identified by time-of-flight mass spectrometry. In the NanoSIMS instrument used in this thesis, seven ion masses can be recorded simultaneously [128]. The fast erosion rate of SIMS enables μm -scale 3D bulk analysis. SIMS is able to detect all the elements and isotopes with parts of billion sensitivity, and NanoSIMS has a spatial resolution of tens of nm because of the fine primary beam diameter.

An overall comparison of APT and NanoSIMS techniques is shown in **Table 3-10**. NanoSIMS complements APT by offering a much larger analysed volume and improved

mass resolution of APT. In this thesis, NanoSIMS analysis was used on the isotopically spiked oxide to help distinguish O and H isotopes and interpret the APT data in Sections **6.2 ^{18}O -spiking** and **6.3 D-spiking**. A CAMECA NanoSIMS 50L at University of Manchester was used, employing a focused 16 keV Cs^+ ion beam to generate negative secondary ions from the sample surface.

The ion sputtering direction (z direction in **Figure 3-21**) has a higher spatial resolution of 10-20 nm, while the lateral direction has a spatial resolution of only ~ 50 nm [104, 128]. During the NanoSIMS experiments, the oxide samples were aligned so that the corrosion direction is along the z direction to get a better spatial resolution of corrosion species in the direction that they propagate through the growing oxide.

Table 3-10. Comparison of APT and NanoSIMS [86, 128].		
Technique	APT	NanoSIMS
Mass Resolution ($M/\Delta M$)	500-1,500	5,000 - 10,000
Spatial Resolution (nm)	~ 0.5	10 (depth) – 200 (lateral)
Chemical sensitivity	Parts per million	Parts per billion
Analysing volume	Cone with 100 nm diameter and ~ 300 nm length	Cube with ~ 10 μm side length
Detection	All ions	Selected 7 ions

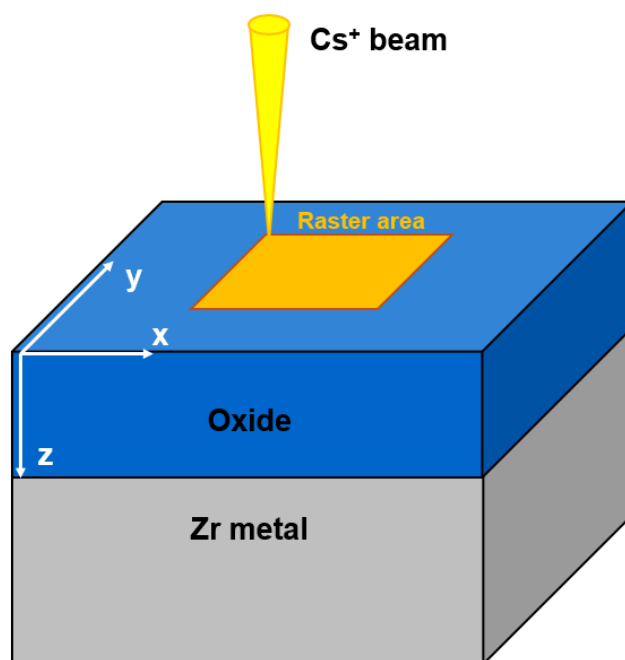


Figure 3-21. Schematic diagram showing the NanoSIMS depth-profiling experiment. The ion sputtering direction is the z axis, and the lateral plane is the xy-plane.

4. Baseline Zr alloys

Before analysing Zr alloys that have been subjected to different corrosion and irradiation conditions, it is essential to thoroughly study their baseline state. A clear understanding about the starting chemistry and microstructure allows for better identification of the dramatic changes during degradation treatments, which helps in the study of the complicated degradation mechanisms.

As mentioned in **2.1.2 Alloy development**, commercial Zr alloys like Zr-2, Zr-4, ZIRLO, X2 and M5 alloys have shown good performance in service [224, 225], and there are some other variant alloys developed to study the impact of alloy chemistry. For example, W13 and W10 alloys are variants of the ZIRLO alloy with the addition of Cu and V, respectively [164]. In this chapter, the nm-scale structure and chemistry of W13, W10, ZIRLO and X2 alloys in the baseline state are studied in **Sections 4.1 to 4.4** using APT in support of electron microscopy analysis carried out by other researchers. The composition and processing history of these alloys can be found in **Section 3.1**.

Baseline W13 in **Section 4.1** will be compared with irradiated W13 in **Section 5.1**. Baseline X2 and ZIRLO in **Sections 4.3 and 4.4** will be compared with autoclave corroded X2 and ZIRLO in **Section 6.1**, irradiated X2 and ZIRLO in **Sections 5.2 and 5.3**, and in-pile corroded X2 and ZIRLO in **Sections 7.2 and 7.3**. There is currently no available data on the irradiated or corroded W10 alloy, so baseline W10 alloy in **Section 4.2** only provides a reference point for the effect of V-addition to the microstructure and microchemistry of baseline W10 alloy.

4.1 Baseline W13 alloy

The Cu-containing W13 alloy was developed by Westinghouse Electric and has a better corrosion performance but worse irradiation resistance (larger irradiation-induced volume growth) compared to ZIRLO alloy. The equiaxed microstructure of the recrystallised W13 alloy, with $\sim 5\ \mu\text{m}$ grain size, is shown in the optical microscopy image in **Figure 4-1(a)**. **Figure 4-1(b-g)** display a bright-field STEM image and corresponding STEM-EDS maps of the solute distribution at a smaller scale. Cu, Nb and Fe are mostly enriched into SPPs and are low in the matrix, as is commonly observed in similar Zr alloys [43, 226]. The thermomechanical history of the sample has resulted in SPPs being distributed in bands of high concentration running across many individual grains. As is shown in **Table 4-1**, the sizes of SPPs follow the sequence of $\text{Zr}_2\text{Cu} > \text{Laves } \text{Zr}(\text{Nb}, \text{Fe}, \text{Cr})_2 > \beta\text{-Nb}$, whereas their area fractions follow the opposite trend. Sn shows a random distribution in the matrix and no evident segregation to any microstructural features, similar to [227]. The distribution of these elements at smaller scale has also been investigated in APT with higher chemical sensitivity.

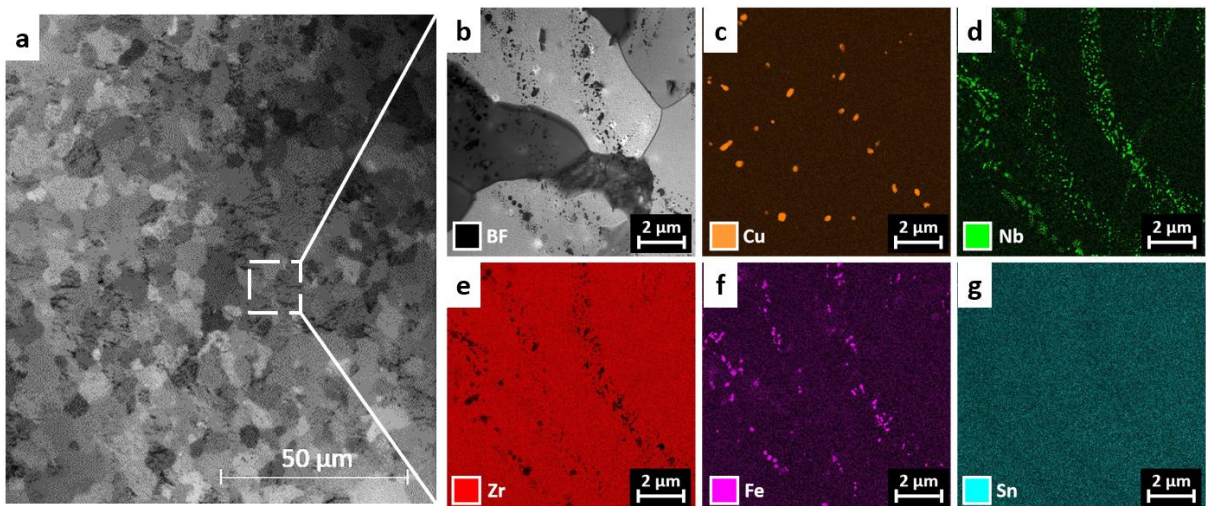


Figure 4-1. Microstructures of the unirradiated W13 alloy. (a) Optical microscopy image showing the equiaxed grain structure, with dashed box showing the scale of (b-g). (b) Bright-field STEM image. (c-g), STEM-EDS maps of Cu, Nb, Zr, Fe and Sn. The size and area fraction of SPPs in **Table 4-1** are measured in this analysed volume. (Courtesy of Callum Andrew, University of Manchester, note the different colours in APT and TEM figures)

Table 4-1. SPP distribution and composition in W13 alloy measured by STEM and STEM-EDS		
SPP type	Mean Diameter (nm)	Area fraction (%)
Zr₂Cu	277 ($\pm$ 119)	0.55
Zr(Nb,Fe,Cr)₂	117 ($\pm$ 71)	1.11
β-Nb	51 ($\pm$ 36)	2.2

Courtesy of Callum Andrew, University of Manchester. Note the area fraction of SPPs is measured based on Figure 4-1, and maybe not representative for overall bulk alloy.

Figure 4-2(a) shows an APT dataset from baseline W13 alloy containing the α -Zr matrix and a β -Nb SPP. The line profile in **Figure 4-2(d)** across the β -Nb SPP shows that there is a uniform concentration of 90% Nb within the SPP as expected from the Zr-Nb phase diagram [228]. The same line profile in **Figure 4-2(e)** shows that W (trace impurity) is enriched within the SPP, and Fe, Cu and Sn are enriched at the interface between SPP and matrix. However, it should be pointed out that, due to possible surface diffusion on the APT tip apex during evaporation, it is difficult to know if the higher Sn content at the interface is real segregation or an APT artefact.

Figure 4-2(b and c) show the separate mass spectra of selected ranges taken from the β -Nb SPP (ROI1) and α -Zr matrix (ROI2). Peaks from solute and impurities are evident in ROI1 but not detected in ROI2, e.g., $^{56}\text{Cr}^{2+}$, $^{63}\text{Cu}^{+}$, $^{184}\text{W}^{2+}$. This indicates that SPP interface acts as sink for solute trace impurities (Fe, Cu, Cr and W) in the baseline state, and is a clear example of that mass spectra for regions from the same APT dataset but with distinct compositions can be very different, and thus should be ranged separately as mentioned in **Specific ranging** in Section 3.4.2 Mass spectrum analysis.

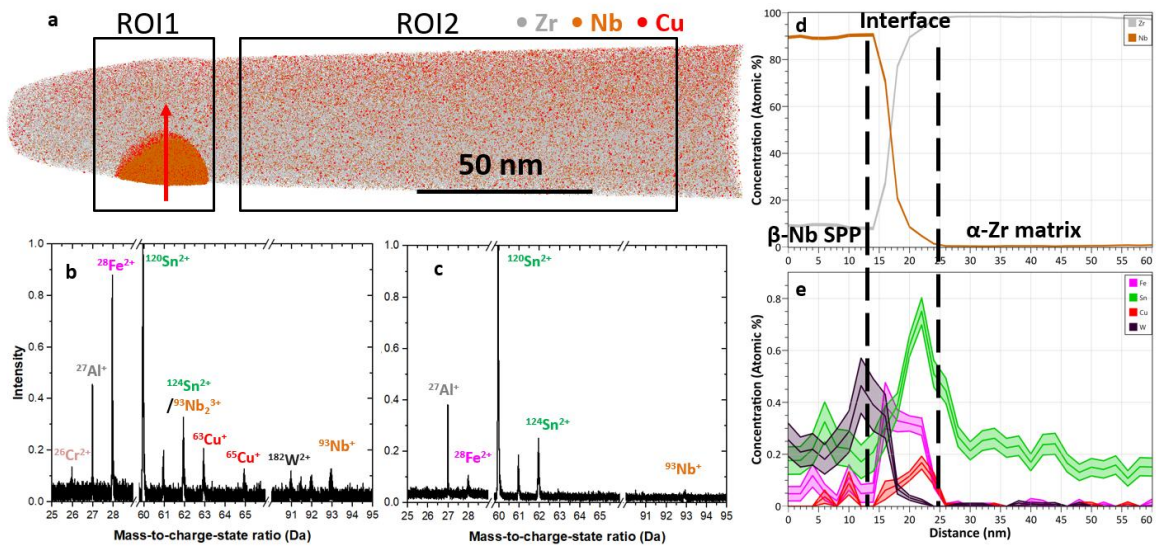


Figure 4-2. APT dataset ‘MCR3_M20’ from the baseline W13 alloy containing a β -Nb SPP. (a) Overlaid spatial distribution map of Cu, Nb and Zr atoms. (In spatial distribution maps, the isotope and charge state will be specified if only one ion is selected to show the distribution of the element, otherwise all ions or more than two ions of the element is used.) (b) and (c) Mass spectra of selected ranges from ROI1 and ROI2, with peak heights normalised to $^{120}\text{Sn}^{2+}$. (d and e) chemical profiles across β -Nb SPP along the red arrow in (a) with bin size of 2 nm.

Figure 4-3(a) shows a spatial distribution map of solutes and trace impurities from an APT dataset containing a Laves phase SPP, and **Figure 4-4** shows the composition profile across the SPP. It is observed that this Laves phase SPP contains 37% Zr, 40% Nb, 20% Fe and 2.5% Cr, giving a $\text{Zr}(\text{Nb}, \text{Fe}, \text{Cr})_2$ composition. Fe, Nb, Cu, W, Ni, Mn and Cr are distributed randomly in the matrix with very low counts, and are strongly enriched within the Laves phase SPP, and Cu is segregated to the interface. Sn, as an exception, has similar content in matrix and SPP. APT can better detect the enrichment of low contents of Cu, Fe and other trace elements compared with (S)TEM due to the higher chemical sensitivity.

There is much more Cr in the Laves phase SPP ($\sim 3\%$) than in the β -Nb SPP ($\sim 0.1\%$), and this can be used as a criterion to distinguish the two types of SPP after irradiation, when Fe is depleted, as the Cr is expected to be released from the Laves phase SPP to the surroundings during irradiation.

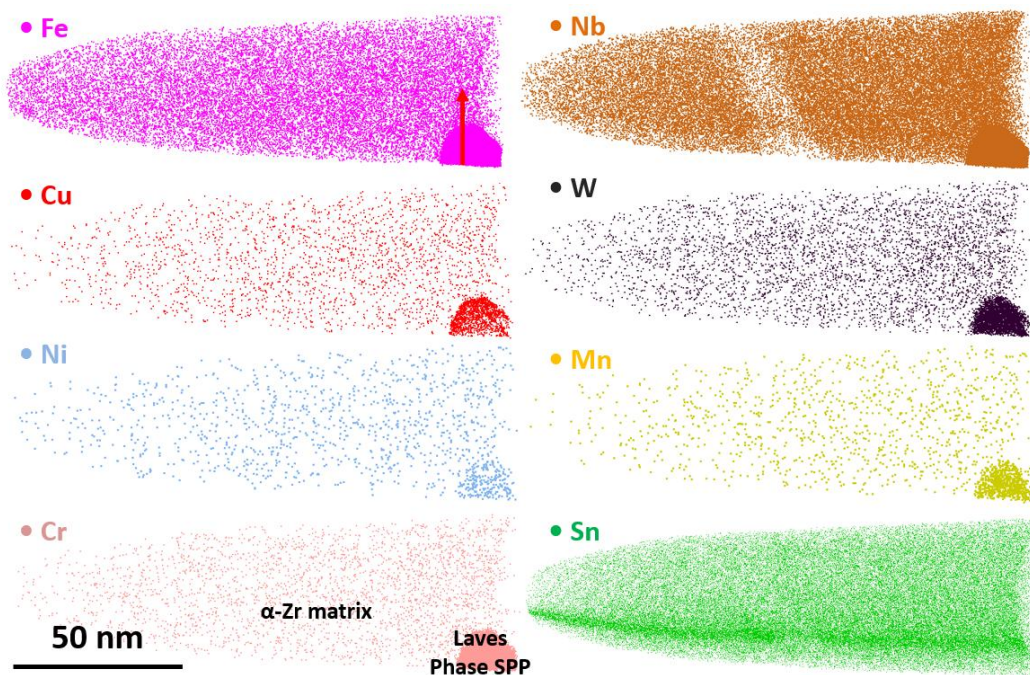


Figure 4-3. APT dataset ‘MCR3_M2’ from a volume of an unirradiated W13 alloy containing a Laves phase SPP. Spatial distribution maps of Fe, Nb, Cu, W, Ni, Mn, Cr and Sn. (This dataset was from a sample resharpener with a Ga-FIB at room temperature, and the band with low Nb is a hydride formed during this FIB process. The Sn line is Sn segregation to a crystallographic pole.)

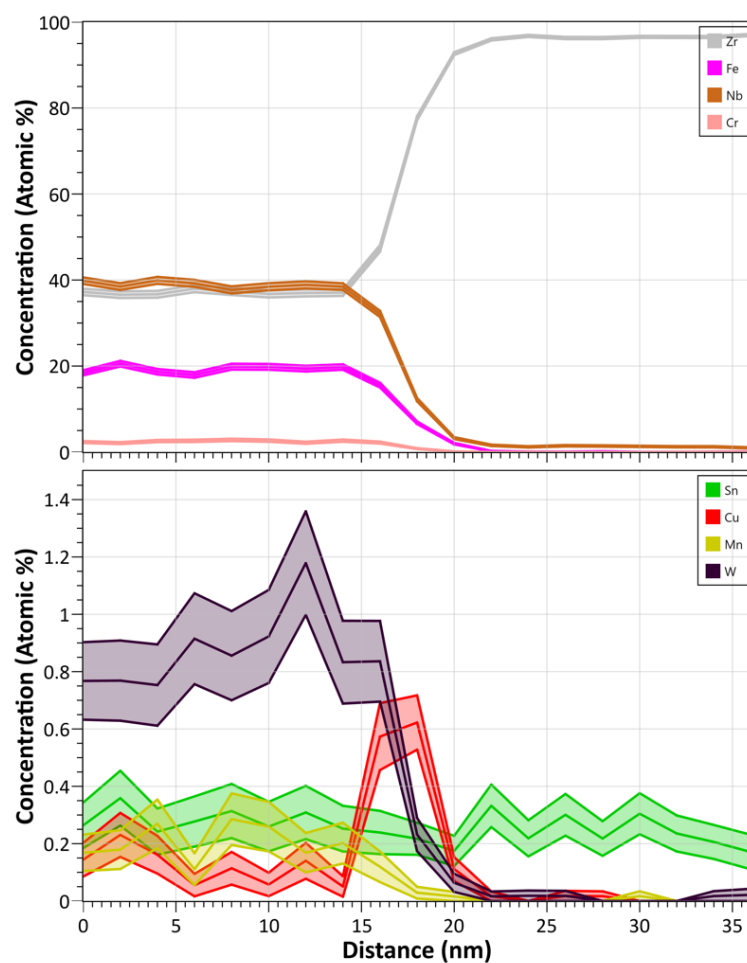


Figure 4-4. Composition profile of a Laves phase SPP measured along the arrow in **Figure 4-3**.

Figure 4-5 shows a typical APT dataset from the unirradiated alloy containing a Cu SPP more than 200 nm in diameter. This is much larger than all the β -Nb and Laves phase SPPs observed by APT, agreeing with the SPP mean size distributions measured by TEM in **Table 4-1**. **Figure 4-5(b)** presents a 1D chemical profile along the arrow in (a), showing a uniform concentration of $\sim 28\%$ Cu, 69% Zr and 1.6% Fe in the SPP, giving a near Zr_2Cu composition. The Zr_2Cu SPP composition and $\sim 0.002\%$ Cu in the matrix align well with the Zr-Cu phase diagram, **Figure 4-6** [229]. Nb presents the same $\sim 0.4\%$ concentration in the Zr_2Cu SPP and matrix, and Sn is slightly depleted in the Zr_2Cu SPP. As indicated by the black box, the Cu concentration remains the same from the core to the edge, and sharply decreases at the interface to near detection limit in the α -Zr matrix. Comparison will be made later with Cu concentrations at the edge of irradiated Zr_2Cu SPPs in **Figure 5-4**.

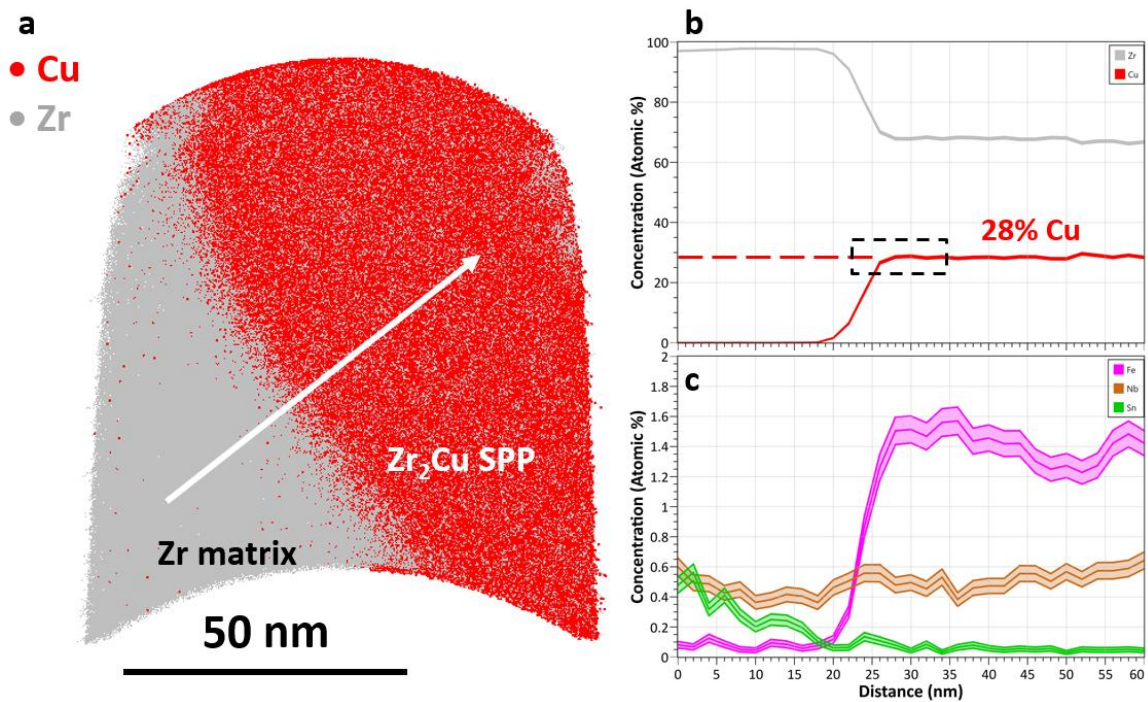


Figure 4-5. APT dataset ‘MCR4_M15’ in the unirradiated W13 alloy containing a Zr_2Cu SPP. (a) Overlaid spatial distribution map of Cu and Zr. (b) Chemical profile across the Zr_2Cu SPP along the arrow. The dashed black box shows that the Cu concentration at the edge remains the same as in the core.

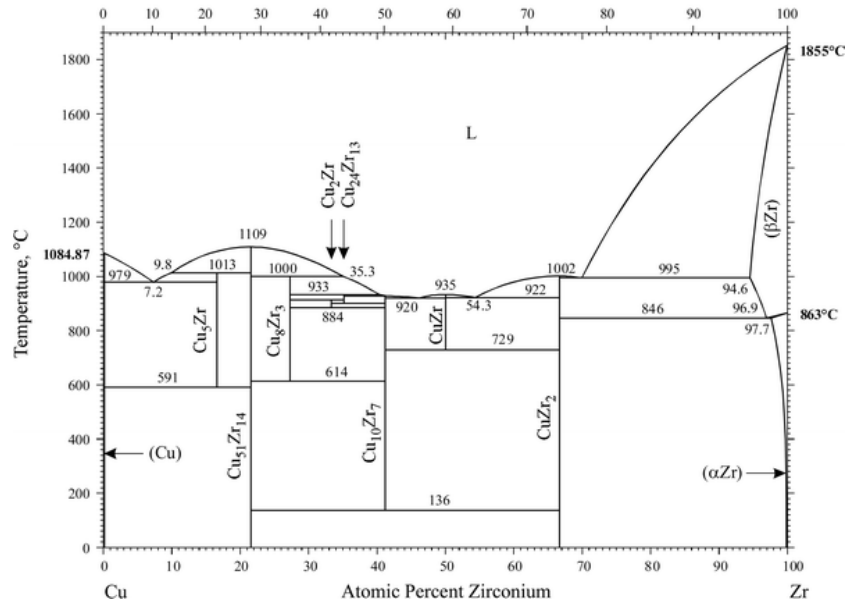


Figure 4-6. Zr-Cu phase diagram [229].

Segregation to a planar feature is also observed in **Figure 4-7(a)**, which is very likely to be a grain boundary since it is often reported in Zr alloys that Fe decorates GBs both in metal and oxide [14, 103, 166]. The line profile in **Figure 4-7(b)** along the red arrow in (a) shows that Fe, Cu and Al are enriched to 2.5%, 1.2% and 0.2% at this grain boundary, respectively. **Figure 4-7(c and d)** show the detector hit map extracted from grain 1 and grain 2, and the change in pole position indicates that there is a misorientation between the two regions, confirming that this planar feature is a GB.

Finally, compositions measured from the bulk of the unirradiated alloy and the three types of SPPs are summarised in **Table 4-2**. Similar to previous observations in ZIRLO [43], and the EDS map in **Figure 4-1**, in W13 the Sn is distributed randomly, at a level of ~0.25% in the matrix, but relatively depleted from SPPs, indicating that all the Sn addition (0.22%) is in solid solution in the α -Zr matrix and does not evidently segregate to any features. Nb has a solubility of ~0.4% in the matrix and is significantly enriched in β -Nb (~90%) and Laves phase (40%) SPPs. Cu, similar to Fe, shows low solubility in the α -Zr matrix (0.001-0.004%), and segregates strongly to β -Nb SPP and Laves phase SPP, GBs and interfaces, but also

forms Zr_2Cu SPPs. Other trace impurities Al, Cr, Ni, Si, Mn, W and V are nearly undetectable in the matrix but are detected at higher concentrations within three types of SPPs, SPP interfaces and GBs. Therefore, these features act as **sinks** to Fe, Cu and trace impurities in the unirradiated state.

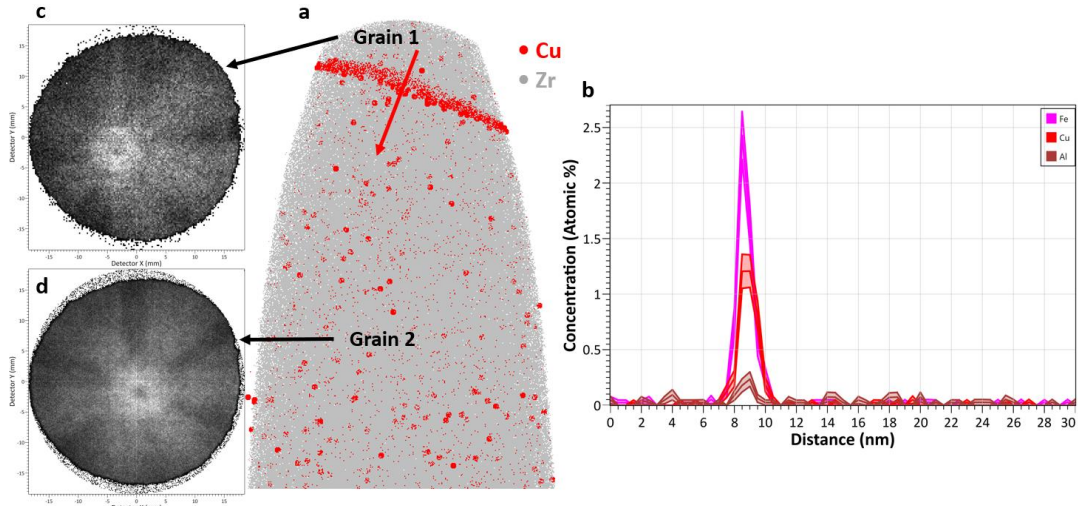


Figure 4-7. APT dataset ‘MCR1_M17’ in unirradiated W13 alloy containing a metal GB. (a) Overlaid spatial distribution map of Cu and Zr. (b) Chemical profile across a GB along the arrow in (a) with 0.5 nm bin size, showing Fe, Cu and Al segregation on the GB. (c and d) Detector hit maps from sampled region in grain 1 and grain 2.

Table 4-2. Compositions of different phases in the baseline W13 alloy*				
	α -Zr Bulk	Laves SPP	β -Nb SPP	Zr_2Cu SPP
Nb	0.39	39.03	89.85	0.73
Sn	0.28	0.10	0.11	0.059
Fe	0.004	19.02	0.079	1.34
Cu	0.001	0.14	0.036	28.65
Al	0.015	0.037	0.028	0.001
Cr	-	2.61	0.036	0.004
Ni	-	0.057	-	0.019
Si	0.002	0.023	0.014	0.10
Mn	-	0.21	-	0.003
W	-	1.31	0.71	-
V	-	0.012	-	-

*One Zr_3Si SPP was also detected in the W13 alloy, however, due to its rarity, this type of SPP is not further studied. Compositions of three types of SPPs were all taken from the SPP core, to avoid the influence of composition changes near interfaces. **Solutes** and **trace impurities** are highlighted in blue and green, respectively.

‘-’ denotes the concentration is below detection limit, in this study, ~ 0.001 at%.

4.2 Baseline W10 alloy

Similar to the W13 alloy, the baseline W10 alloy contains many SPPs in the matrix that are enriched with Nb, V and Fe as shown in the STEM-EDS maps in **Figure 4-8(c-d)**. V and Fe have similar enrichments in the Laves phase SPP, while Nb segregates mostly to β -Nb SPPs. Laves phase SPP and β -Nb SPPs account for volume fractions of $\sim 0.4\%$ and $\sim 0.6\%$ of the bulk material, respectively. The compositions of these SPPs and matrix were further investigated by APT.

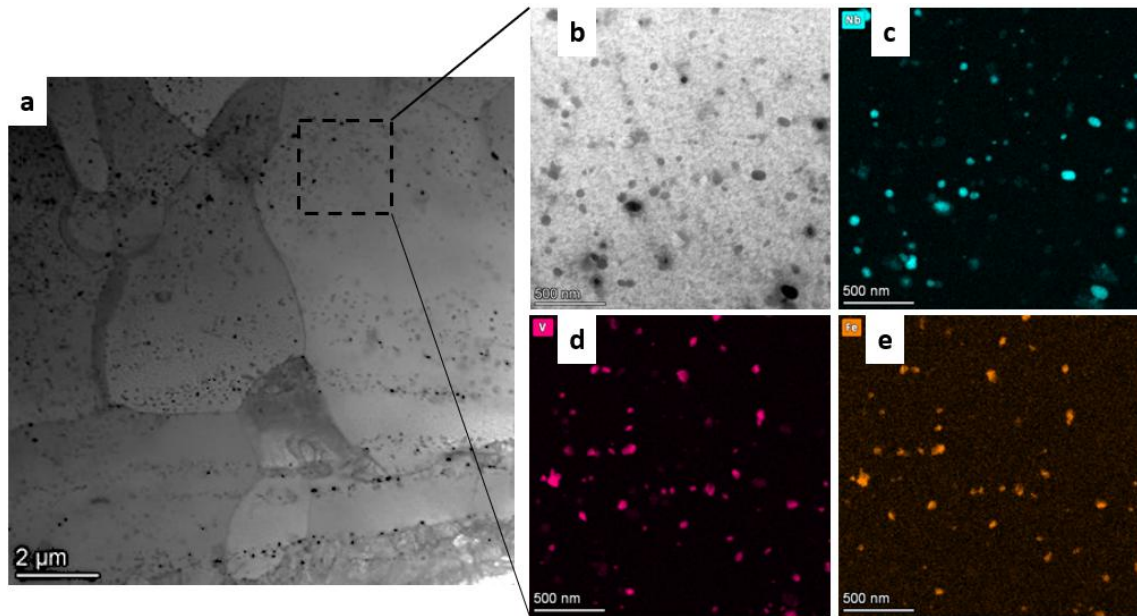


Figure 4-8. Microstructures of the unirradiated W10 alloy. (a) Bright-field STEM image showing the equiaxed grain structure, with dashed box showing the scale of (b-e). (b) Bright-field STEM image shows the distribution of SPPs. (c-e), STEM-EDS maps of Nb, V and Fe. (Courtesy of Kieran Lynch, University of Manchester)

Figure 4-9 shows the distribution map of solutes and impurities from an APT dataset from the baseline W10 alloy, containing the α -Zr matrix and a Laves phase SPP. **Figure 4-10** shows the composition profile from matrix to the Laves SPP along the arrow in **Figure 4-9**. There are $\sim 40\%V$, $15\% Fe$, $15\% Nb$, and $30\% Zr$ within the Laves SPP, giving a $Zr(V,Fe,Nb)_2$ composition. It is observed that Sn is slightly depleted in the SPP, Cu is enriched at the SPP interface, and all other solutes and impurities, including Nb, Fe, Al, V, Cr, Mn, Ni and Si, are present in low contents in the matrix but significantly enriched in the

Zr(V,Fe,Nb)₂ SPP. The diffraction pattern from the TEM analysis confirms a hexagonal Laves phase crystal structure. The matrix composition is displayed in **Table 4-3**, and is similar to W13 with ~0.4% Nb, 0.30% Sn, and Fe, V and Al in tens of ppm. The mass peaks of all other impurities are below the background level, so their contents in the matrix are below the APT detection limit.

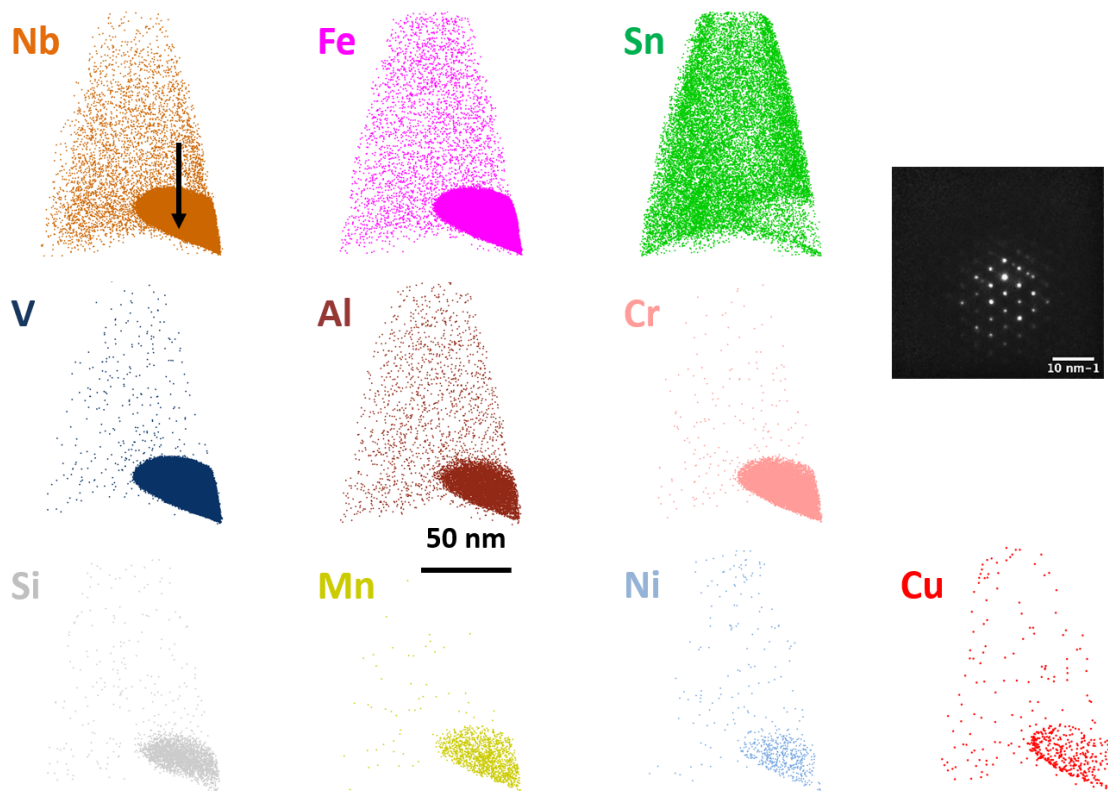


Figure 4-9. APT dataset ‘MCR5_M21’ from a baseline W10 sample containing matrix and a Laves phase SPP. Diffraction pattern of a Laves SPP from the [3-31] zone axis (courtesy of Kieran Lynch, University of Manchester).

Table 4-3. W10 baseline matrix composition	
Solute	Concentration at%
Nb	0.44
Sn	0.30
Fe	0.005
V	0.008
Al	0.004

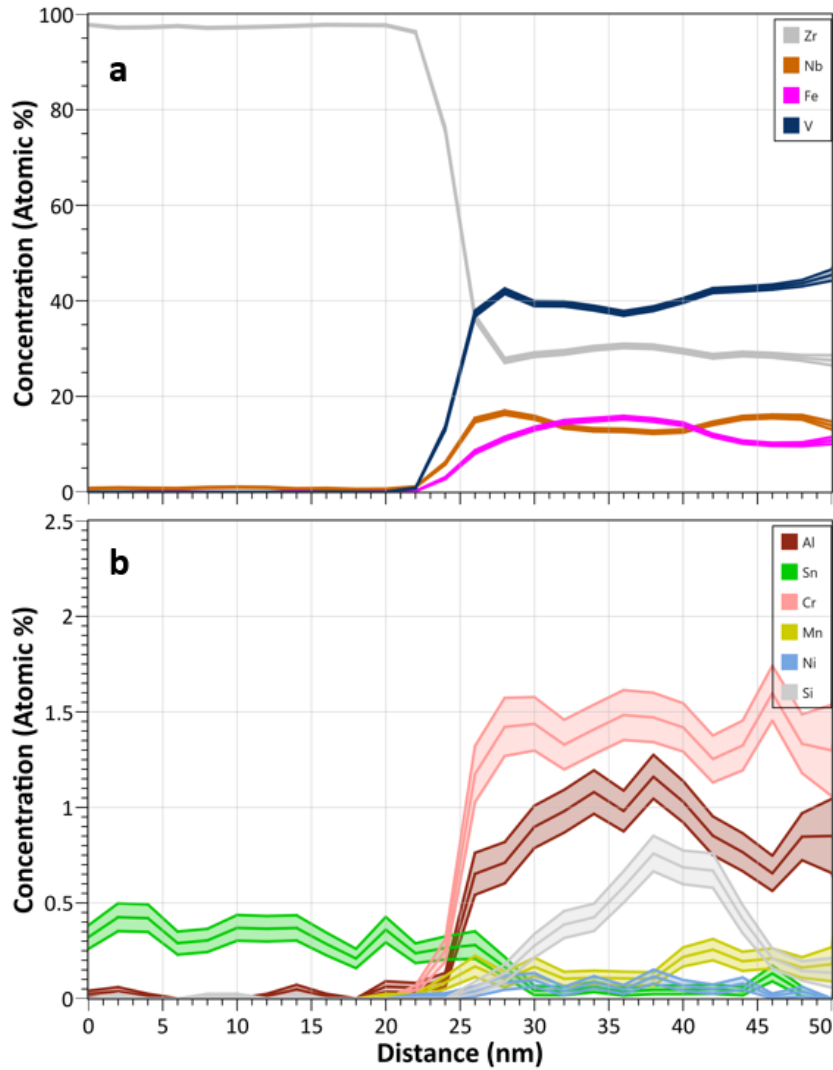


Figure 4-10. Composition profile of a Laves phase SPP measured along the arrow in **Figure 4-9**. (a) Zr, Nb, Fe and V. (b) Al, Sn, Cr, Mn, Ni and Si.

Figure 4-11 shows another APT dataset from the baseline W10 alloy that contains three Laves phase SPPs and one β -Nb SPP, as labelled on the V distribution map. The diffraction pattern (**Figure 4-11(d)**) confirms the body-centred cubic (BCC) crystal structure of the β -Nb SPP. **Figure 4-11(b and c)** show the composition profiles across the β -Nb SPP containing 80-85% Nb, similar to β -Nb SPP in W13, but with 5-10% Nb replaced by V. Sn is depleted in the β -Nb SPP, and Fe, Al and Cr are observed enriched within the β -Nb SPP.

The composition of Laves phase SPP 2 is measured in **Figure 4-12(b)**, showing a $\text{Zr}(\text{V,Fe,Nb})_2$ composition. Sn is depleted from the SPP, whereas enrichments of Al, Si, Mn, Ni, W and Ti are observed. It is interesting to note that the solute concentrations in the Laves

phase SPPs are not as uniform as in W13 SPPs, and the content of V seems to correlate with Nb but anti-correlate with Fe, **Figure 4-10(a)** and **Figure 4-12(a)**, although these alloys have the same fully recrystallised annealing. The ratio map of the STEM-EDS signal of Nb/V and V/Fe (**Figure 4-13**) confirms this non-uniformity. It is uncertain if this non-uniformity is caused by the V addition.

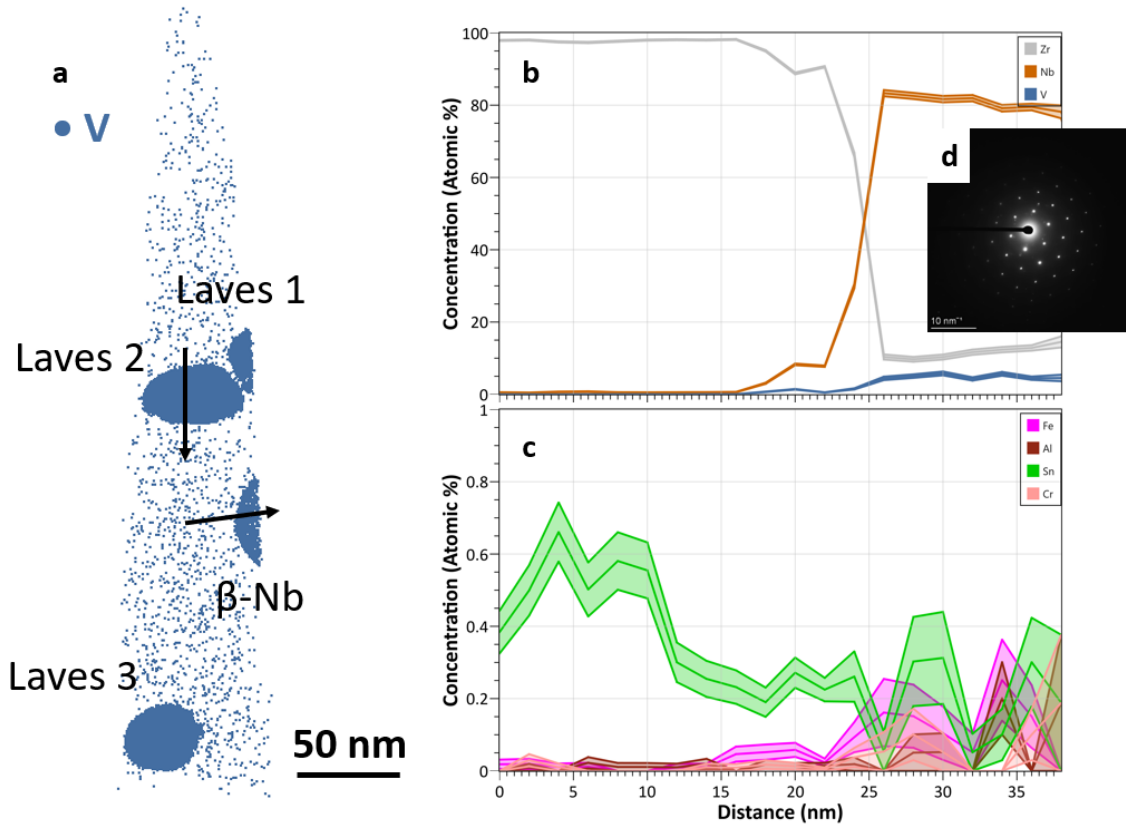


Figure 4-11. APT dataset ‘MCR5_M4’ from baseline W13 alloy, (a) V spatial distribution map, containing three Laves phase SPPs and one β -Nb SPP. (b and c) chemical profile of the β -Nb SPP along the arrow. (d) Diffraction pattern of the Laves SPP from the [11-1] zone axis (courtesy of Kieran Lynch, University of Manchester).

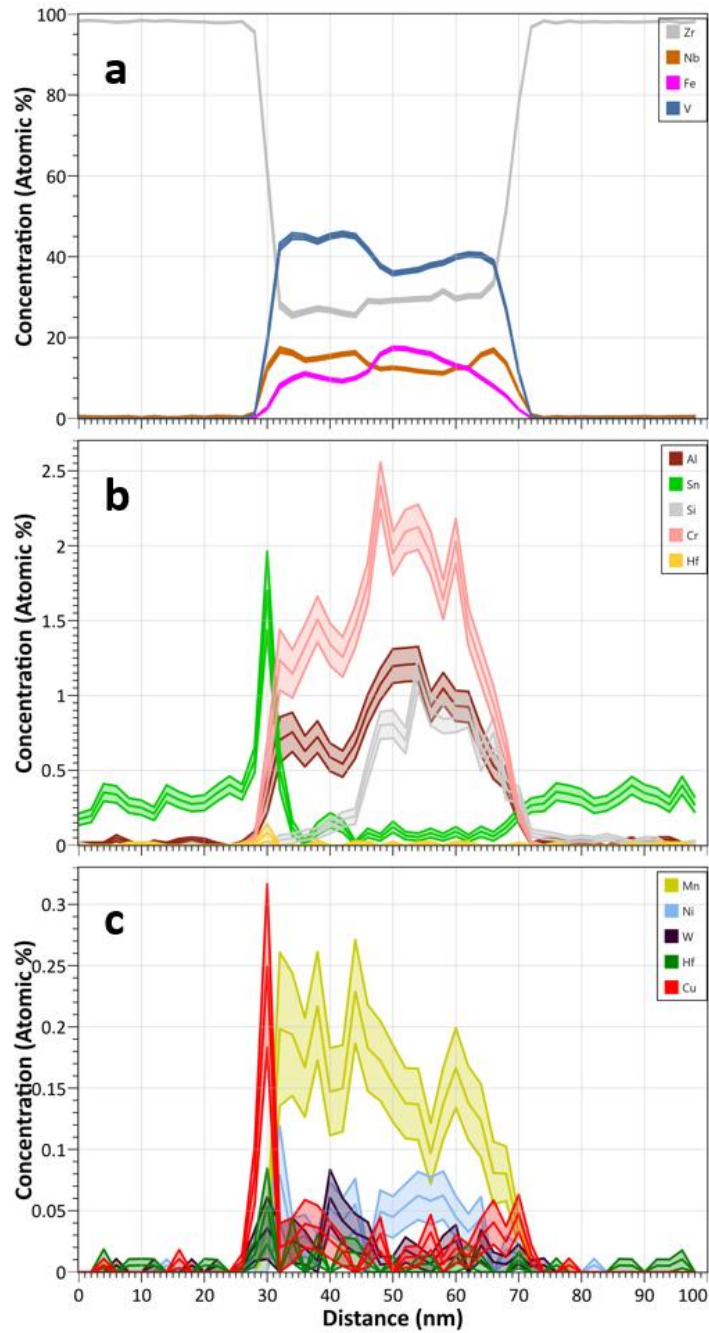


Figure 4-12. Composition profile of Laves phase SPP 2 measured along the arrow in **Figure 4-11**, binning with 2 nm.

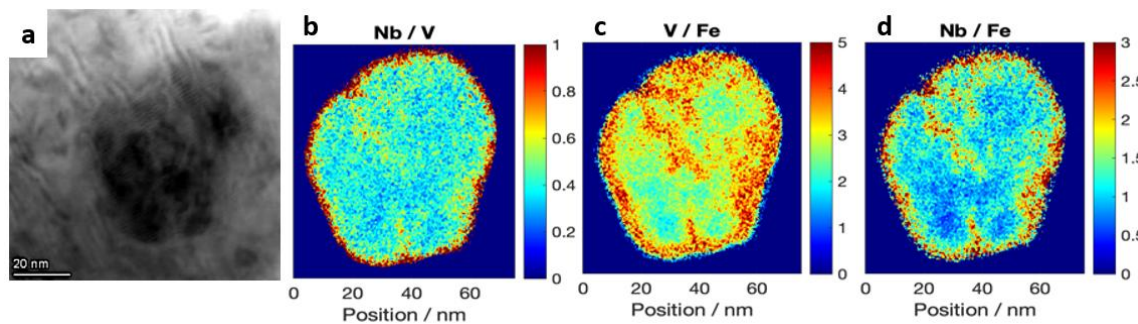


Figure 4-13. (a) Bright-field image of a Laves phase SPP in W10 alloy. (b-d) Intensity maps of STEM-EDS Nb/V, V/Fe and Nb/Fe ratio. (Courtesy of Kieran Lynch, University of Manchester)

4.3 Baseline X2 alloy

After the full recrystallization at 580 °C for 4 hours, an equilibrium state has been achieved in the X2 alloy, forming β -Nb SPPs and $\text{Zr}(\text{Nb},\text{Fe})_2$ Laves phase SPPs in the equiaxed-grained α -Zr matrix [25, 167], with $\sim 5\ \mu\text{m}$ grain diameter, **Figure 4-15**. The typical APT dataset from the baseline X2 matrix in **Figure 4-16** shows that Nb, Fe and Al are randomly distributed in the matrix, giving a composition of 0.39% Nb, 0.005% Fe and 0.004% Al.

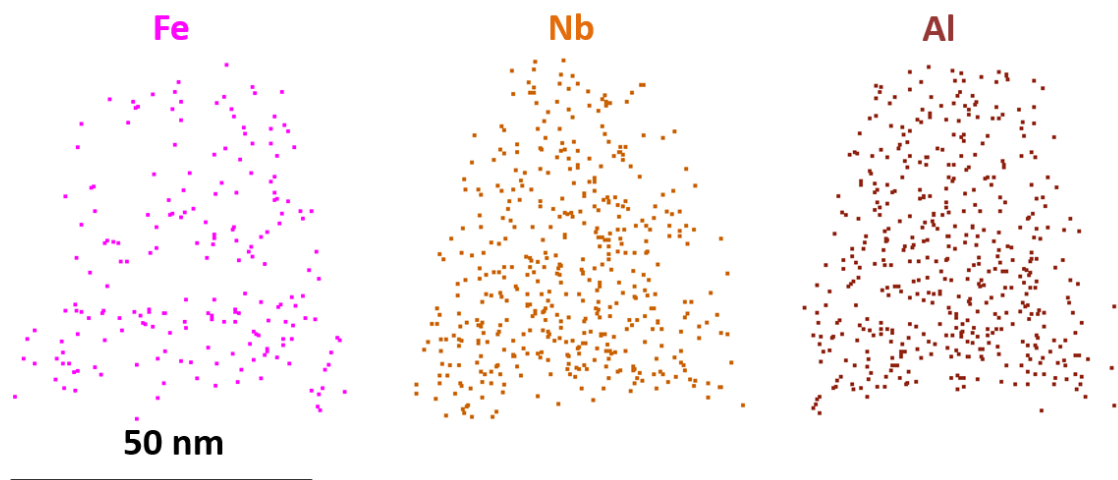


Figure 4-14. Typical APT dataset ‘SC10_M04’ from the baseline X2 matrix. Distribution maps of selected signals.

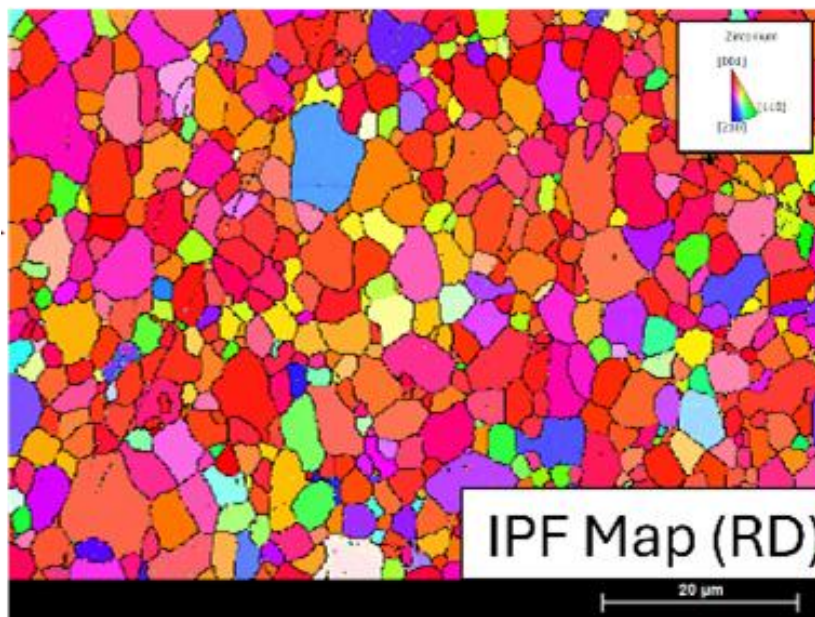


Figure 4-15. EBSD IPF (inverse pole figure) map of baseline X2 tube alloy from the radial direction. (Courtesy of Rajat Nama, University of Oxford)

4.4 Baseline ZIRLO alloy

The typical APT dataset from the baseline ZIRLO matrix in **Figure 4-16** shows that Nb, Sn and Al are randomly distributed in the matrix, but Fe segregates to curved lines, which could be some dislocations left from the processing history. The matrix composition is measured to be 0.42% Nb, 0.72% Sn, 0.008% Fe and 0.004% Al, where Nb and Fe have reached their solubility and the 0.77% addition of Sn is almost fully soluble in the α -Zr matrix. In contrast to the other three Zr alloys, only a stress-relieving final annealing was conducted on this ZIRLO alloy to maintain the strength, and there can still be some defects induced from cold working. The SRA processing has led to a very non-homogeneous grain structure, which is dominated by columnar grains with 100-300 nm grain width, **Figure 4-17**. Therefore, when considering the solute distribution in irradiated (**Chapter 5**) or corroded (**Chapters 6 and 7**) ZIRLO samples, this chemical non-uniformity in the starting alloy needs to be taken into consideration. This non-uniform grain morphology and the typical Laves phase SPPs (~40% Nb) and β -Nb SPPs (~90% Nb) in the optimised ZIRLO alloy have also been recently reported [230].

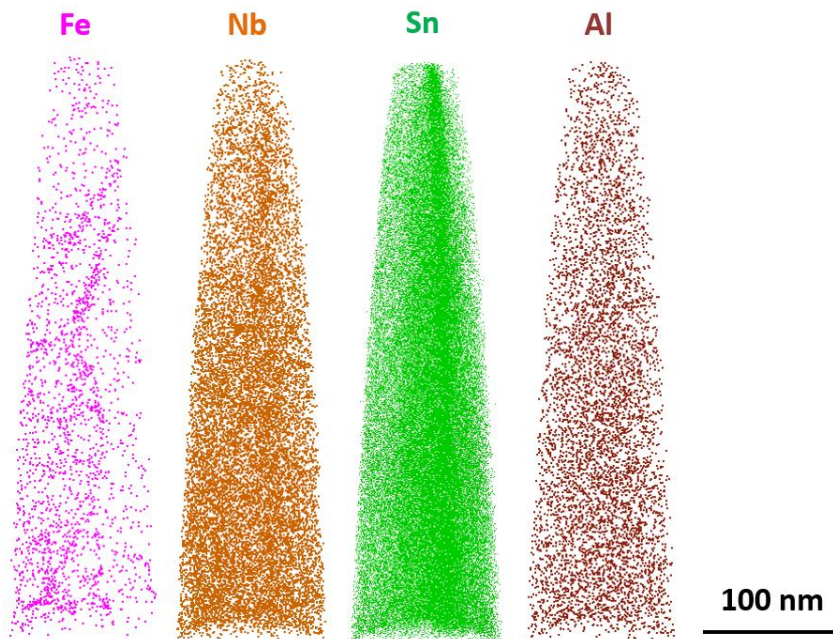


Figure 4-16. APT dataset ‘PZ11_M22’ from the baseline ZIRLO matrix. Spatial distribution of Fe ($^{56}\text{Fe}^{2+}$), Nb ($^{93}\text{Nb}^{3+}$), Sn and Al.

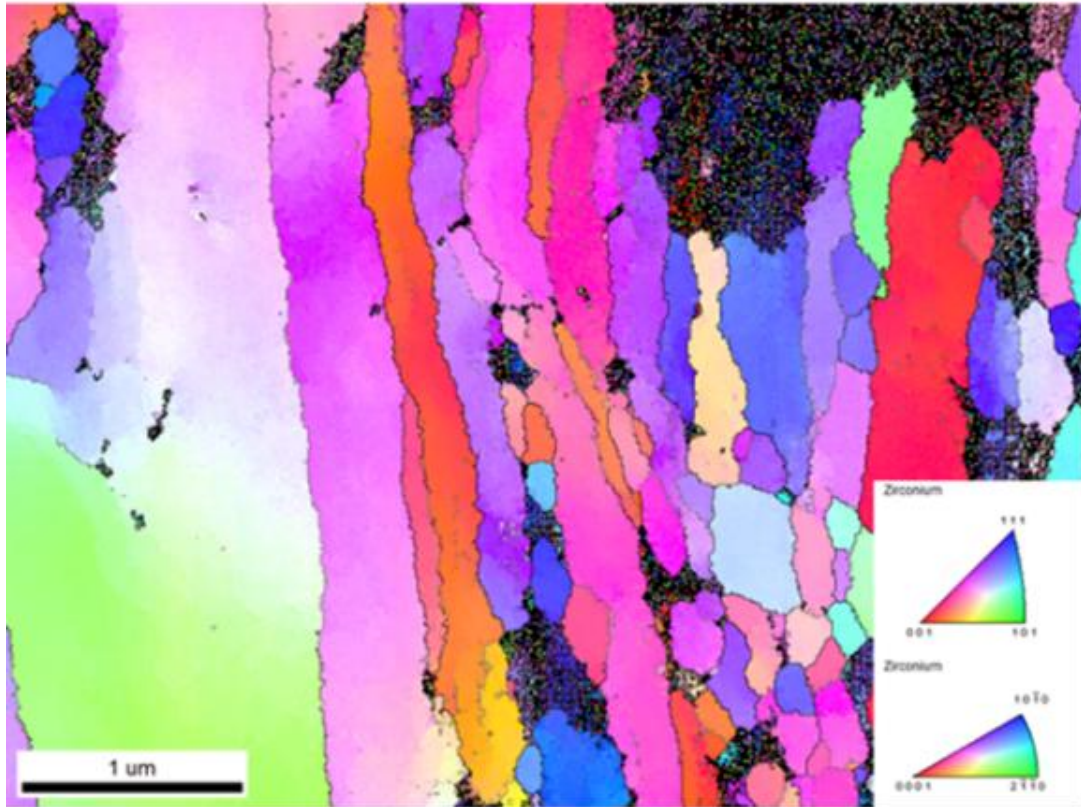


Figure 4-17. EBSD IPF (inverse pole figure) map of baseline ZIRLO tube alloy. (Courtesy of Rajat Nama, University of Oxford)

4.5 Discussion and conclusions

The baseline W13, W10, X2 and ZIRLO alloys are studied in this chapter, giving a clear starting point that can be compared with their degraded states. The SRA and RXA treatments have made solute compositions in matrix and SPPs achieve the equilibrium state. Except for the Fe segregation to residual dislocations in the SRA ZIRLO alloy, all solutes in all these alloys are randomly distributed in the matrix.

The solute compositions in the matrix of these baseline alloys are summarised in **Table 4-4**, in comparison with the nominal composition. Sn is fully soluble in the α -Zr matrix so the APT measured Sn concentrations in the matrix of the four alloys are similar to the nominal concentrations, or slightly higher because Sn is depleted in some SPPs. Al, as a trace impurity, is detected at ~0.004% in all four alloys. Nb, Fe, Cu and V are saturated in the

matrix, and are detected around their equilibrium solubilities of 0.4%, 0.004%, 0.002% and 0.004%, respectively. The supersaturated fraction of solutes is enriched mostly in SPPs, and also at GBs or interfaces. Cu in the W13 alloy shows a similar distribution to Fe but also forms Zr_2Cu SPPs. V in the W10 alloy is enriched in β -Nb SPPs (5%) and $Zr(V,Nb)_2$ Laves phase SPPs (40%). Nb is enriched at β -Nb SPPs (90%), $Zr(Nb,Fe)_2$ (40%) Laves phase SPPs and $Zr(V,Nb)_2$ (20%) Laves phase SPPs. Other trace impurities are below the APT detection limit in the α -Zr matrix but strongly segregate at sinks like SPPs, interfaces and grain boundaries.

Table 4-4. Nominal and measured matrix composition of W13, W10, X2 and ZIRLO alloys								
Element	Nominal composition (at.%)				APT matrix composition (at.%)			
	W13	W10	X2	ZIRLO	W13	W10	X2	ZIRLO
Nb	0.95	0.95	0.97	0.95	0.40 ± 0.02	0.44 ± 0.03	0.41 ± 0.02	0.42 ± 0.01
Sn	0.22	0.22	-	0.77	0.28*	0.26	-	0.73
Fe	0.08	0.08	0.1	0.18	0.004	0.005	0.005	0.008
Cu	0.24	-	-	-	0.002	-	-	-
V	-	0.32	-	-	-	0.008	-	-
Al	-	-	-	-	0.004	0.004	0.004	0.004

* Errors less than 0.01% are omitted in this thesis.

5. Irradiation damage in Zr alloys

In the baseline state, most solute elements and trace impurities are either randomly distributed in the α -Zr matrix or enriched at sinks (interfaces, GBs and SPPs), as shown in **Chapter 4**. During irradiation, as reviewed in **Section 2.2 Irradiation**, a high concentration of point defects as well as microstructural defects are formed, and the solutes can redistribute by being lost from original segregation sites or by the formation of new clusters. This chapter studies this irradiation damage by comparing the microchemistry changes in irradiated W13, X2 and ZIRLO alloys with their unirradiated microstructures in **Chapter 4 Baseline Zr alloys**. This also provides an irradiated-only reference state for further analysis of the ex-reactor X2 and ZILRO samples in **Chapter 7**, that have undergone in-situ irradiation and corrosion.

Samples in this chapter are extracted from the metal matrix (unless otherwise stated), so should not show any effect of O, but these radioactive APT specimens need to be exposed to air (sometimes for extended periods to be tested for residual activity and released by MRF staff) before being loaded into the vacuum environment in APT, which induces a thin ZrO oxide layer on the top and sides of the tip [231].

Irradiation-induced growth (IIG) has been measured on many Zr alloys exposed in the BOR-60 reactor [163]. Smaller IIG values indicate better structural stability of the alloy under irradiation. The three RXA samples studied here have similar structural stability, following the decreasing sequence of ZIRLO, W13 and W10, **Figure 5-1**. The irradiation performance of RXA X2 alloy relative to these alloys is unknown, but according to [25], it should be better than SRA ZIRLO and similar to the RXA alloys. However, SRA ZIRLO alloy has a much worse IIG stability, suggesting that the final annealing is very important in determining the radiation resistance. The most evident difference is that SRA ZIRLO alloy has a non-

uniform columnar grain structure ([232] and **Figure 4-17**), while RXA alloys have equiaxed grains with 3-5 μm diameter.

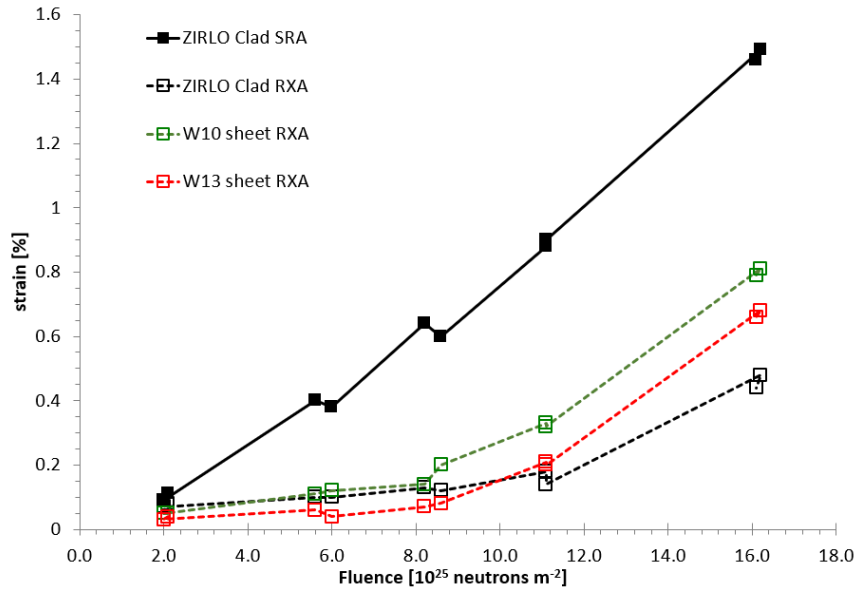


Figure 5-1. Irradiation-induced growth of neutron irradiated Zr alloys in the BOR-60 reactor (reproduced from [163]).

5.1 Irradiated W13 alloy

Correlative APT and (S)TEM analysis was applied to the irradiated W13 alloy to characterise the effect of irradiation on the solute distribution over a range of length scales.

Figure 5-2 presents TEM observations on the W13 alloy after neutron irradiation to 17.5 dpa. Larger $\langle c \rangle$ -type dislocation loops are observed in the α -Zr bulk in **Figure 5-2(a)** in a region of material containing a Zr_2Cu SPP and β -Nb SPPs. **Figure 5-2(b)** shows that Cu is released from the Zr_2Cu SPP during irradiation, as already reported for Fe being released from Laves phase SPP in Zr-2 alloy [233], likely leading to supersaturation in the bulk. In the STEM-EDS maps in **Figure 5-2(b-e)**, Cu, Nb, Fe and Sn form banded structures on the basal plane, as previously observed by TEM and APT in Zr-2 and ZIRLO alloys [49]. As shown in the overlaid bright-field image and EDS map in **Figure 5-2(a)**, some of the solute bands and the position of $\langle c \rangle$ loops are spatially correlated, suggesting that the

supersaturated solutes released to the bulk are trapped at or around the $\langle c \rangle$ loops. The Nb-rich bands seem to consist more of equiaxed Nb-rich clusters with diameters of several nm. Details of the solute redistribution at increasing levels of irradiation damage is now further studied by APT. In order to be clear about the definitions of different regions of materials to which we are referring in the APT datasets, here we define **bulk** as all the analysed volume excluding SPPs and GBs, and **matrix** as the bulk excluding irradiation-induced clusters and bands of segregated solute. **Bulk** and **matrix** compositions are by definition the same in the unirradiated state. In this way, the comparison of solute compositions in irradiated bulk and baseline matrix can be used to explore if solutes are released from sinks during irradiation, and comparison of the solute compositions in irradiated matrix and irradiated bulk can indicate the fraction of solutes used to form solute clusters. The irradiated matrix composition is also important in determining the corrosion resistance of the irradiated metal.

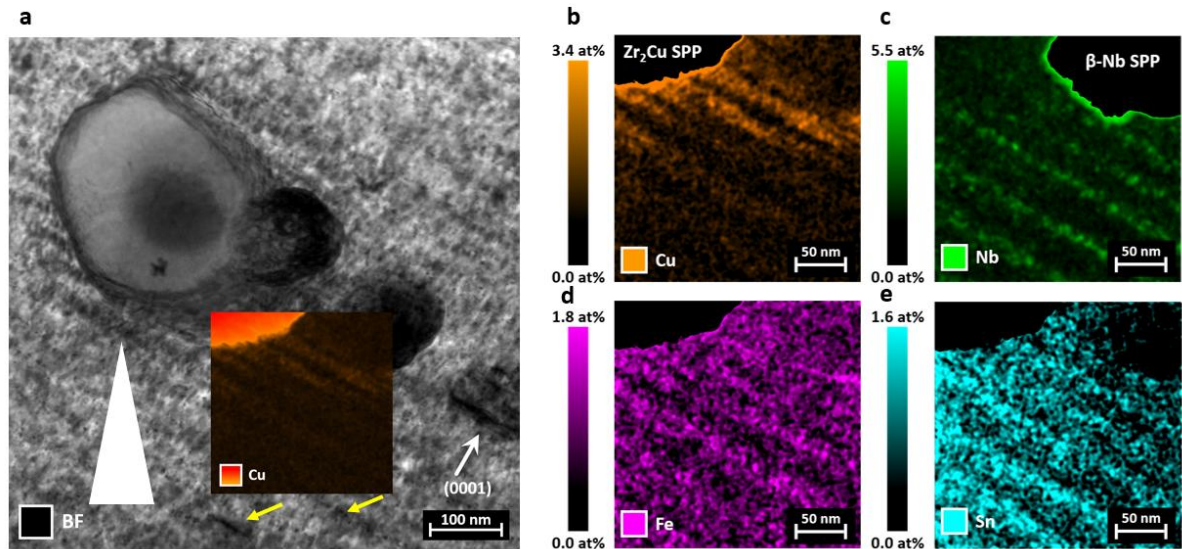


Figure 5-2. TEM observations of the W13 alloy after irradiation to 17.5 dpa. (a) Bright-field TEM image, with overlaid STEM-EDS Cu map identifying the analysis volume in (b-e) of a region containing Zr₂Cu SPPs in the α -Zr bulk. Yellow arrows indicate $\langle c \rangle$ loops on the basal plane. The white triangle indicates the approximate volume of an APT dataset. (b-e) STEM-EDS maps of Cu, Nb, Fe, and Sn distributions in the α -Zr bulk surrounding the SPPs (Only signals in the bulk are shown for better contrast). These STEM-EDS maps have an applied Gaussian blur added to identify the solute banding structures more clearly. (Courtesy of Callum Andrew)

5.1.1 4.1 dpa

Figure 5-3 presents an APT dataset from W13 alloy neutron irradiated to 4.1 dpa that contains four β -Nb SPPs. The SPPs are labelled 1-4 in **Figure 5-3(a)**, and the Zr and Nb chemical profiles along the arrows are displayed in **Figure 5-3(b-e)**. The largest SPP1 still has 80% Nb in the core, with a decreasing gradient to 60% at the periphery, whereas there is only 40% Nb throughout the smallest SPP4. SPPs 2 and 3 have sizes between those of 1 and 4, and show intermediate levels of Nb, 60-70% at the core and 50%-60% at the peripheries. This indicates a gradual decrease of the Nb concentration within the β -Nb SPPs during irradiation, with the larger SPPs retaining a higher Nb concentration than the smaller SPPs. A concentration of 40% Nb is the lowest point observed in β -Nb SPPs after irradiation to 4.1 dpa. The Nb distribution in the bulk is no longer homogeneous as observed in unirradiated state in **Figure 4-3(a)** due to the formation of nanoscale Nb clusters even at this low irradiation dose. Similar nanoscale clusters have often been reported in Nb-containing Zr alloys after irradiation [36, 43].

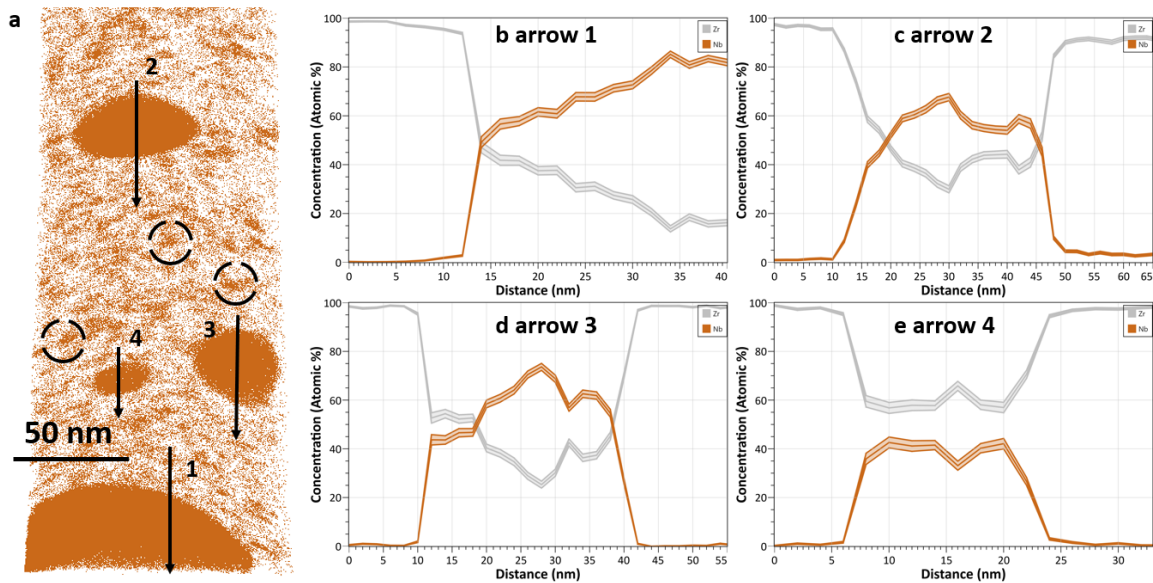


Figure 5-3. APT dataset ‘PZ05_M1’ from the W13 alloy irradiated to 4.1 dpa. (a) Nb spatial distribution map. Four β -Nb SPPs are labelled in the sequence of decreasing size. Irradiation-induced Nb clusters are not very evident at this dose, and are indicated by dashed circles. (b-e) Line profiles across the four SPPs identified in (a) along arrows 1-4.

Figure 5-4 shows another APT dataset from the sample after irradiation to 4.1 dpa, containing both Laves phase and Zr_2Cu SPPs. In clear contrast to the random distribution of solutes in the bulk detected in the unirradiated state (**Figure 4-3**), in **Figure 5-4(a)** substantial concentrations of Fe, Cu, Cr and Nb are found distributed heterogeneously in the matrix. Laves phase SPPs lose Fe rapidly during irradiation [30], because the ordered interstitial arrangement of Fe [157] is more easily destroyed [156] during the amorphization of $\text{Zr}(\text{Nb,Fe})_2$ SPP under irradiation, leaving an enrichment in Nb that makes them hard to distinguish from $\beta\text{-Nb}$ SPPs. Using the observation of Cr segregation, we can identify it as a Laves phase particle, because before irradiation Cr is normally segregated inside Laves phase SPPs but not in $\beta\text{-Nb}$ (**Table 4-2**). Fe enrichment both at the interface of the Laves phase SPP and inside the Zr_2Cu SPP is still present. In addition, the dashed box in **Figure 5-4(a)** which is expanded in **Figure 5-4(b)** shows segregation of Fe to ~ 20 nm planar features inside the Zr_2Cu SPP. Such features are not seen in the unirradiated state Zr_2Cu SPPs, so are likely to be solute-segregated dislocation loops formed within the SPP during neutron irradiation.

Higher concentrations of Cu are clearly observed at the surrounding bulk around both the Zr_2Cu and Laves phase SPPs, but not far away, because at this low irradiation dose not very much Cu is released from the sinks and they can only diffuse limited distance. This is clear in the line profile in **Figure 5-4(c)**, where the core of the Zr_2Cu SPP remains at the unirradiated Cu concentration ($\sim 27\%$), but the edge of the SPP starts to lose Cu, compared to the constant Cu concentration throughout the baseline Zr_2Cu SPP shown in **Figure 4-5(b)**. Cu content increases in the bulk surrounding the Zr_2Cu SPP are indicated with arrows in the composition profile in **Figure 5-4(d)**, and these four peaks correlate well with the four Cu-rich bands seen in the Cu spatial distribution map. The band closest to the SPP has 1% Cu enrichment, but this decreases to 0.2% further away from the SPP, exactly as seen in the

TEM results in **Figure 5-2** where the intensity of the Cu bands fades further away from the SPP. Although $\langle c \rangle$ loops could act as segregation sites for solute bands, they are normally observed after ~ 5 dpa [30], and at 4.1 dpa, it is more likely that these solute bands are segregating to other microstructural defects on the basal plane, possibly arrays of $\langle a \rangle$ loops [30, 49].

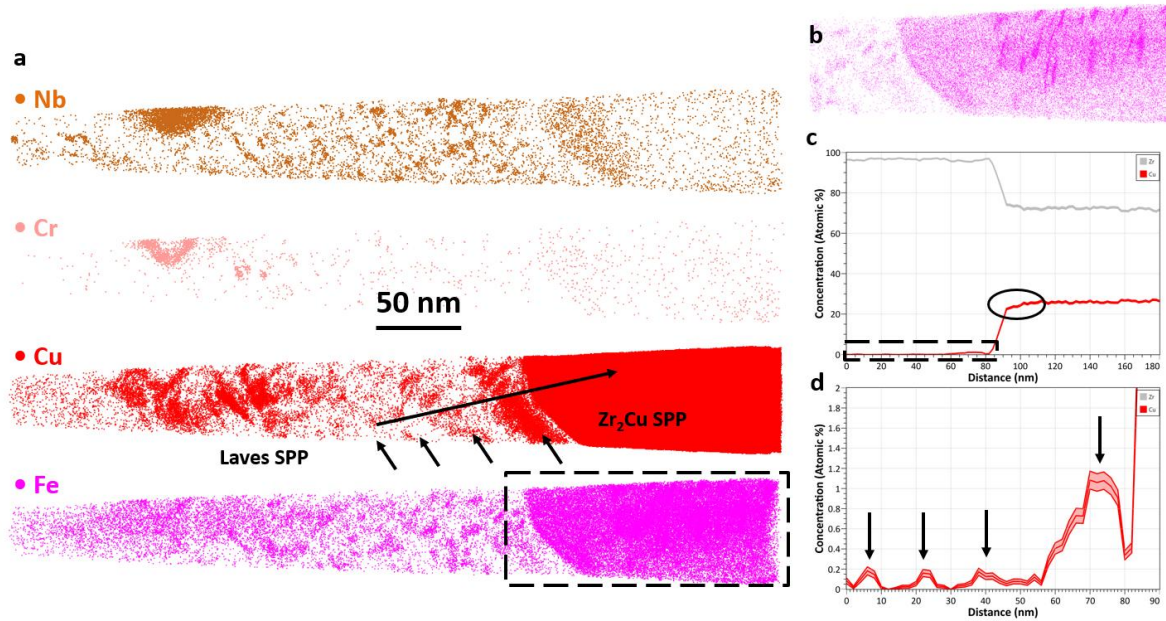


Figure 5-4. APT dataset ‘PZ05_M6’ from W13 alloy irradiated to 4.1 dpa containing a Zr_2Cu SPP and a Laves phase SPP. (a) Fe, Cu, Cr ($^{56}\text{Cr}^{2+}$) and Nb ($^{93}\text{Nb}_2^{3+}$) spatial distribution maps. (b) Magnified Fe distribution from the dashed box in (a) showing Fe segregation to planar features within the Zr_2Cu SPP. (c) Chemical line profile along the red arrow in (a). Decrease of Cu concentration at the SPP edge is indicated by a black circle. (d) Magnified dashed box region in (c), showing the Cu banding composition in the bulk around the Zr_2Cu SPP. The black arrows indicate the locations of the Cu-rich bands identified by arrows in (a).

5.1.2 17.5 dpa

A typical APT dataset from the 17.5 dpa irradiated W13 alloy is displayed in **Figure 5-5**, showing that Nb clusters in the bulk are now much more evident than in the 4.1 dpa sample.

Figure 5-5(b) and (c) show the composition profiles across a $\beta\text{-Nb}$ SPP and a Zr_2Cu SPP, where the Nb concentration in the $\beta\text{-Nb}$ SPP core further decreases to $\sim 35\%$ at this higher damage level, and the Cu concentration is evidently decreased at the edge of the SPP to form Cu-enriched bands lying on the basal plane. These Cu bands, indicated with correlated

arrows in **Figure 5-5(a)** and (c), are also better defined than that at 4.1 dpa in **Figure 5-4(a)**, and correspond closely with the TEM observations at the same dose shown in **Figure 5-2**. The nearest band is now enriched with 10% Cu, both because at this higher dose more Cu atoms are released from the Zr_2Cu SPP and also because that the longer exposure time allows diffusion further into the bulk. At the same time, at 17.5 dpa a higher density of $\langle c \rangle$ loops are expected [30], and they may be more effective at trapping solutes than the arrays of $\langle a \rangle$ loops present at 4.1 dpa. Despite the influence of the Sn segregation to crystal poles, Sn banding segregation on the basal plane is observed, and its segregation at the SPP interfaces also seem to be more evident.

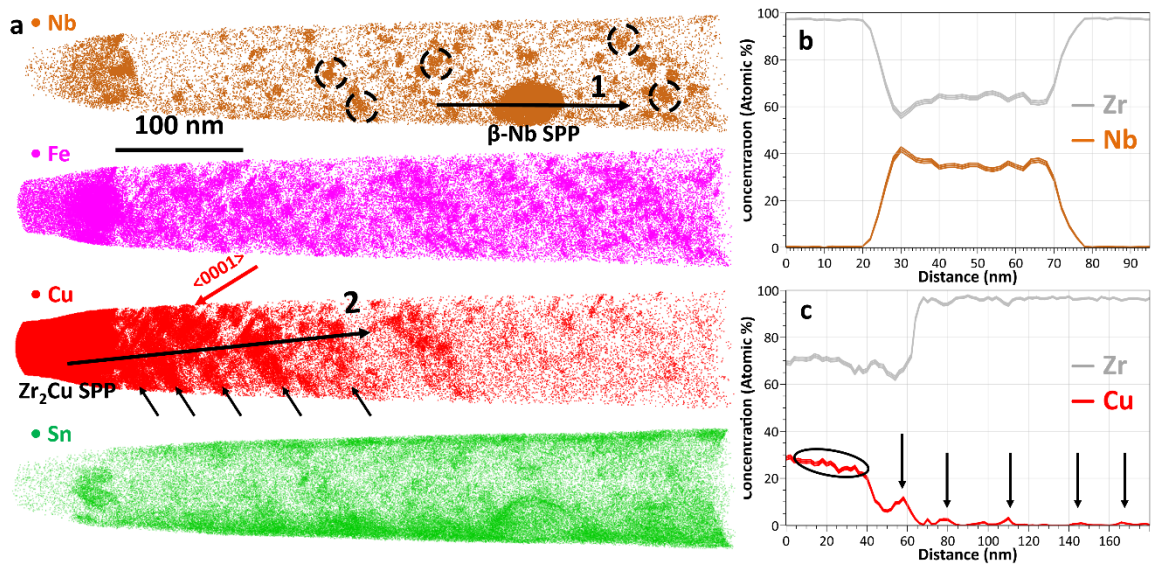


Figure 5-5. Typical APT dataset ‘PZ06_M1’ from W13 alloy irradiated to 17.5 dpa containing β -Nb and Zr_2Cu SPPs. (a) Nb (Nb_2^{3+}), Fe, Cu and Sn spatial distribution maps. Red arrows show the $\langle 0001 \rangle$ direction (determined in the APT hit map). Dashed circles indicate Nb clusters, which are better defined than those formed at 4.1 dpa. (b) Chemical line profile across the β -Nb SPP along arrow 1 in (a). (c) Chemical line profile along arrow 2 in (a). The black arrows indicate Cu bands identified in (a). The decrease of Cu concentration at SPP edge is indicated with black circle, for comparison with similar circles in unirradiated state (**Figure 4-5(b)**) and 4.1 dpa (**Figure 5-4(c)**).

5.1.3 33.5 dpa

Finally, a set of solute maps from a typical APT dataset from the 33.5 dpa sample are displayed in **Figure 5-6(a)**. Fe, Cu and Sn clearly form bands of segregation on the basal plane throughout the bulk, in evident contrast with solute banding that is only visible near

SPPs at lower irradiation doses. At lower dose levels, not much Fe and Cu are released from the SPPs, and the time for diffusion is shorter, and so only the bulk immediately surrounding the SPPs becomes supersaturated, and the banding is only visible within a few tens of nm (**Figure 5-2, Figure 5-4 and Figure 5-5**). At higher doses, the SPPs are further depleted, more Fe and Cu are released with longer diffusion time, hence the solute bands reach higher concentrations and not limited only to regions around the SPPs. The progress of formation of crystallographic defects in irradiated Zr alloys follows the sequence of $\langle a \rangle$ type dislocation loops (~ 4 nm in diameter [36]) at lower irradiation dose, which gradually line up on the basal plane as $\langle a \rangle$ loop rafts [30]. Much larger $\langle c \rangle$ loops (50-200 nm) start to form after ~ 5 dpa [36]. It is thus reasonable to assume that these arrays of $\langle a \rangle$ loop rafts and $\langle c \rangle$ loops are the segregation sites that result in the observed banding of Fe, Cu and Sn.

Interestingly, species with atomic mass of 94 and 95 are detected (peaks at 94, 95, 62.6 and 63.3 Da in mass spectra), and 62.6 Da signal having the same distribution with Nb is presented in **Figure 5-6(a)** as an example. This has not been observed in unirradiated or low-dose samples. Therefore, we consider these signals as transmutation products from Zr or Nb. Given that no such peaks are seen in the 33.5 dpa BOR-60 Zr-2 sample (which contains no Nb) and that Nb (1.15 barns) has a 6 times higher neutron cross section than that of Zr (0.185 barns) so captures neutrons more efficiently during irradiation and transmutes into ^{94}Nb and ^{95}Nb , etc. These isotopes will then follow the decay processes of $^{94}\text{Nb} \rightarrow \beta^- \rightarrow ^{94}\text{Mo}$ and $^{95}\text{Nb} \rightarrow \beta^- \rightarrow ^{95}\text{Mo}$ with half-life of ~ 2000 years and ~ 35 days, respectively [234], and thus by the time of analysis the detected species should be ^{94}Nb and ^{95}Mo . It is an interesting question what this content of Mo might do to affect the corrosion resistance during further exposure. Sabol et al [22, 235] have reported that Mo can improve the corrosion resistance if it is mainly contained in cubic ZrMo_2 SPPs, whereas in-solution Mo degrades the

corrosion resistance. Other research suggests that the addition of Mo in Zr contributes to increased tensile strength but is bad for corrosion resistance.

The chemical profile across a β -Nb SPP along the red arrow in **Figure 5-6(b)** shows that the core of the SPP now only has a concentration of 30-40% Nb. **Figure 5-6(c)** shows that Al, Fe and Cu are still segregated at the β -Nb SPP interface, indicating this must be a preferential site for these elements even at this highly damaged state. The 30-40% Nb concentration has been measured in several other β -Nb SPPs in this 33.5 dpa material, indicating that this is the minimum level of Nb reached in these SPPs at very high irradiation doses.

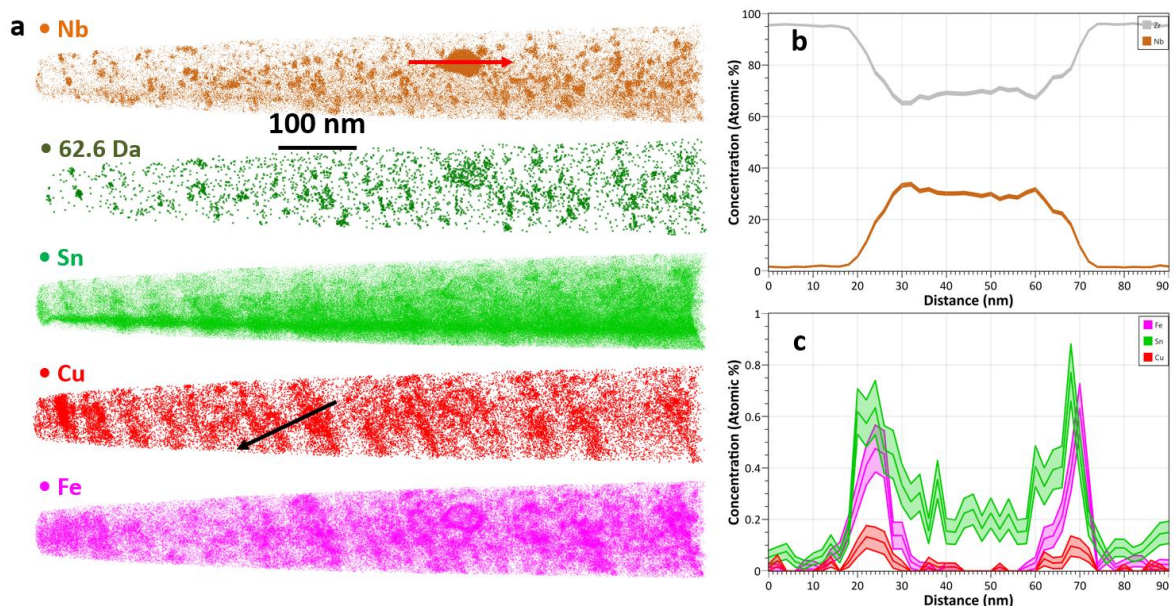


Figure 5-6. Typical APT dataset ‘PZ02_M8’ of W13 alloy irradiated to 33.5 dpa. (a) Nb ($^{93}\text{Nb}_2^{3+}$), 62.6 Da ($^{94}\text{Nb}_2^{3+}$), Sn, Cu and Fe spatial distribution maps, containing α -Zr bulk and a β -Nb SPP. The black arrow indicates the $\langle 0001 \rangle$ direction. (b) and (c) Chemical line profiles across the β -Nb SPP along the red arrow in (a).

Figure 5-7(a) and (b) compare composition line profiles along the $\langle 0001 \rangle$ direction measured on the 17.5 dpa sample using STEM-EDS and APT. In both datasets Fe and Cu segregate strongly to the same bands separated by about 20-30 nm. The distribution of Nb measured in both techniques is less ordered because Nb tends to form clusters instead of bands (**Figure 5-5**). In the STEM profile, Sn banding is clearly out of phase with Fe and Cu, as previously reported [30]. This is difficult to confirm in the APT analysis because the Sn

distribution is distorted by the well-known APT pole artefact where Sn segregates at particular crystallographic directions on the specimen surface during field evaporation [236]. Similar APT and TEM observations of solute banding on the basal plane, the out-of-phase banding of Fe and Sn, and clustering of Nb have been reported in Zr-2 and ZIRLO alloys by Jenkins et al [49].

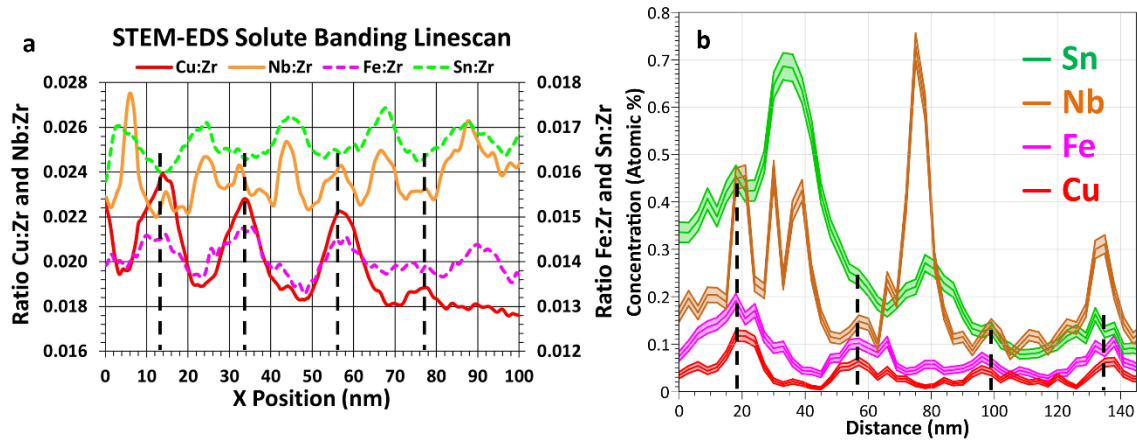


Figure 5-7. Chemical profiles of the Cu, Nb, Fe and Sn along the $\langle 0001 \rangle$ direction measured on the 33.5 dpa sample using (a) STEM and (b) APT.

5.1.4 Composition analysis

In-pile corrosion usually occurs at a much higher rate than measured in proxy autoclave corrosion tests [237]. Three factors, which may act simultaneously, have been suggested to explain this, (i) the accumulating microstructural defects [37], (ii) changes in microchemistry in the bulk [40], and (iii) acceleration of the key mechanisms of the metal-to-oxide transformation at the oxide/metal interface [37]. Here we focus on (ii).

The composition of solutes in the bulk in the W13 alloy from 0 to 33.5 dpa is displayed in **Table 5-1** and **Figure 5-8**. The equilibrium solubility of Fe and Cu is very low in the unirradiated bulk, measured as 0.004% and 0.001%, respectively, whereas the bulk compositions of both increase by more than a factor of 10 during irradiation, confirming that

they are significantly released from SPPs into the bulk, where they are trapped by planar defects and show as solute bands.

The bulk composition of Sn and Nb remains the same at ~0.4% and 0.25%, respectively. Sn is randomly distributed in the unirradiated material with no clear segregation to any microstructural features, therefore it is as expected that there is no evidence of extra Sn entering the bulk after irradiation. The Sn banding, which is out of phase with the Fe and Cu bands, seems to be composed of Sn in solid solution in the bulk before irradiation. Sn diffusion is normally considered to be very slow in the α -Zr matrix because of its large atom size, but must become easier as a result of the vacancies induced into the lattice during irradiation. The out-of-phase banding of Sn with Fe and Cu is currently not understood, possibly suggesting a different segregation mechanism of Sn driven by local strains or activity gradients rather than trapping by defects.

Considering the dramatic decrease of Nb concentration in the β -Nb SPPs, from 90% to 40% at the core, we might expect the bulk Nb concentration to also increase. However, it remains ~0.37% after even 33.5 dpa irradiation, possibly because any Nb atoms released from the well-dispersed β -Nb SPPs have only a limited effect on the bulk composition. However, in the profiles across irradiated Nb SPPs, **Figure 5-5(a)** and **Figure 5-2(c)**, if Nb is leaving β -Nb SPPs, the Nb map should show a similar concentration gradient in the bulk around the β -Nb SPPs as Cu does around the Zr_2Cu SPPs, perhaps with an even steeper gradient due to the slower diffusion rate of Nb than Cu in α -Zr [238]. Noting that this is not seen, it is reasonable to suggest that the decrease in Nb concentrations in the β -Nb SPP after irradiation is induced by SPP growth and intermixing with Zr, instead of releasing of Nb to the bulk. He et al [226] confirm a ~5% growth in diameter of β -Nb SPPs after heavy ion irradiation using in-situ TEM techniques, and that these β -Nb SPPs remain fully crystalline after high dose irradiation [226] because the intermixed Zr atoms substitute for Nb maintaining the

BCC crystal structure. The observation in **Figure 5-6(c)** that the segregated elements remain at the interface of the β -Nb SPP suggests that these segregating species move as the SPPs coarsen because they are nearly insoluble in both the HCP α -Zr and BCC β -Nb SPPs, so the interface is still the preferred segregation site even after high irradiation damage. By contrast, Laves phase and Zr_2Cu SPPs gradually become amorphous [239] starting from the outer edge due to the depletion of Cu and Fe (**Figure 5-5 (c)**).

Table 5-1. Bulk composition of solutes in W13 alloy before and after neutron irradiation (at%)*				
	0 dpa	4.1 dpa	17.5 dpa	33.5 dpa
Nb	0.39 $\pm$ 0.01	0.36 $\pm$ 0.01	0.37	0.36 $\pm$ 0.01
Sn	0.28	0.28	0.21	0.26
Fe	0.004	0.007	0.053	0.065
Cu	0.001	0.004	0.008	0.024

* Trace impurities are also partially released from the sinks during irradiation leading to slightly higher bulk concentrations. Here the focus is only solutes.

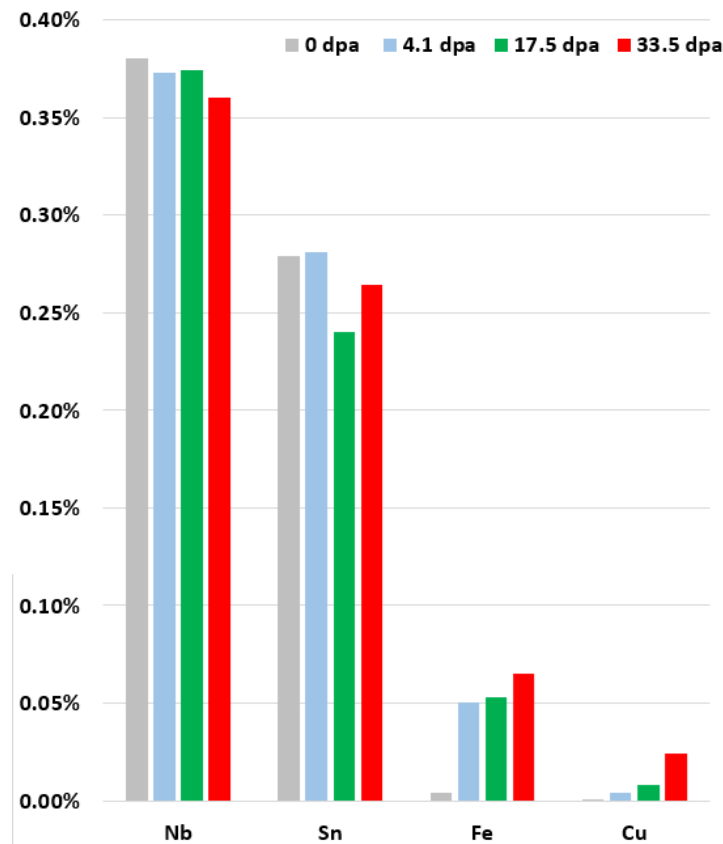


Figure 5-8. Solute bulk composition in W13 alloy after 0, 4.1, 17.5 and 33.5 dpa. The data is taken from **Table 5-1**.

All of these microchemical changes involve the diffusion of solute elements during irradiation, taking Nb as an example, the diffusion distance, d , of Nb in α -Zr can be estimated from

$$d = \sqrt{Dt},$$

where t is diffusion time, D is the diffusion coefficient

$$D = A \exp (-Q/RT).$$

A = the frequency factor of Nb in α -Zr, $6.6 \times 10^{-10} \text{ m}^2/\text{s}$ [240],

Q = the activation energy of Nb in α -Zr, $1.32 \times 10^5 \text{ J/mol}$ [240],

R = the gas constant, $8.31 \text{ J/mol} \cdot \text{K}$,

T = temperature, 593 K.

The diffusion coefficient of Nb in α -Zr is $D = 1.53 \times 10^{-21} \text{ m}^2/\text{s}$.

The irradiation times for the 4.1, 17.5, 33.5 dpa samples are 4 months, 11 months and 16 months [164]. Hence, the diffusion distance can be estimated as ~40, 66 and 80 nm, respectively. However, we expect irradiation to significantly accelerate solute diffusivity [31, 241], so the actual Nb diffusion distances during BOR-60 exposure must be greater. The diffusion coefficient in α -Zr follows the sequence of $\text{Fe} > \text{Cu} > \text{Cr} > \text{Nb} > \text{Sn} > \text{Zr}$ [238], so Fe and Cu can diffuse much further than Nb, whereas Sn is less mobile. This calculation aligns well with the APT observations that the in-solution Nb and Sn in the bulk at relatively higher concentrations diffuse only tens of nm to form clusters and bands, while the Fe, Cu and trace elements released from sinks diffuse hundreds of nm to any potential sinks for segregation.

Nb cluster analysis

The content of Nb is particularly important in determining the local electrochemical properties of the oxide and thus the corrosion resistance. As mentioned above, the Nb concentrations at the core of β -Nb SPPs dramatically decrease from 90% to 40-60% at 4.1

dpa, and to ~35% at 17.5 and 33.5 dpa, meanwhile Nb clusters with up to 40% Nb form in the bulk. APT enables observation and atom-by-atom analysis of the size and composition of nanoscale irradiation-induced clusters. Here we use APT data to define Nb clusters and investigate the local Nb content changes at increasing doses. Detailed quantitative analysis of the Nb microchemistry in bulk, clusters and matrix after 0, 4.1, 17.5 and 33.5 dpa is carried out, **Table 5-2**.

Figure 5-9(a-c) show the Nb clusters in APT datasets from 4.1, 17.5 and 33.5 dpa samples identified using the isosurface method illustrated in **Section 3.4.4 Cluster analysis**. Cluster interface for the different analysis purposes of matrix, cluster core, and cluster statistics follow the considerations in **Figure 3-15**. Proxigrams showing averaged Nb content changes from the matrix to Nb cluster core are displayed in **Figure 5-9(d-f)**. At 4.1 dpa, the Nb content plateaus at ~35% and at ~40% in both 17.5 and 33.5 dpa datasets.

The matrix Nb concentration decreases from 0.38% in the unirradiated state to 0.26% after 4.1 dpa, and further decreases to 0.14% after 17.5 dpa, but then stays around 0.16% at 33.5 dpa, **Figure 5-10(a)**. Combined with the fact that the bulk Nb concentration remains the same, it is obvious, as concluded above, that the in-solution Nb is depleted from the α -Zr matrix to form the Nb clusters. It is interesting to note that most of the compositional changes (SPP dissolution, matrix depletion, and cluster growth) happen during the early stage of exposure, 0-4.1 dpa.

Cluster size distribution histograms at three doses are displayed in **Figure 5-9(g-i)**, and a clear shift to larger volumes is observed. The cluster sizes mostly fall in the range of 0-300 nm³ for the 4.1 and 17.5 dpa datasets, whereas 15% of the clusters have volumes larger than 300 nm³ when irradiated to 33.5 dpa. The cluster volume fraction increases from 0.51 vol% at 4.1 dpa to 0.78 vol% at 17.5 dpa and then to 1.10 vol% dpa at 33.5 dpa, with the cluster number density following opposite trend from $7.47 \times 10^{22} \text{ m}^{-3}$ at 4.1 dpa to $4.92 \times 10^{22} \text{ m}^{-3}$ at 33.5

dpa, indicating smaller clusters tend to coarsen into bigger clusters at higher doses. Similar observations on the increasing volume fraction of Nb clusters at higher irradiation doses can be found in [36, 242].

Therefore, we conclude that once the cluster reaches a 40% Nb at the core at around 17.5 dpa, the clusters grow in size rather than becoming richer in Nb. We note that this value is similar to the Nb concentration to which β -Nb SPPs are reduced to by irradiation (35% in **Figure 5-3**, **Figure 5-5** and **Figure 5-6**), indicating that the pre-existing β -Nb SPPs in the unirradiated materials and the irradiation induced Nb-rich clusters eventually achieve a similar thermodynamically-stable composition after severe irradiation, **Figure 5-10(b)**. Although here has been evidence for spatial correlation between clusters and dislocation loops [48], in most of other cases in this thesis and literature, this correlation is very rarely observed, so I conclude that there are two mechanisms for the formation of solute clusters: (i) segregation on crystal defects, like the strained region of $\langle a \rangle$ loops and irradiation-induced nanovoids, and (ii) nucleation and growth randomly within the bulk.

Table 5-2. Nb microchemistry analysis on W13 alloy at different irradiation doses				
Dose (dpa)	0	4.1	17.5	33.5
Nb concentration at β -Nb SPP core (%)	90	40-60	35	35
Nb concentration in bulk (%)	0.38	0.37	0.37	0.36
Nb concentration in matrix (%)	0.39	0.26	0.14	0.16
Nb concentration at Nb cluster core (%)	-	35	40	40
Nb cluster volume fraction (%)	-	0.51	0.78	1.10
Nb cluster number density ($\times 10^{22} \text{ m}^{-3}$)	-	7.47	5.94	4.92

Bulk denotes all material excluding SPPs and GBs. **Matrix** denotes the bulk also excluding all Nb clusters defined in the isosurfaces.

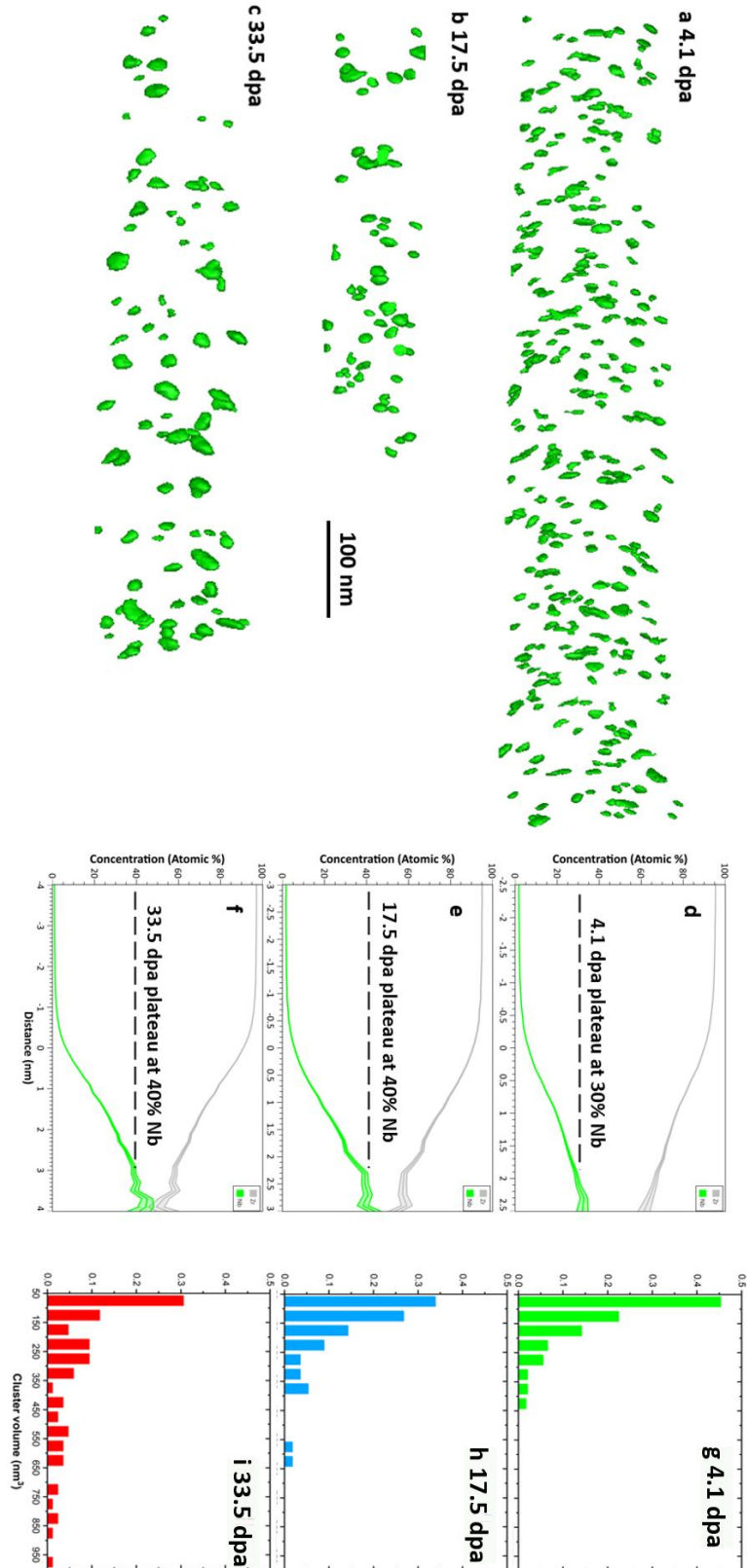


Figure 5-9. Nb clusters defined with 6% Nb isosurfaces and with greater than 50 nm³ in typical APT datasets from (a) 4.1 dpa, (b) 17.5 dpa, and (c) 33.5 dpa samples. (d-f) Average Nb concentration vs distance proxigrams for Nb clusters in (a-c), where distance 0 is approximately set at the interface between cluster and bulk. The distance in proxigrams from 0 to where the measurement ends indicates the cluster radius, i.e., 2.5 nm, 3 nm and 4 nm, respectively. (g-i) Nb cluster size distribution histograms for (g) 4.1, (h) 17.5, and (i) 33.5 dpa, with 50 nm³ binning size. The count of clusters within each volume range is normalised to the total cluster count.

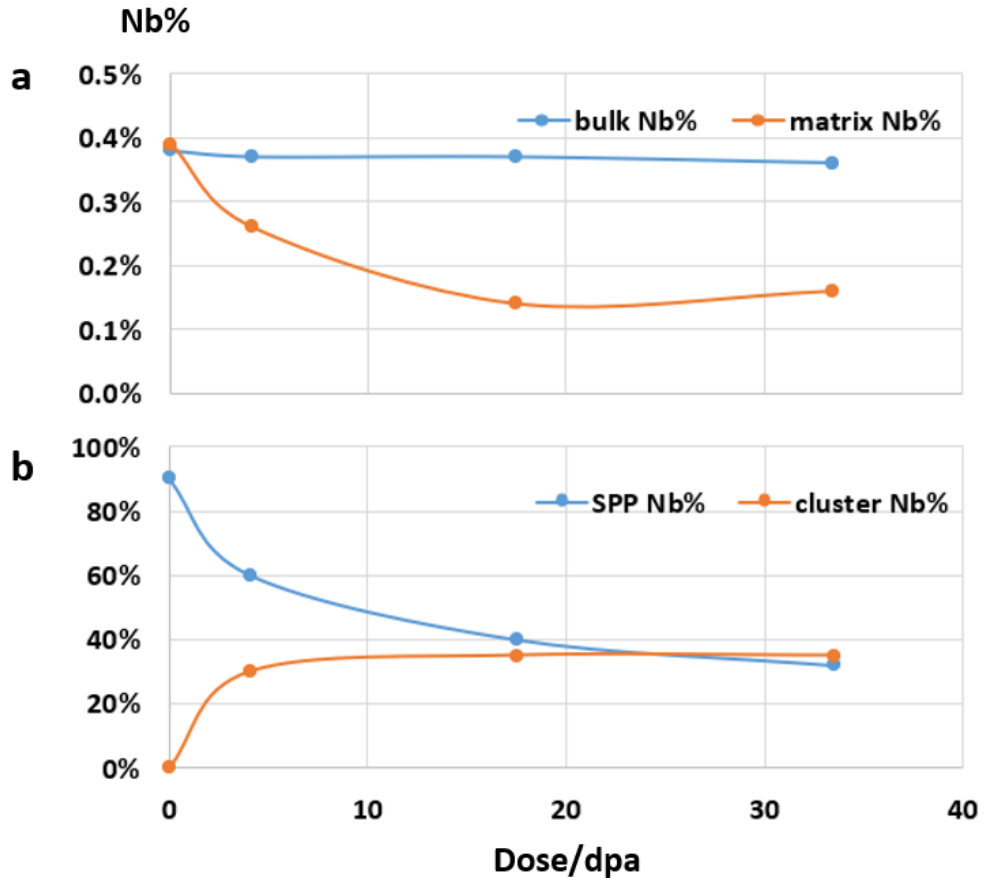


Figure 5-10. Nb microchemistry analysis (a) Nb concentrations in matrix and bulk after different doses, (b) Nb concentrations at the cores of SPPs and clusters.

5.1.5 W13 alloy summary

Because of its noble electrochemical properties, Cu is added into several alloy systems to improve corrosion performance [243, 244]. For instance, the addition of Cu can improve the intergranular corrosion of Al-Mg alloys [245]. As indicated in recent studies, the oxides GBs formed by aqueous corrosion of Zr alloys act as preferential diffusion paths for corrosion species [166]. Although we have observed Cu to strongly segregate to grain boundaries in W13 (**Figure 4-7**), there is currently no data on the distribution of Cu in the oxides formed on this alloy. Some encouraging modelling data suggests that Cu can improve the tensile strength of zirconia grain boundaries [71], and it may also prevent the formation of cracks and nanovoids on grain boundaries during corrosion, limit the easy penetration through interconnected pathways and improve the overall corrosion rate. It is also still unknown why

a little addition of Cu makes W13 alloy less stable under irradiation than RXA ZIRLO alloy. These would be an interesting next stage in understanding the influence of Cu additions to Zr cladding alloys on the corrosion and irradiation performance.

The microchemical variations in Westinghouse W13 Zr-Nb-Sn-Cu-Fe alloy samples in the unirradiated, 4.1, 17.5, and 33.5 dpa neutron irradiated states were investigated using APT and by Callum Andrew by (S)TEM. In the unirradiated state, solutes in W13 alloy show similar behaviour as the ZIRLO alloy, where 0.28% Sn is distributed randomly throughout the matrix, but is depleted in SPPs. Nb has a 0.39% solubility in α -Zr and is enriched at β -Nb SPPs (90%) and Laves phase (40%) SPPs. Cu, Fe and other trace impurities are present at very low concentrations in α -Zr and segregate at sinks like SPPs, interfaces and GBs, and most of the Cu is contained in the Zr_2Cu SPPs. After irradiation Fe and Cu are depleted from these sinks to the α -Zr bulk, leading to an increase in bulk concentration of a factor of ten. This excess of Fe and Cu forms enriched bands on the basal plane, probably around arrays of $\langle a \rangle$ dislocation loops or $\langle c \rangle$ dislocation loops. The Nb content of β -Nb SPPs is reduced from 90% to 35% at 33.5 dpa by mixing with Zr atoms and SPP growth. In-solution Nb and Sn is depleted from the matrix to form Nb clusters and Sn bands. The Sn bands are out-of-phase with the Fe and Cu bands. The core composition of the irradiation-induced Nb clusters plateaus after 17.5 dpa at 40%, and they then grow with increasing dose, accounting for a larger volume fraction. The β -Nb SPPs and Nb clusters eventually achieve a similar concentration of Nb of $\sim 40\%$, which must be some kind of dynamic equilibrium concentration under irradiation.

5.2 Irradiated X2 alloy

The microchemistry of X2 alloy irradiated to 8 dpa (1 cycle) and 32 dpa (4 cycles) in the Vogtle reactor was studied with APT. These APT tips were made from the metal matrix at least 50 μm away from the O/M interface on the axial cross section bulk samples to study the irradiation effect separately, unless otherwise stated. Details have been given in **Section 3.3.1**.

5.2.1 8 dpa

Figure 5-11 shows a typical APT dataset from the 8 dpa X2 alloy, containing a Nb-enriched SPP and the irradiated metal bulk. Some Nb and Fe clusters have formed in the bulk and are weakly aligned on the basal plane. This Nb-rich SPP still has 80% Nb or 4:1 Nb/Zr ratio at the core, **Figure 5-11(b)**, so before irradiation must be a β -Nb SPP, because unirradiated Laves phase SPPs only have a 1:1 Nb/Zr ratio, and this should decrease during irradiation. Fe segregation at the SPP interface is still present.

These APT tips are extracted from the metal matrix, and should only contain trace-level of elements like C, H and O. However, as shown in the Fe mass spectrum in **Figure 5-12**, two Fe-containing peaks are apparently significantly affected by gas species. The $^{56}\text{Fe}^{2+}$ peak partially overlaps with $^{12}\text{C}^{16}\text{O}^+$, and the $^{56}\text{Fe}^+$ peak completely overlaps with $^{94}\text{Zr}^{16}\text{O}^1\text{H}^{2+}$ and $^{96}\text{Zr}^{16}\text{O}^{2+}$, respectively. Because the extracted tips are far from the oxide, these contamination signals must arise from residual gas in the analysis chamber. Estimated from the isotope concentrations, the contribution of $^{94}\text{Zr}^{16}\text{O}^1\text{H}^{2+}$ and $^{96}\text{Zr}^{16}\text{O}^{2+}$ to the 56 Da peak is indicated by an arrow and a horizontal line, so the majority of the 56 Da signal is not from Fe, making accurate compositional analysis of Fe very difficult. In order to include all the real Fe counts during the composition analysis, these two peaks are labelled as Fe, as shown in the purple ranges. As an example to show the distribution of these gas-related signals, the

54 Da $^{94}\text{Zr}^{16}\text{O}^1\text{H}^{2+}$ signal is randomly distributed in the bulk, **Figure 5-12(c)**, so this ranging method inevitably introduces background noise in the Fe spatial map in **Figure 5-11(a)**.

Notably, the 55.5 Da peak is not seen in other datasets, and is not from ZrOH species, and from experience we would not expect Nb to be evaporated as $^{93}\text{Nb}^{16}\text{O}^1\text{H}_2^{2+}$ because the high electric field would encourage such complex ions to dissociate. However, the position of the 55.5 Da counts shows segregation to the Nb SPP, **Figure 5-12(d)**, clearly contrasting with the 54 Da $^{94}\text{Zr}^{16}\text{O}^1\text{H}^{2+}$ counts that show a random distribution in the bulk, **Figure 5-12(c)**. So I conclude that the 55.5 Da signal must be a Nb-containing signal, i.e. $^{93}\text{Nb}^{16}\text{O}^1\text{H}_2^{2+}$. This emphasizes the idea that the evaporation and detection of ions during APT analysis can be very different from different samples, and careful interpretation of the mass spectrum regarding the specific material composition, running conditions and tip morphology of each dataset is essential prior to detailed analysis.

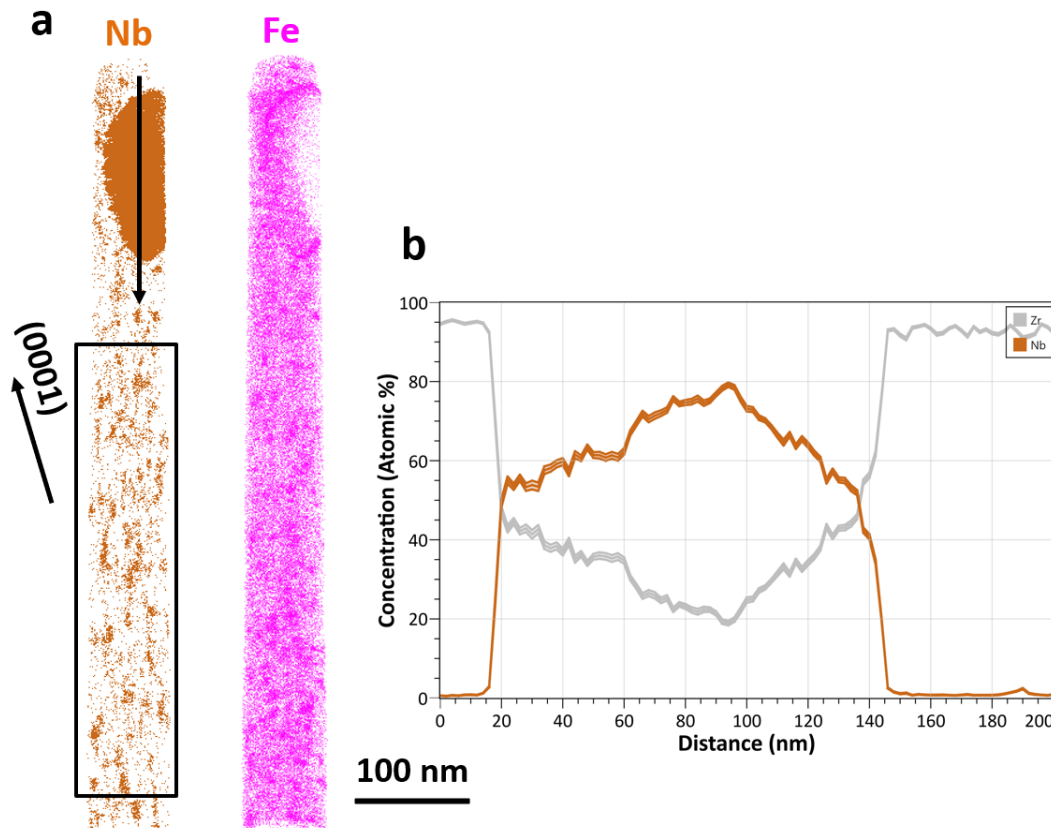


Figure 5-11. APT dataset ‘PZ14_M3_1cXA’ from an 8 dpa irradiated-only X2 alloy. (a) Spatial distribution of Nb ($^{93}\text{Nb}_2^{3+}$) and Fe. (b) Chemical profile across the SPP, binning with 2 nm. Materials in the boxed region is taken for bulk composition analysis.

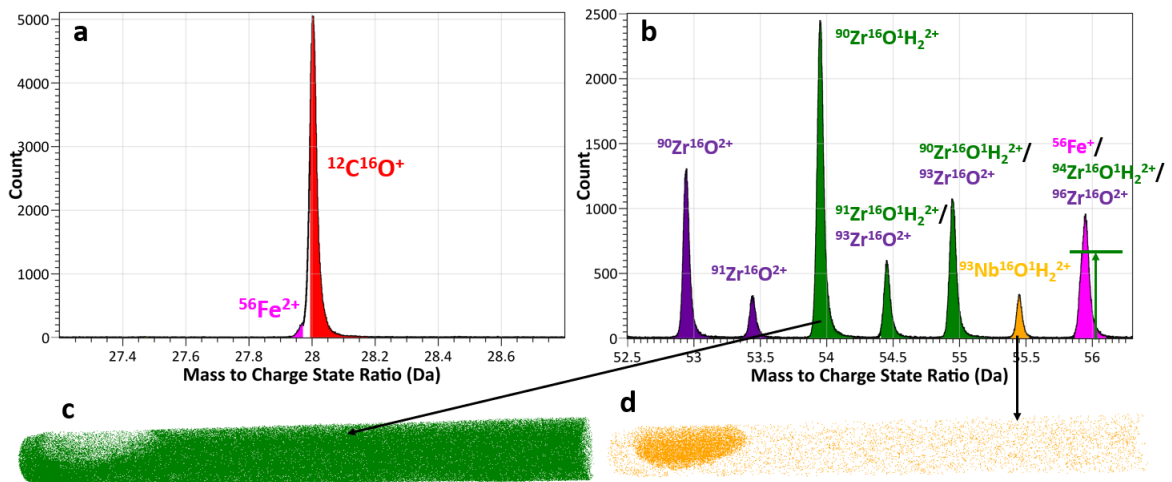


Figure 5-12. Mass spectrum of Fe-containing peaks in ranges of (a) 27.2-28.8 Da, and (b) 52.5-56.3 Da from the APT dataset in **Figure 5-11**. Height of the horizontal green line indicates the level of contribution from $^{94}\text{Zr}^{16}\text{O}^1\text{H}_2^{2+}$ and $^{96}\text{Zr}^{16}\text{O}^{2+}$ signals in the 56 Da peak. (c and d) Spatial distribution maps of 54 and 55.5 Da signals.

5.2.2 32 dpa

Figure 5-13 shows a typical APT dataset from a 32 dpa irradiated-only X2 alloy, containing a Nb-rich SPP and the irradiated metal bulk. The Nb and Fe clusters grow larger and are evidently aligned on the basal plane, compared to those at 8 dpa. The distributions of Cr and Al are examples showing that trace impurities are hardly detectable before irradiation but are significantly released from sinks during irradiation, becoming supersaturated in the bulk. They diffuse away from the SPP and can be trapped in planar defects forming bands of solute segregation. These impurities are only present in low concentrations, and only the composition and distribution of Fe and Nb are studied in detail. Transmutation products from ^{95}Nb at 63.2 Da having the same distribution with ^{93}Nb are detected, similar as in **Figure 5-6**.

The Nb concentration remains at ~50% at the core of this SPP, but reduces to below 20% at the periphery, **Figure 5-14(a)**. Considering the substantial amount of Cr in the surrounding bulk, this should be a Laves phase SPP before irradiation. However, it becomes more

difficult to determine the original type of Nb-rich SPPs in highly-irradiated samples, and this differentiation seems to be less important because both Laves phase and β -Nb SPPs will eventually have a Nb/Zr ratio less than 1:1, so when oxide front progresses to consume this region of metal, both types of SPPs should have similar electrochemical properties and effect on the delayed oxidation.

The chemical profile across the solute bands in **Figure 5-13** (yellow arrow) clearly shows that Nb and Fe are enriched at similar positions, with a 80-100 nm spacing, **Figure 5-14(b)**. This spacing is quite larger than that of Fe and Cu bands seen in irradiated W13 alloy (20-30 nm). Due to the limited dimensions of an APT dataset, measurement vertical to the solute bands is difficult if they are steeply inclined to the tip axis, and the profile needs to include many bands to give good statistics on the position of Fe and Nb bands. This profile only aims to show the co-banding of Nb and Fe, and the quantitative information should not be overinterpreted.

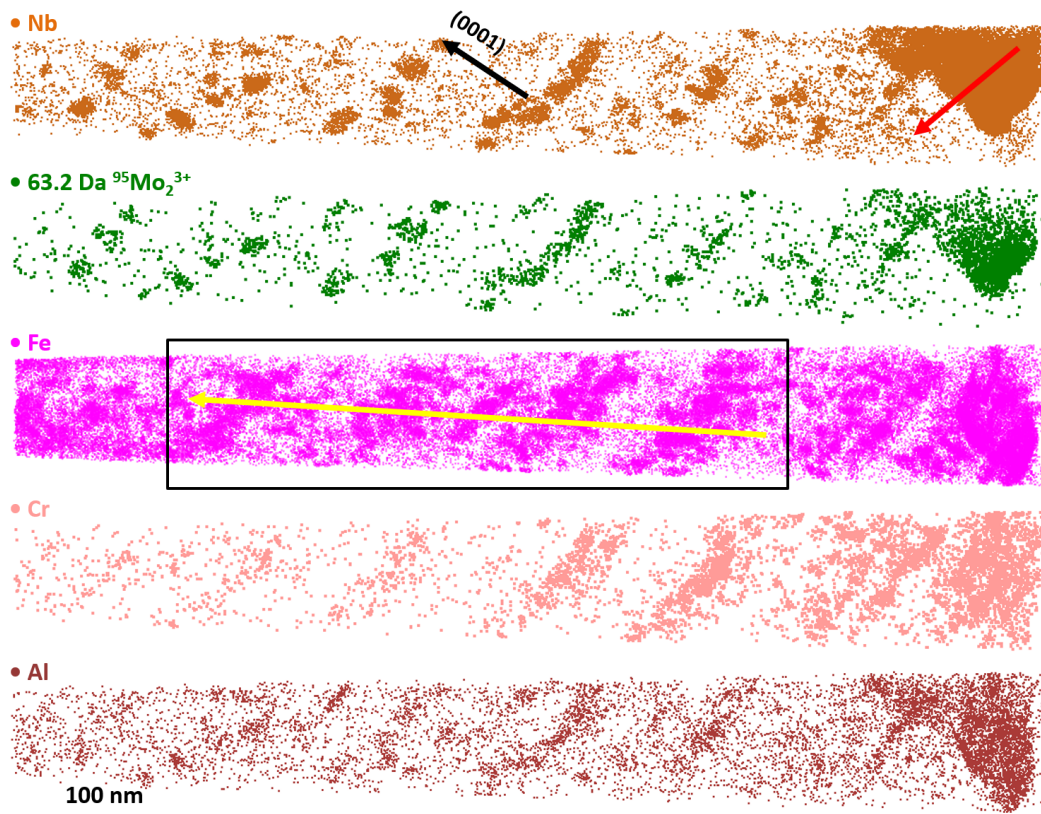


Figure 5-13. APT dataset ‘PZ13 M09 4cXR’ from a 32 dpa irradiated-only X2 alloy. Spatial distribution of Nb ($^{93}\text{Nb}_2^{3+}$), Mo ($^{95}\text{Mo}_2^{3+}$), Fe, Cr and Al. The $\langle 0001 \rangle$ direction is indicated by the black arrow. A composition profile across the Nb-rich SPP is measured along the red arrow. Material in the boxed region is selected for bulk composition analysis. (This APT tip was made from the radial cross section Vogtle bulk samples aiming at the O/M interface but ended up in the underlying metal below the O/M interface. These regions of metal seem to have little effect from oxidation, and are used for analysis of the effect of irradiation on the metal matrix.)

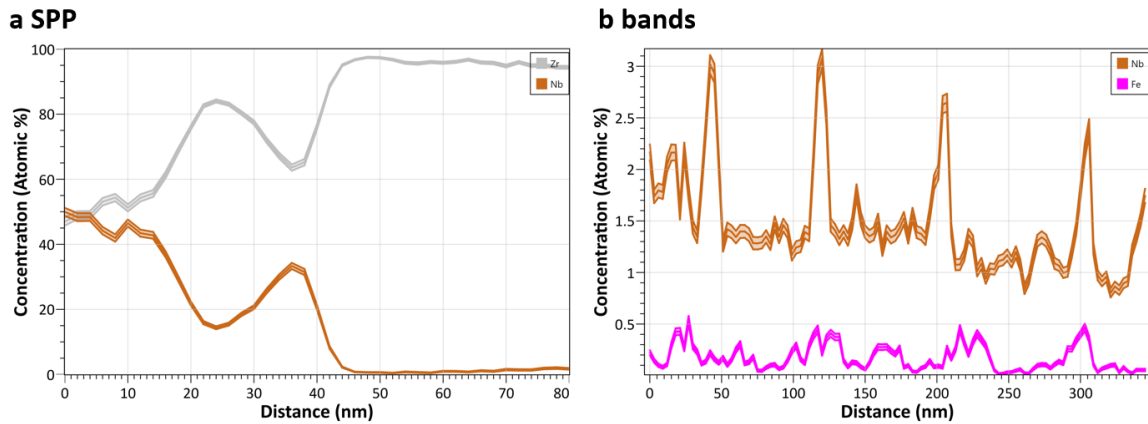


Figure 5-14. Chemical profile of the SPP (binning with 2 nm) and bulk solute bands (binning with 3 nm) measured along red and yellow arrows in **Figure 5-13**, respectively.

5.2.3 Composition analysis

Bulk

The boxed regions in **Figure 5-11(a)** and **Figure 5-13** are selected for compositional analysis on X2 datasets, and there are 0.33% Nb, 0.05% Fe and 0.04% Al in the 8 dpa bulk, and 0.38% Nb, 0.08% Fe and 0.04% Al in the 32 dpa bulk, **Table 5-3**. Therefore, compared with the unirradiated bulk composition, no additional Nb is released from the SPP, so the decrease in Nb content observed in SPPs must be achieved by the intermixing of Zr, and the formation of Nb clusters in the Zr matrix is from the solid solution Nb. The significant increase in the Fe and Al contents in the bulk indicates that they are substantially released from segregation sinks in the unirradiated state. This explains why no Fe-containing SPPs can be observed in STEM-EDS after even early-stage irradiation, and that it is difficult to distinguish the Laves phase and β -Nb SPPs [37, 151, 232].

Table 5-3. Bulk composition of solutes in X2 alloy before and after neutron irradiation (at%)			
Dose /dpa	0	8	32
Nb	0.41 $\pm$ 0.02	0.34 $\pm$ 0.01	0.38 $\pm$ 0.01
Fe	0.005	0.05	0.08
Al	0.004	0.04	0.04

Clusters

A similar isosurface method for clusters in irradiated W13 alloy as described in **Section 3.4.4** was used to define clusters in the 8 and 32 dpa X2 alloy, **Figure 5-15**. The same $c_{iso}=6\%$ and $v_{iso}=50 \text{ nm}^3$ thresholds were used to define Nb clusters. Due to the much lower Fe content, Fe clusters are considered smaller and less enriched, therefore lower thresholds, $c_{iso}=1.5\%$ and $v_{iso}=50 \text{ nm}^3$ are applied to define Fe clusters. It is clear that both Nb and Fe clusters are relatively randomly distributed in the 8 dpa dataset, but they are clearly aligned on the basal plane in the 32 dpa dataset as well as being considerably larger. It is difficult to imagine that existing clusters move during further irradiation, so the less banded clusters at 8 dpa can be explained as there are not enough of them to provide the visualisation of banding at 8 dpa, whereas at 32 dpa, after the formation of enough clusters, the banding becomes much more obvious. It can also be observed that at 32 dpa each solute band consists of many equiaxed small clusters on the basal plane instead of planar segregation or banding. This analysis also shows that the background signals from ZrOH species as shown in **Figure 5-12(c)** can be effectively filtered out using the composition and volume threshold when defining Fe clusters.

Proxigrams of these clusters are shown in **Figure 5-16**, where Nb clusters plateau at 30% Nb and 40% Nb at 8 and 32 dpa, respectively, while at both 8 and 32 dpa the Fe clusters plateau at $\sim 6\%$ Fe. The algorithm for the proxigram stops the calculation at halfway from

the cluster interface (i.e. approximately at the cluster centre), and thus the right end of the horizontal axis can be used to estimate the cluster radius. Nb clusters grow from 3 nm to 4.2 nm and Fe cluster grow from 2 to 2.5 nm, consistent with the growing size observed in **Figure 5-15**. The composition of Nb, Cr and Al is also shown in the 32 dpa Fe proxigram, **Figure 5-16(d)**. It is clear that Nb content does not increase within Fe clusters, and Al and Cr increase from trace level to ~0.2%. This indicates that Al and Cr are co-clustering with Fe in the bulk, and although Fe and Nb are enriched at similar banding positions, **Figure 5-14(b)**, they form separate clusters.

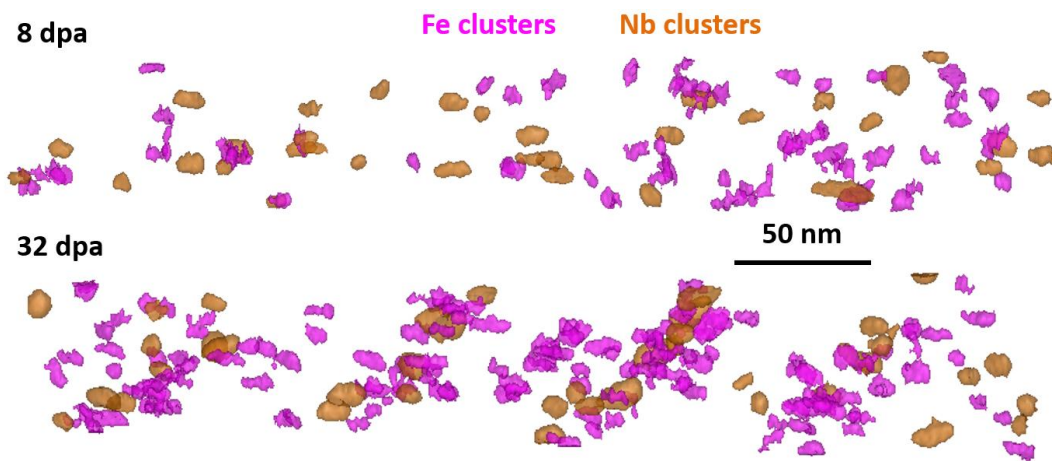


Figure 5-15. Nb and Fe clusters identified in 8 and 32 dpa datasets using isosurfaces with $c_{\text{iso}}=6\%$, $v_{\text{iso}}=100 \text{ nm}^3$ and $c_{\text{iso}}=1.5\%$, $v_{\text{iso}}=50 \text{ nm}^3$, respectively.

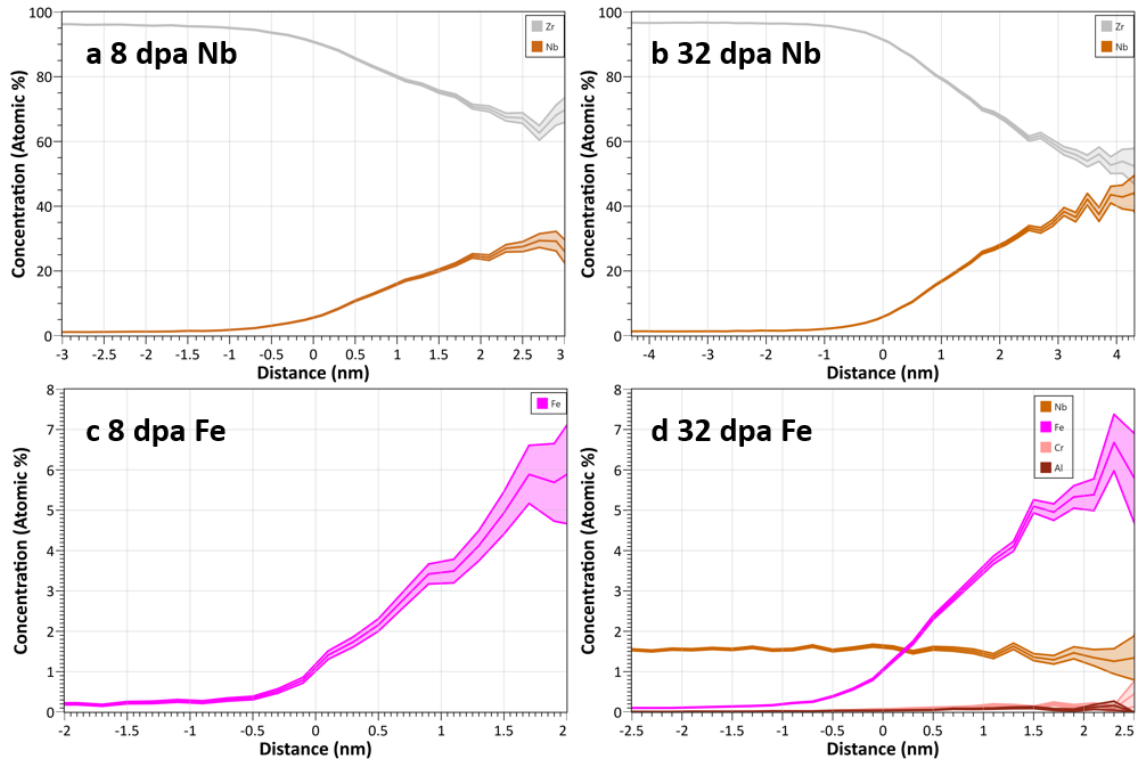


Figure 5-16. Proxigrams of Nb and Fe clusters identified in 8 and 32 dpa X2 alloys, showing the averaged cluster composition change from matrix to the core.

5.2.4 X2 alloy summary

Fe, together with other trace impurities, are released from sinks during irradiation to segregate as clusters and bands. Nb is not released from the Nb-rich SPPs and Nb in the solid solution is depleted to form Nb clusters. The Nb and Fe clusters grow larger and become more aligned on the basal plane from 8 to 32 dpa. Fe and Nb form banding segregation at similar positions, with the interval of ~80 nm and many small Fe and Nb clusters constitute one band, but the Fe and Nb clearly cluster separately. Al and Cr are also enriched within Fe clusters. At higher damage levels, ^{94}Nb and ^{95}Mo , the transmutation product of ^{93}Nb , are detected and have the same distribution with Nb.

5.3 Irradiated ZIRLO alloy

Finally in this chapter on the irradiated metal matrix, the microchemistry of SRA ZIRLO samples irradiated for ~8 dpa (1 cycle), 16 dpa (2 cycles), 24 dpa (3 cycles) and 32 dpa (4 cycles) in the Vogtle reactor are studied with APT.

5.3.1 8 dpa

A typical APT dataset from the 8 dpa irradiated-only ZIRLO alloy is shown in **Figure 5-17**. Small Fe clusters are observed in the bulk. Nb clusters are observed to be more stripy, and Sn shows a heterogeneous distribution in the bulk. Sn, Nb, Fe and Al all clearly segregate at a metal GB after irradiation, as shown in the composition profile in **Figure 5-17(b)**. Sn does not evidently segregate at metal GBs in the unirradiated state, as the addition of Sn is fully soluble in α -Zr. The strong Sn segregation at GBs after irradiation could be due to the accelerated Sn diffusivity in the irradiated bulk in relative with the very slow Sn diffusion in unirradiated matrix, which makes the knocked-out Sn to diffuse to and get trapped at GBs.

5.3.2 16 dpa

A typical APT dataset from the 16 dpa irradiated-only ZIRLO alloy is shown in **Figure 5-18**. Some Nb clusters are observed randomly distributed in the bulk. Despite the segregation to two crystal poles in the Sn distribution map, Sn banding segregation in the bulk can be observed, possibly on the basal plane, but the detector hit map for most ZIRLO alloy datasets is not clear enough to determine the $\langle 0001 \rangle$ direction. Fe clusters are observed also slightly aligned on the same plane directions as Sn.

5.3.3 24 dpa

A typical APT dataset from the 24 dpa irradiated-only ZIRLO alloy is shown in **Figure 5-19**. Nb, Sn, Fe and Al all clearly segregate to a GB. Sn forms complex networks within the bulk.

Fe form clusters randomly in the bulk. Nb and Al form clusters in the bulk and these clusters align on parallel bands. These Nb and Al bands are similar with those seen in irradiated W13 and X2 alloys, however it is difficult to determine if these are solute banding segregation on the basal plane, because these bands are less ordered and Fe is not banding at similar regions.

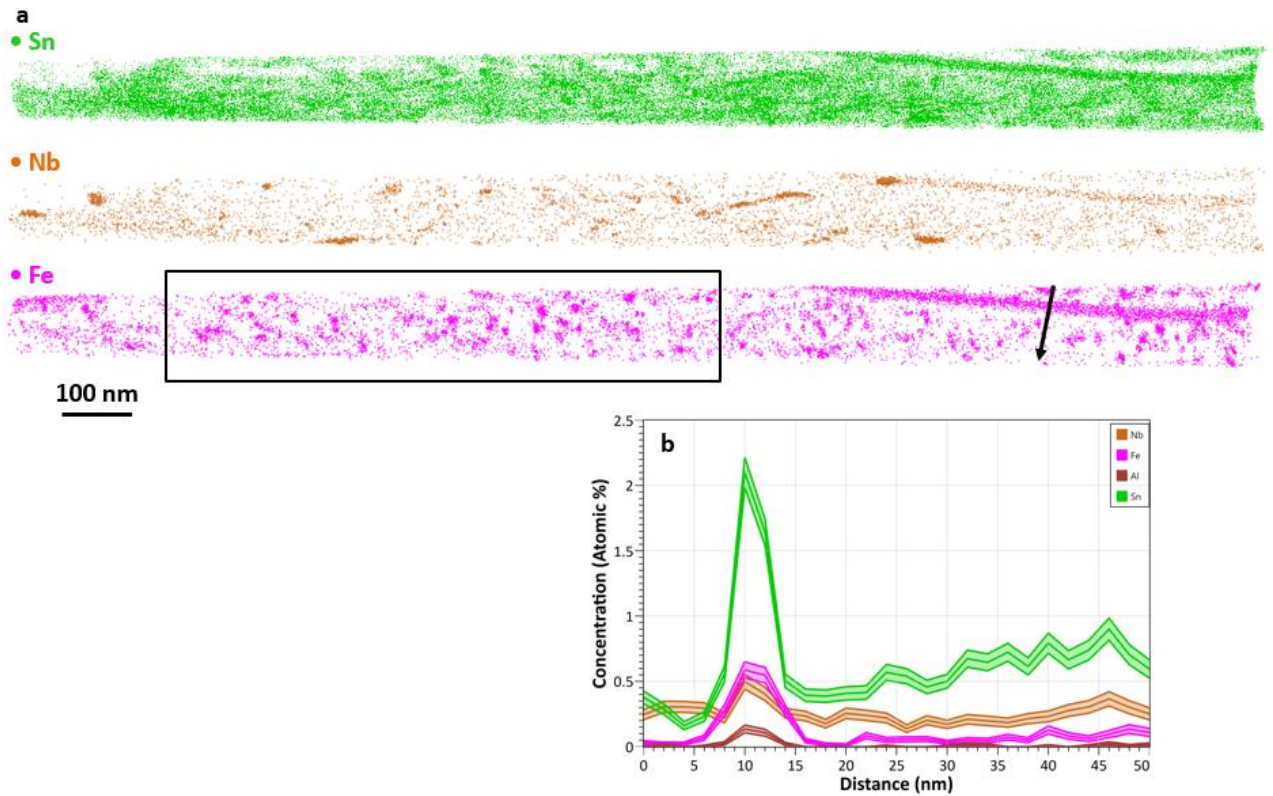


Figure 5-17. (a) Spatial distribution of Sn, Nb ($^{93}\text{Nb}_2^{3+}$) and Fe in a 10-nm slice from APT dataset ‘PZ14_M20_1cZA’ from 8 dpa irradiated-only ZIRLO. (b) Composition profile across GB along the black arrow in (a). The boxed region is selected for bulk composition analysis.

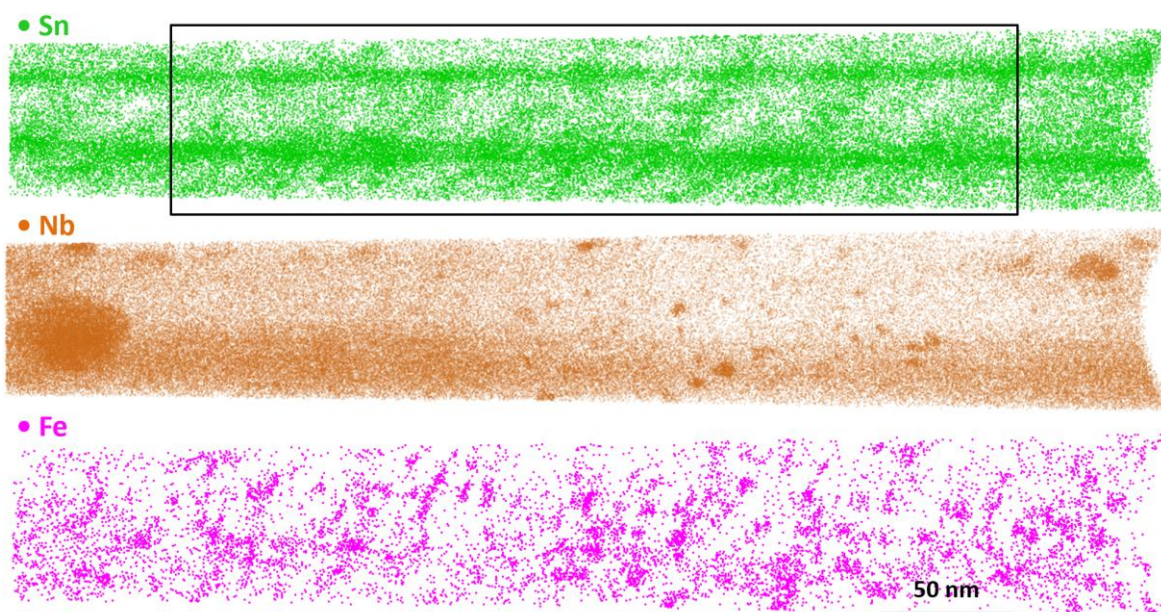


Figure 5-18. 20-nm slice of APT dataset ‘PZ13_M12_2cZA’ from 16 dpa irradiated-only ZIRLO alloy. The boxed region is selected for bulk composition analysis.

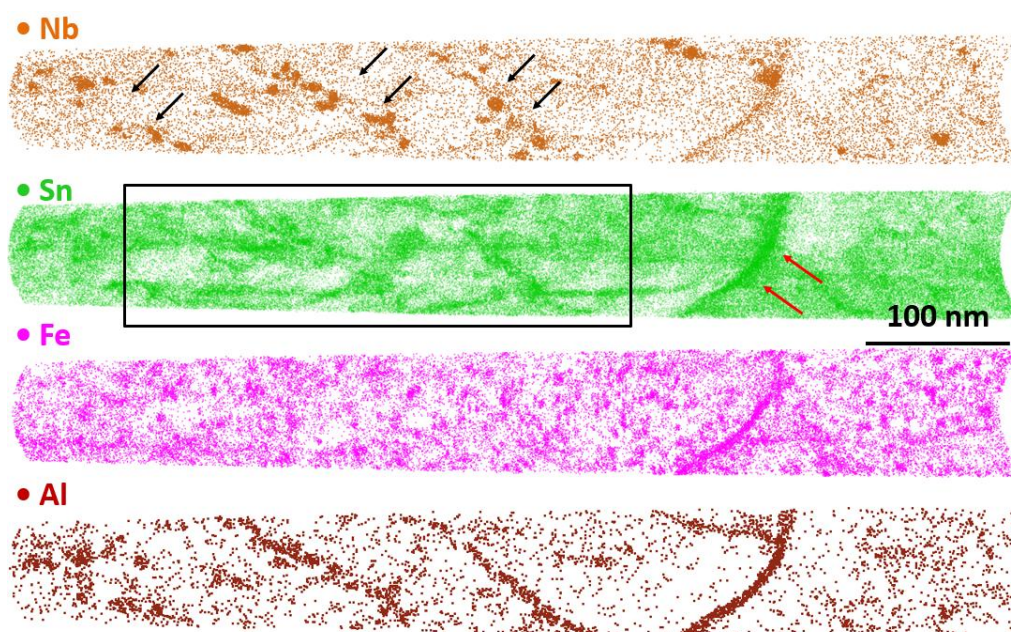


Figure 5-19. 20-nm slice of APT dataset ‘PZ10_M14_3cZR’ from 24 dpa irradiated-only ZIRLO alloy. GBs and cluster bands are indicated by red and black arrows, respectively. The boxed region is selected for bulk composition analysis. (This APT tip was made from the radial cross section Vogtle bulk samples aiming at the O/M interface but ended up in the underlying metal below the O/M interface. These regions of metal seem to have little effect from oxidation, and are used for analysis of the effect of irradiation on the metal matrix.)

5.3.4 32 dpa

The solute distribution in 32 dpa irradiated-only ZIRLO sample is shown in **Figure 5-20**.

Many small Fe clusters are observed randomly distributed in the bulk. Sn and Al form

complex interconnected networks, and similar Sn networks have been previously reported in SRA low-tin ZIRLO alloy irradiated in the BOR-60 reactor by Jenkins et al [49]. Nb segregates on some part of the networks and also forms clusters on the networks. The Nb clusters are evidently larger than Fe clusters. Sn, Fe and Al are all enriched at the interface of the Nb-rich SPP, and the composition profile across the SPP shows that it contains ~35% Nb and 65% Zr after 32 dpa irradiation, similar to the β -Nb composition in 33.5 dpa W13.

The nature of these Sn networks is not very obvious from these results. Another two datasets acquired from the same APT tip were put together to investigate the network structure, **Figure 5-21**. It is clear that Nb and Sn are segregating on parallel planes, with ~50 nm separation, similar to the solute banding seen in the irradiated X2 and W13 alloys. However, these bands are less ordered and not always straight, and Nb is observed to be segregated to what looks like planar features instead of forming clusters within the bands. Considering that this ZIRLO alloy is not fully recrystallised, and has a columnar grain structure with grain width sometimes even less than 100 nm, **Figure 4-17**, it is also possible that these features are solute segregation to columnar GBs. If this is the case, the GBs play a key role during the redistribution of solutes in ZIRLO alloy, where Sn is significantly enriched to GBs, and Nb forms elongated clusters mainly on these same GBs. The interconnected networks could also be related to residual strains and dislocations induced during the cold work process.

It is difficult to determine which of these is more likely (solute bands, GBs or dislocation networks) because APT analysis cannot analyse a large enough volume to show the real microstructure whereas TEM may not have the chemical sensitivity to image these enriched planes. However, the one insight we can at least extract from this is that the redistribution of solutes during irradiation and thus the final microchemistry, depends strongly on the starting microstructure of the alloy. This different solute redistribution mechanism in SRA ZIRLO

to that seen in the RXA W13 and RXA X2 alloys possibly explains the much worse structural stability of SRA ZIRLO during irradiation compared to the RXA alloys, **Figure 5-1**.

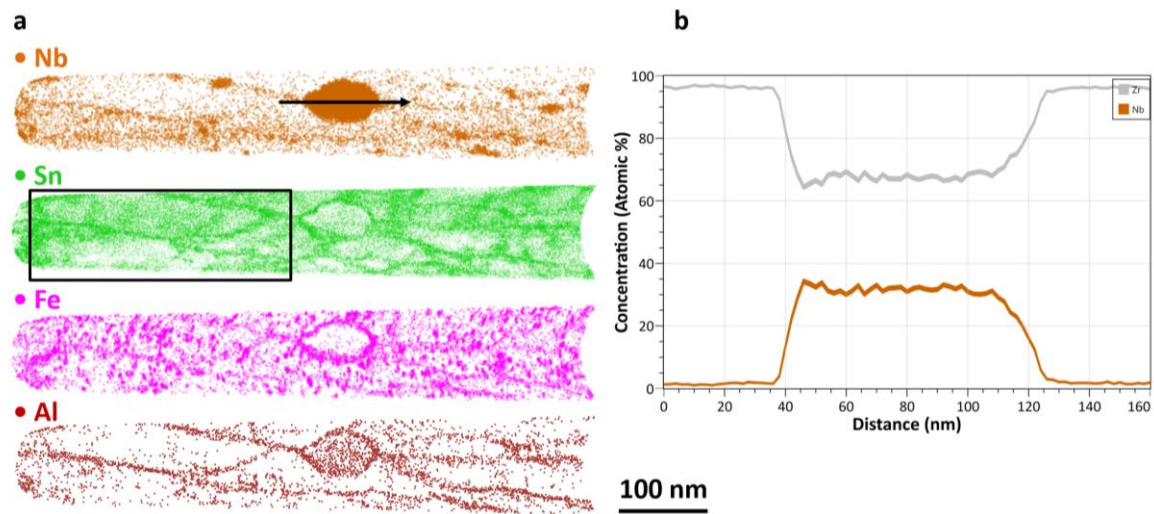


Figure 5-20. 10-nm slice of APT dataset ‘PZ15_M19_4cZA’ from 32 dpa irradiated-only ZIRLO alloy. (b) Composition profile across SPP along the arrow. The boxed region is selected for bulk composition analysis.

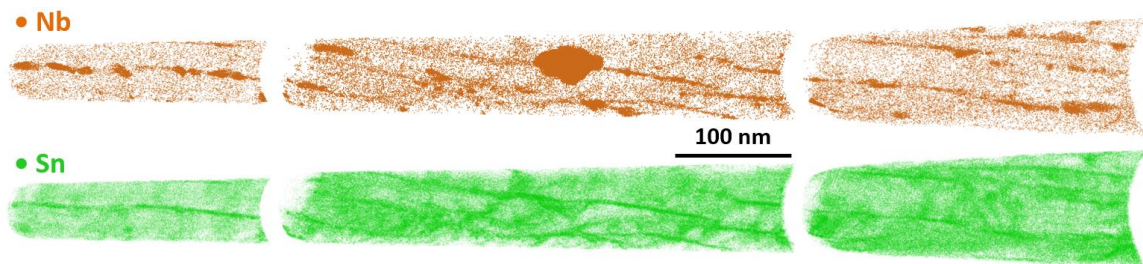


Figure 5-21. 30-nm slice of APT dataset ‘PZ15_M19_4cZA’ from 32 dpa irradiated only ZIRLO alloy.

5.3.5 Composition analysis

The bulk composition of unirradiated samples and irradiated samples at four doses is analysed in the boxed regions in the above APT datasets. Despite the distinctive solute distribution after irradiation compared to X2 and W13 alloys, the bulk composition shows a similar trend, where the composition of Nb and Sn remains the same, and much more Fe and Al are released from sinks to the bulk.

Fe and Nb clusters after these four doses are defined using the same isosurface method as that used for irradiated X2 samples, **Figure 5-22**. Fe clusters seem to remain at same sizes but increase in number density, while the Nb clusters grow in size at increasing dose. The

proxigrams of these cluster are presented in **Figure 5-23**. Indeed, the composition and size do not change much in the Fe clusters, with the Fe content at the cluster core only increasing from 4% to ~5% from 8 to 16 dpa, with ~1.5 nm radius after 32 dpa. The Nb clusters plateau at 25% concentration at 8 dpa and saturates at 40% after 24 dpa, with the radius growing from 2.5 to 4.5 nm. Both Fe and Nb clusters saturate at similar values of ~5% and 40% in the X2 and ZIRLO alloys after 32 dpa irradiation, and thus these values are likely to be the metastable saturation point of Fe and Nb clusters under severe irradiation, respectively.

Table 5-4. Bulk composition of solutes in ZIRLO alloy before and after neutron irradiation (at%)					
	0	8	16	24	32
Nb	0.42±0.01	0.34±0.02	0.36±0.01	0.42±0.01	0.36±0.01
Sn	0.73	0.78±0.01	0.80±0.02	0.72	0.75
Fe	0.008	0.06	0.06	0.08	0.07
Al	0.004	0.03	0.02	0.02	0.05

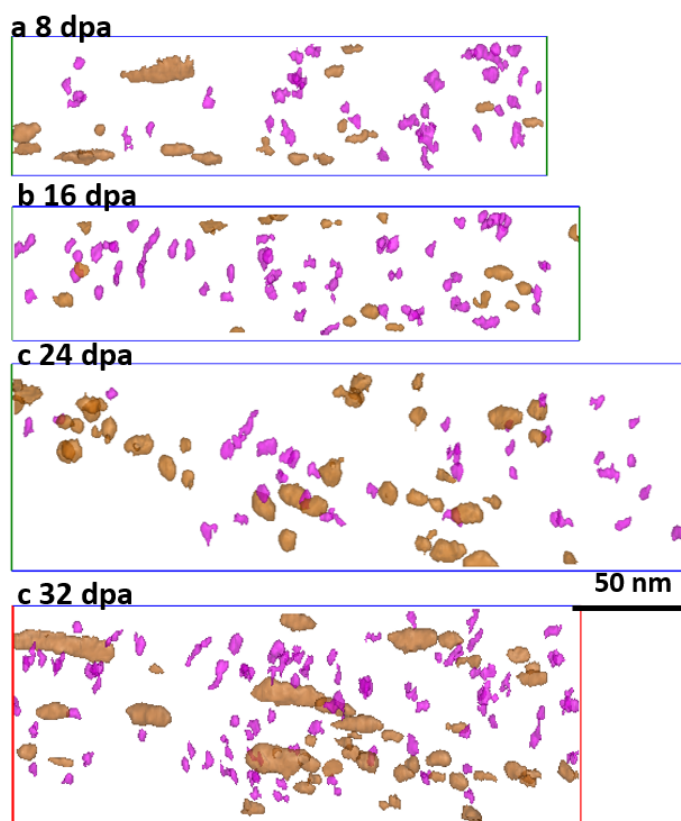


Figure 5-22. Nb and Fe clusters identified in the boxed region of **Figure 5-17**, (a) 8 dpa, (b) 16 dpa, (c) 24 dpa, and (d) 32 dpa. Fe isosurface thresholds: $c_{iso}=1.5\%$ and $v_{iso}=50 \text{ nm}^3$. Nb isosurface thresholds: $c_{iso}=6\%$ and $v_{iso}=50 \text{ nm}^3$.

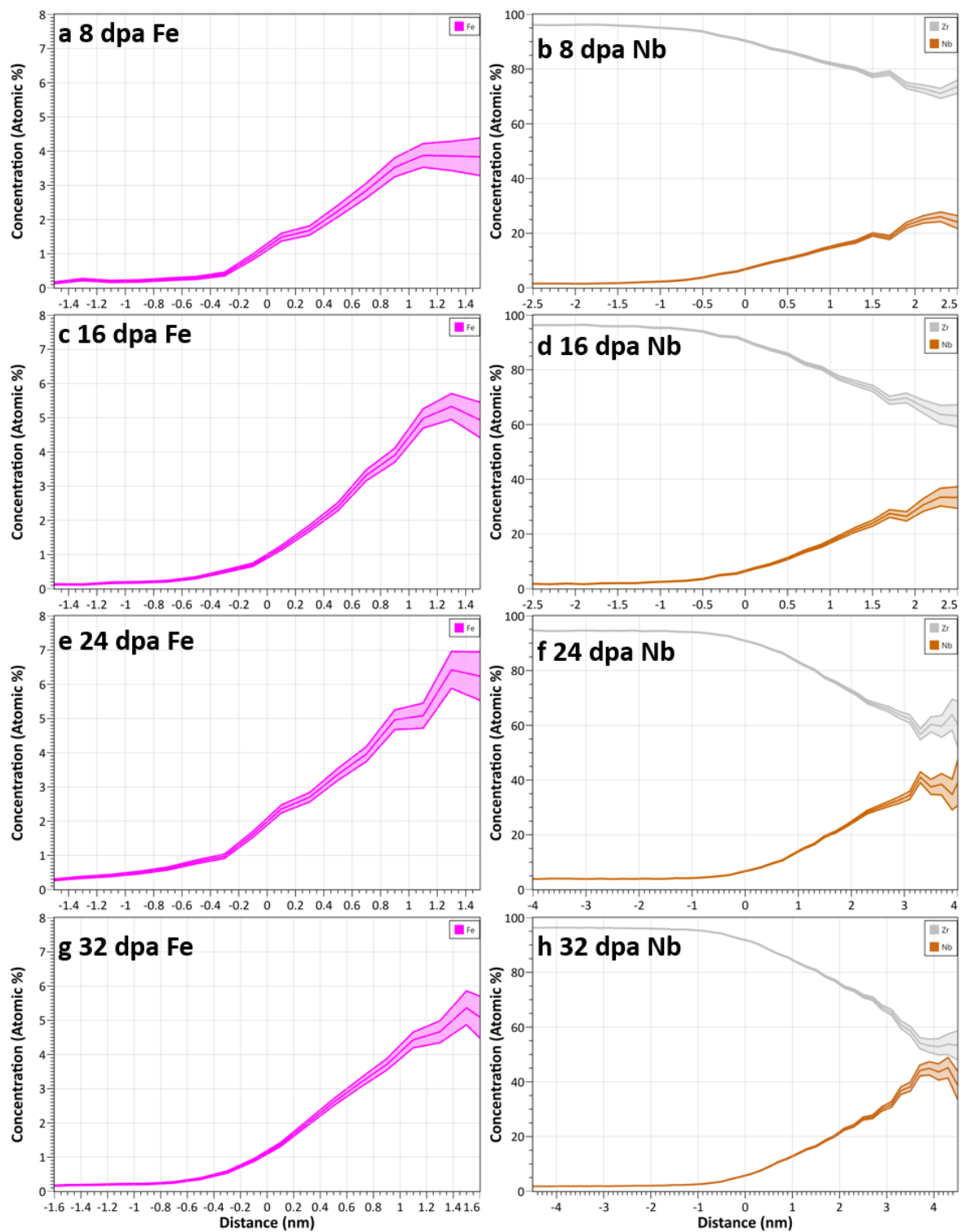


Figure 5-23. Proxigrams of Nb and Fe clusters identified in **Figure 5-22**. (a) 8 dpa Fe clusters, (b) 8 dpa Nb clusters, (c) 16 dpa Fe clusters, (d) 16 dpa Nb clusters, (e) 24 dpa Fe clusters, (f) 24 dpa Fe clusters, (g) 32 dpa Fe clusters, and (h) 32 dpa Nb clusters.

5.3.6 ZIRLO alloy summary

In this alloy, the bulk compositions of Nb and Sn remain the same after irradiation, and that of Fe and Al increase significantly due to release from sinks. Solute segregation at GBs and SPP interfaces can still be observed after irradiation, and Sn more strongly segregates at GBs after irradiation. Fe clusters saturate at 5% with 1.5 nm radius, Nb clusters with less ordered shape saturate at 40% and grow from radius of 2.5 to 4.5 from 8 to 32 dpa. β -Nb SPP after 32 dpa irradiation also has a 35% Nb composition, similar with that in 33.5 dpa W13 alloy. The other solute distributions are rather complicated, with Sn and Al forming complex network structures, possibly due to the non-uniform columnar grain structure and dislocations left by SRA processing, and thus APT analysis on irradiated ZIRLO alloy lacks representativeness. Comparison with the irradiated microstructure of the W13 and X2 alloys, suggest that the way that solute redistributes during irradiation depends strongly on the starting microstructure.

5.4 Discussion and conclusions

The atomic- to μm - scale solute distribution and composition at different neutron irradiation doses have been carefully studied in RXA W13, RXA X2 and SRA ZIRLO alloys. Because of the equilibrium RXA equiaxed grain structure, and well-distributed SPPs, APT datasets from W13 and X2 alloys are very similar at all levels of irradiation, indicating that the neutron irradiation damage is uniformly influencing the equiaxed bulk material, and that the limited volume of material analysed in APT dataset is enough to summarise the solute redistribution behaviours. However, the SRA processing has made the initial microstructure and so the final solute distribution in irradiated ZIRLO rather non-homogeneous, especially the apparent Sn segregation possibly due to the columnar grain structure, and limited dataset volume of APT analysis is not sufficient to be representative of the irradiated microstructures.

But despite the differences in alloy compositions and processing histories, there are some common findings listed below, that should reflect the fundamental thermodynamic behaviour of the solutes in Zr alloys under irradiation. This understanding of as-irradiated microstructure will be applied to interpret the in-pile corroded datasets in **Chapter 7**.

Starting with Sn, this solute is fully soluble in the unirradiated metal matrix, so is randomly distributed and does not obviously segregate to any features. However, it redistributes during irradiation forming banded segregation in the bulk that is out-of-phase with Fe and Nb bands, and also segregate to GBs and SPP interfaces. The out-of-phase banding of Sn and other elements could be because solute atoms in the HCP Zr crystal lattice have anisotropic diffusivities, where interstitial atoms (Fe and Cu) diffuse faster along the c direction [246] while the substitutional atoms (Sn and Nb) diffuse faster along the a direction [247].

Nb, Fe, Cu and other trace impurities have limited solubility in the unirradiated metal matrix, with 0.4% for Nb and tens of ppm for the rest, and so are enriched strongly at sinks like SPPs, GBs and interfaces. Except for Nb, they are released to the bulk metal after irradiation, inducing a significant increase in their bulk concentrations and becoming supersaturated, but their original segregation sites are normally not fully depleted and can still be observed at these locations with the high chemical sensitivity offered by APT analysis. As they diffuse away from the sinks, they are trapped by planar defects, likely $\langle a \rangle$ loop rafts or $\langle c \rangle$ loops, forming banded segregation on the basal plane. Each of these bands is composed of many small clusters. Fe and Cr depletion from Laves SPPs happens at a very early stage of irradiation, with Fe even faster than Cr [248], explaining why STEM-EDS cannot see Laves phase SPP after irradiation. The Fe clusters have a slightly growing radius of 1.5-2 nm and saturate at ~5% Fe.

Nb, on the other hand, is not released from Nb-rich SPPs, and the Nb content decrease, from 90% in β -Nb SPPs or 40% in Laves SPPs both to 35%, is achieved by the intermixing of Zr

atoms and coarsening of the SPPs. The solid solution level of Nb is depleted from 0.4% to <0.2% to form Nb clusters in the bulk, which have 30% Nb in the core at 8 dpa and saturate at 40% at 24 dpa. The radius of these Nb clusters grows from 2.5 nm to 4.5 nm with increasing dose. It is interesting to note that most of the microchemistry changes and formation of clusters have been completed at relatively low doses. This seems related to the observation that the hardness of the W13 alloy increases sharply from 0 to 4 dpa, but remains similar from 4 to 33 dpa, **Figure 5-24**, suggesting the precipitation of solute clusters can be a main strengthening factor.

The dose rate in BOR-60 is four times higher than that in the Vogtle reactor. A higher dose rate generates a higher density of point defects, which can accelerate solute diffusion, but a slower dose rate allows a longer diffusion time. The proxigrams of Nb clusters in the BOR-60 W13 alloy and the Vogtle ZIRLO alloy are compared in **Figure 5-25**. These Nb clusters are identified using the same isosurface parameters, and there is similar level of Nb in the alloys and in the unirradiated matrix, so the cluster size and Nb content in the clusters can be directly compared from these proxigrams. The general trend of the development of Nb clusters is similar in these two alloys, but the rate at which it proceeds is significantly different. In W13 alloy at 4 dpa the clusters have already plateaued at >30% Nb, while there is only ~25% Nb in the Nb clusters in the ZIRLO alloy at 8 dpa. At around 16 dpa, the W13 clusters are already saturated at 40% Nb, whereas the clusters in ZIRLO alloy do not achieve 40% Nb until 24 dpa. Therefore, it is very clear that with higher dose rate, Nb is depleted faster from the matrix to form more highly enriched Nb clusters. And it is also interesting to note that, for all three alloys at 33 dpa, the Nb clusters saturate at ~40% Nb in the core and have a ~4 nm radius. This indicates that the thermodynamic endpoint of Nb clustering after severe irradiation is the same in very different starting alloys, with the dose rate affecting principally the kinetics of this process. It is also interesting to note that the banding spacings

seen in 32 dpa W13, X2 and ZIRLO alloys are 30, 80 and 50 nm, however, it is unclear what is the major determining factor.

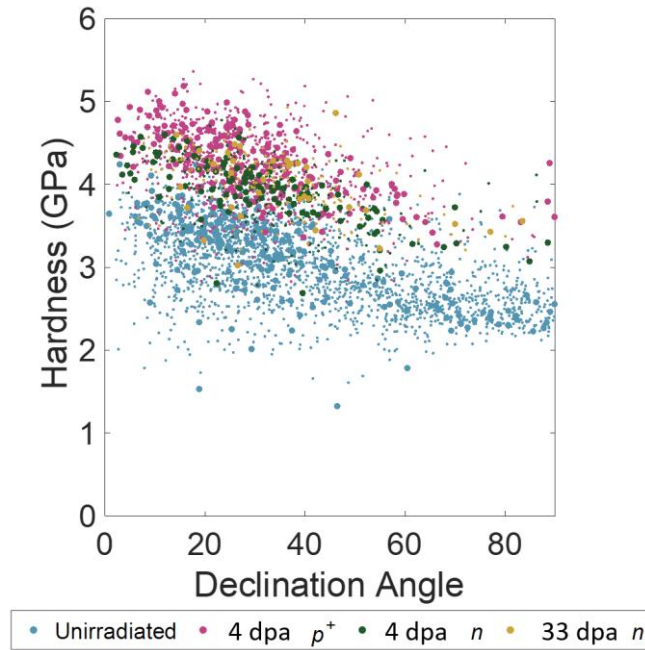


Figure 5-24. Berkovich hardness on W13 alloy in unirradiated, proton 4 dpa, neutron 4 dpa, and neutron 33 dpa, with a variation of declination angles. (Courtesy of Kay Song, University of Oxford)

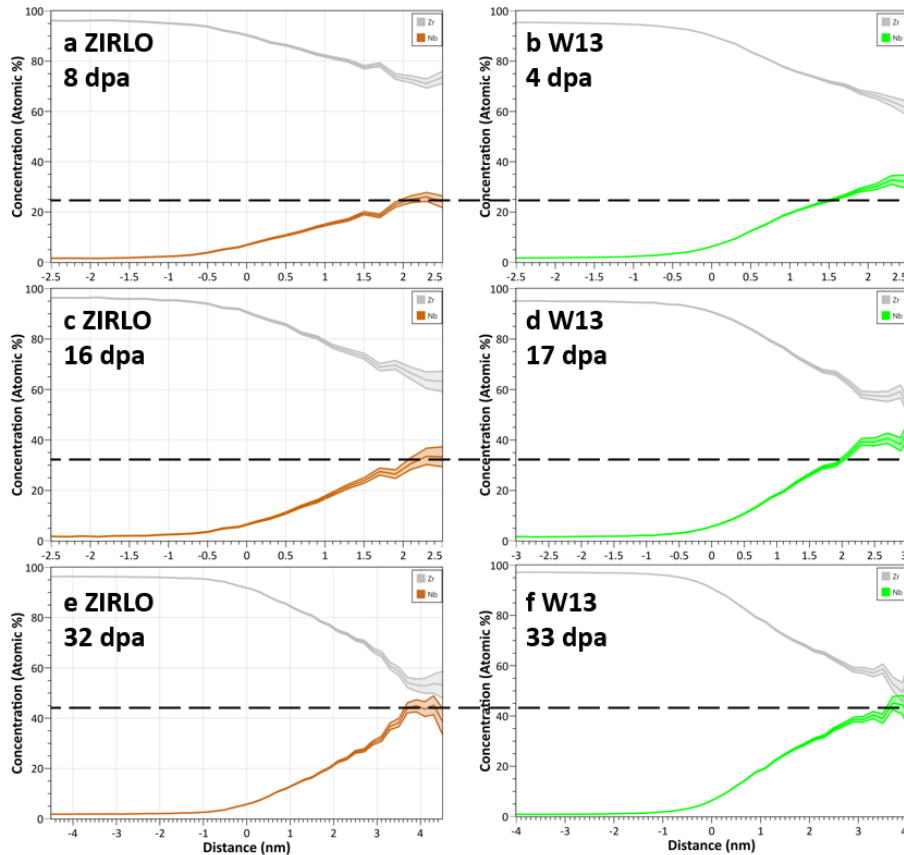


Figure 5-25. Comparison of proxigrams of Nb clusters in irradiated W13 alloy and ZIRLO alloy. (a) ZIRLO alloy at 8 dpa. (b) W13 alloy at 4 dpa. (c) ZIRLO alloy at 16 dpa. (d) W13 alloy at 17 dpa. (e) ZIRLO alloy at 32 dpa. (f) W13 alloy at 33 dpa.

6. Autoclave corrosion of Zr alloys

This chapter studies Zr alloys that have been corroded in the autoclave to simulate PWR water conditions. The aim is to understand the corrosion mechanisms by comparing the characterisation results around the O/M interface using APT, TEM and NanoSIMS with the baseline state in **Chapter 4**. These corrosion results are induced by irradiation-free corrosion, providing control corrosion data for the in-pile corroded samples subjected to in-situ irradiation and corrosion.

This chapter includes corrosion in natural water, **Section 6.1**, ^{18}O -spiked water, **Section 6.2**, and D-spiked water, **Section 6.3**. The addition of ^{18}O and D in the spiked water are designed to help study the in-diffusion processes involved in the transport of O and H during corrosion.

6.1 H_2O water corrosion

The O/M interface

Figure 6-1 shows an APT dataset around the O/M interface from an autoclave-corroded ZIRLO alloy with an oxide thickness of $\sim 0.7\ \mu\text{m}$. **Figure 6-1(b)** shows the characteristic Zr-O ratio change at the O/M interface as previously reported by Dong et al [14] and Ni et al [249, 250], and reviewed in **Section 2.3.5**. Specifically, as defined in **Table 6-1**, the full range of the characteristic Zr-O stoichiometry at the O/M interface between the ZrO_2 oxide and $\alpha\text{-Zr}$ metal substrate is clearly observed over a range of $\sim 100\text{-nm}$ -thick material, as identified by dashed lines A to D. The O/M interface contains several regions with different O contents and different crystal structures, including ZrO_2 oxide with $>60\%$ O, ZrO suboxide with 50% O, O-saturated $\alpha\text{-Zr}$ with $\sim 30\%$ O, O-enriched $\alpha\text{-Zr}$ with $<30\%$ O, and the underlying $\alpha\text{-Zr}$ metal matrix with a low level of O (around the equilibrium solubility of

O in α -Zr). The ~30% O solubility limit in HCP α -Zr and equilibrium oxide phase of ZrO_2 aligns with the Zr-O phase diagram in **Figure 6-2**. This region is significant in defining the corrosion performance, because both solute redistribution [34] and the phase transformations to create the ZrO suboxide and new ZrO_2 grains happen in this region [235]. This Zr-O profile will be compared with that measured from an in-pile corroded sample, **Figure 7-2**.

The detected ion type depends on both of the tip composition and the electric field. Looking at the ion map across the interface, **Figure 6-1(c)**, it is a universal observation for all the oxide datasets that, regardless of the running condition or dataset size, O_2^+ , ZrO_2^{2+} and ZrO_3^{2+} ions are only detected in the ZrO_2 region, ZrO molecular ions account for ~65% of the overall ion counts in the ZrO_2 region and become the strongest signal (up to 90%) at the O/M interface. Then Zr^{2+} ions gradually dominate when the analysis passes into the Zr(O) and underlying α -Zr regions. The difference in the detection of ions is the result of a combination of composition, field, and chemical bonding. Although it is difficult to use the ratio of these ion types to approximate the evaporation field, the distribution of O_2^+ , ZrO^{2+} , and Zr^{2+} signals can help to estimate the position of the O/M interface (normally the transition between O_2^+ and Zr^{2+} signals), and, if the dataset does not contain the whole O/M interface, how far a particular region is away from the O/M interface.

Table 6-1. Oxygen contents at the O/M interface from Figure 6-1 [81].					
Region	O content	Type	Phase	Oxidation Extent	Position
ZrO_2	>60%	Oxide	m/t*	Fully	Above A
ZrO suboxide	~50%	Interface	h	Partially	A-B
O-saturated α-Zr	~30%	Interface	h	Partially	B-C
O-enriched α-Zr	<30%	Interface	h	Partially	C-D
α-Zr matrix	<1%	Metal	h	None	Below D

*m = monoclinic ZrO_2 , t = tetragonal ZrO_2 , h = hexagonal α -Zr and ZrO.

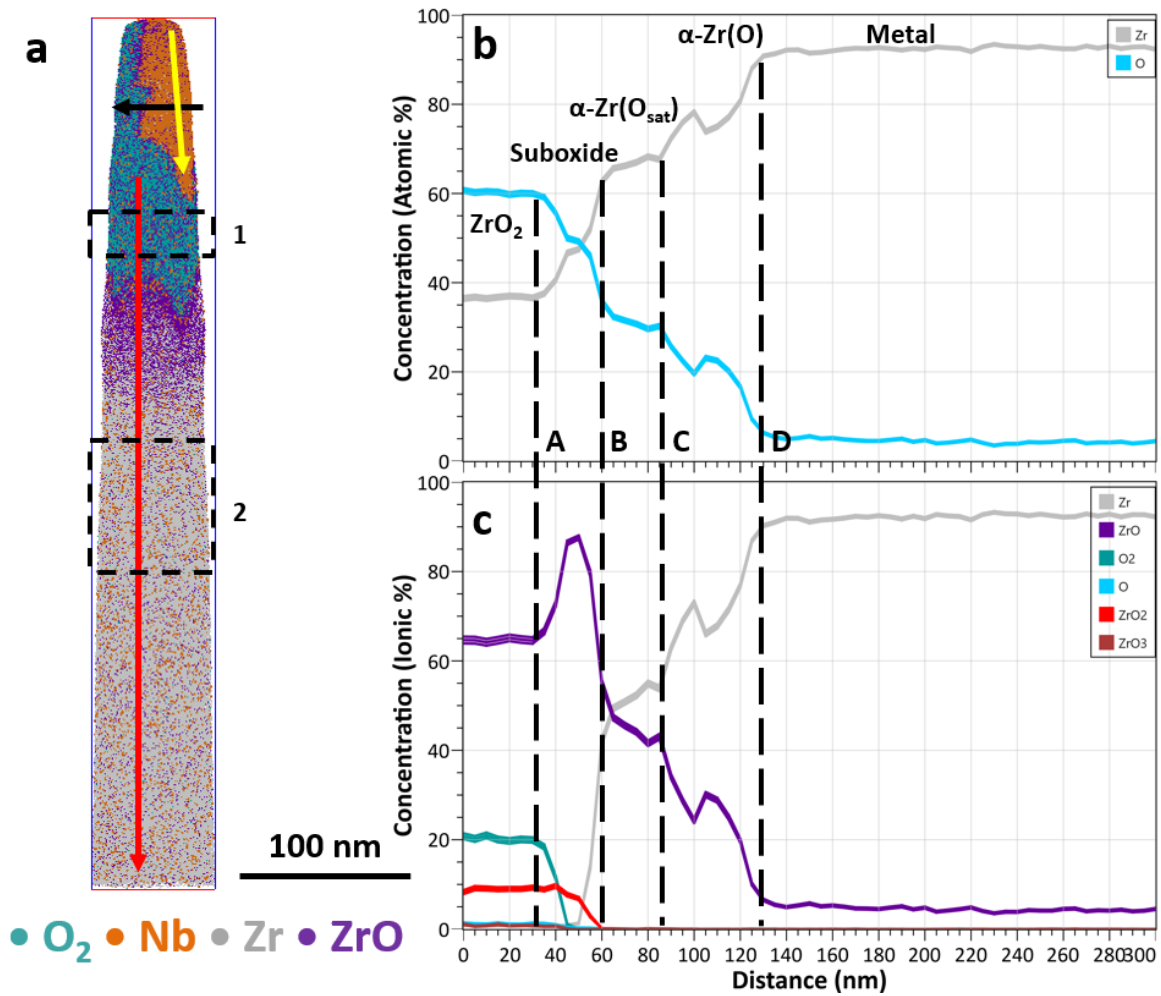


Figure 6-1. APT dataset ‘MCR3_M12’ from the O/M interface of 77-day autoclaved ZIRLO alloy. (a) ion map of O₂, Nb, Zr and ZrO. (b) Composition profile of Zr and O along the red arrow in (a). (c) Ion profile along red arrow in (a), with 2 nm bin size.

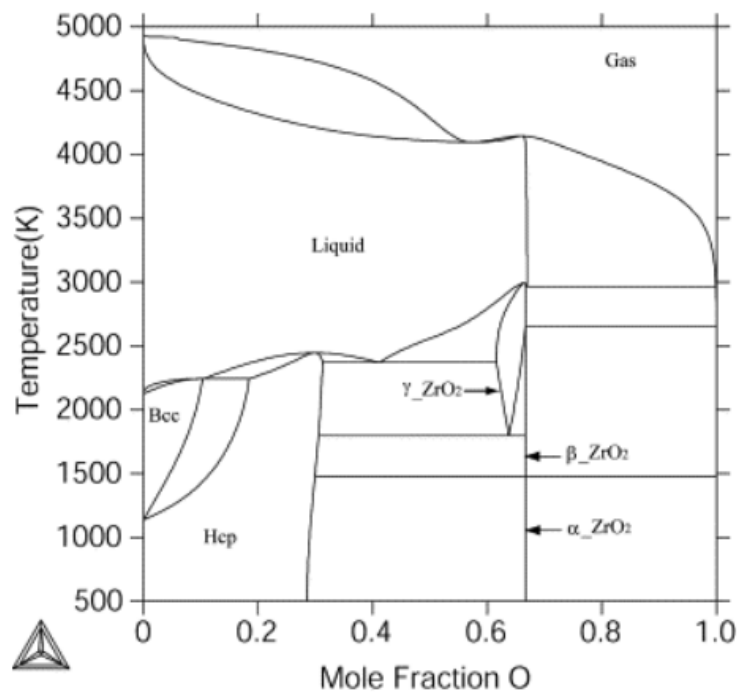


Figure 6-2. Zr-O phase diagram [251].

Solute redistribution at the O/M interface is important in understanding how the microchemistry changes during oxidation. Due to the significant composition changes as the analysis passes from oxidised to metallic regions, it is reasonable to compare values of the solute/Zr ratio instead of the ratio of solute/all atom counts. The $^{56}\text{Fe}^+$ signal detected in the oxide is buried by the $^{96}\text{Zr}^{16}\text{O}^{2+}$ peak, so attempting to measure accurate Fe concentration in the oxide and Fe redistribution at interface is not possible.

The mass spectrum of an oxide region with ~ 1 million ions taken from **Figure 6-1(a)** is shown in **Figure 6-3**. The normal Nb peaks at 31 Da ($^{93}\text{Nb}^{3+}$) and 46.5 Da ($^{93}\text{Nb}^{2+}$) in a metal dataset cannot be observed in the mass spectrum of an oxide dataset, **Figure 6-3(a and b)**, and Nb is detected as NbO_2^{2+} at 62.5 Da and NbO_2^+ at 125 Da, **Figure 6-3 (c and d)**. And we believe most of the Nb atoms in the materials have been taken into account by this ranging strategy.

Sn is mostly detected only as $2+$ state, as shown in **Figure 6-3(c)**. $^{122}\text{Sn}^{2+}$ and $^{124}\text{Sn}^{2+}$ are overlapped with $^{90}\text{Zr}^{16}\text{O}_2^{2+}$ and $^{91}\text{Zr}^{16}\text{O}_2^{2+}$ at 61 Da and 62 Da, respectively. These two Sn isotopes account for 10.42%, therefore the actual Sn content can be calculated from other Sn peaks that do not have overlaps and their abundant ratios.

The Nb/Zr and Sn/Zr ratios measured from the oxide (box 1) and metal regions (box 2) in **Figure 6-1** are displayed in **Table 6-2**. The Nb/Zr ratio remains $\sim 0.4\%$ after oxidation, while the Sn/Zr ratio significantly decreases from 0.8% to 0.4%. This indicates that as the O/M interface grow deeper into the metal substrate, Sn is continuously pushed out from the interface to the underlying metal substrate, possibly due to a decreased Sn solubility in ZrO_2 , while in-solution Nb atoms remain at their starting position after being oxidised. The redistribution of Sn is similar to previous studies [14, 145], however, there is little data in the literature on Nb concentration at the O/M interface to compare with.

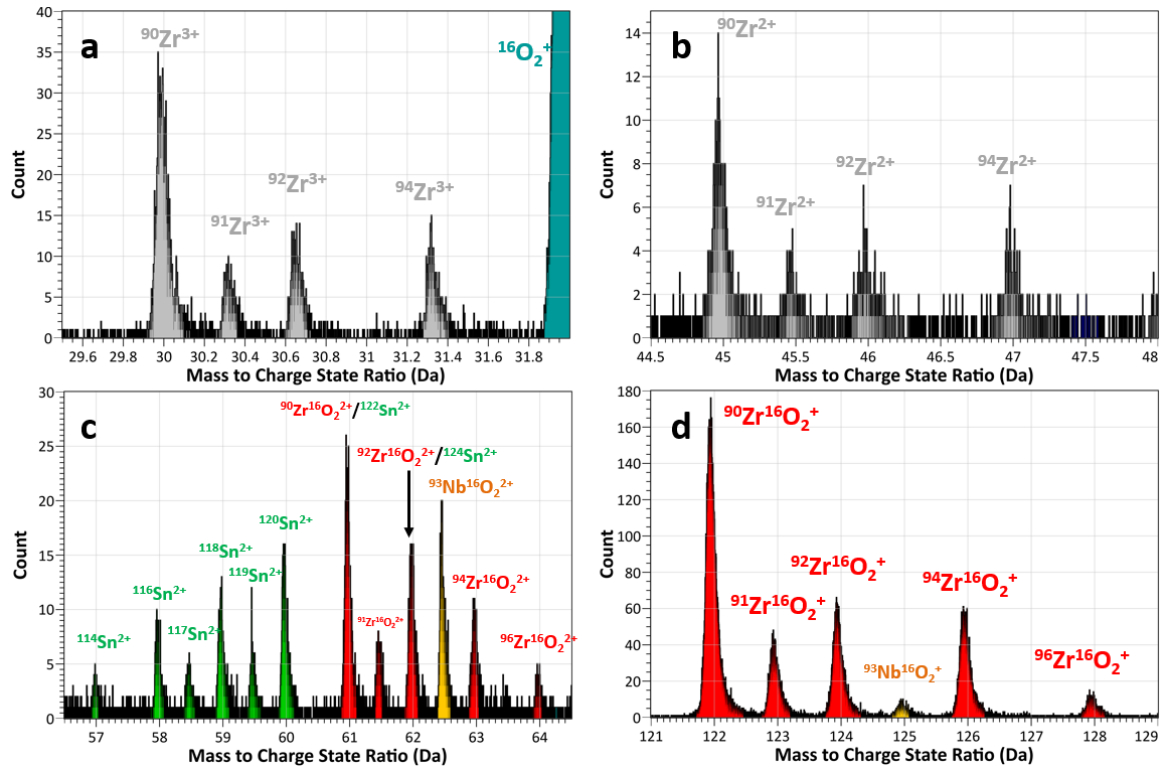


Figure 6-3. Mass spectrum of the box 1 in Figure 6-1(a) in the ranges of (a) 29.5-32 Da, (b) 44.5-48Da, (c) 60.5-64.5 Da, and (d) 121-129 Da. Note the difference in the y-axis.

Table 6-2. Solute composition measured in **Figure 6-1(a)**.

	Oxide	Metal
Nb/Zr	0.39%	0.41%
Sn/Zr	0.40%	0.80%

SPPs

Figure 6-4(a) shows a chemical profile across the Nb-rich SPP along the black arrow in **Figure 6-1(a)** that has been incorporated 300 nm deep into the growing oxide, and so is expected to be partially oxidised [27]. The SPP contains ~30% Nb, 45% Zr and 30% O. Considering the Nb/Zr ratio in Laves phase SPPs (1:1, **Figure 4-3**) and β -Nb SPPs (9:1, **Figure 4-2**) in the baseline state, this SPP must be a Laves phase SPP that is partially oxidised, while the surrounding Zr matrix has been fully oxidised to ZrO_2 , showing delayed oxidation. Often seen accompanied with this delayed oxidation, cracks may form at the SPP edge that is opposite to the O/M interface due to the greater expansion of the surrounding

matrix during oxidation (the Pilling-Bedworth ratio [67]). However, this cannot be observed in this APT analysis.

Figure 6-4(b) shows composition of this SPP along the corrosion direction (yellow arrow in **Figure 6-1(a)**). Although we might expect to observe the end of the SPP furthest from the O/M interface to be more oxidised and have a higher O concentration because that region has been incorporated into oxide matrix for longer time, Zr, O and Nb concentrations are uniform within the SPP along the corrosion direction. This may indicate that oxidation of Laves phase SPPs beyond 30% O require more oxidation time and can only be observed in SPPs that are incorporated deeper into the oxide.

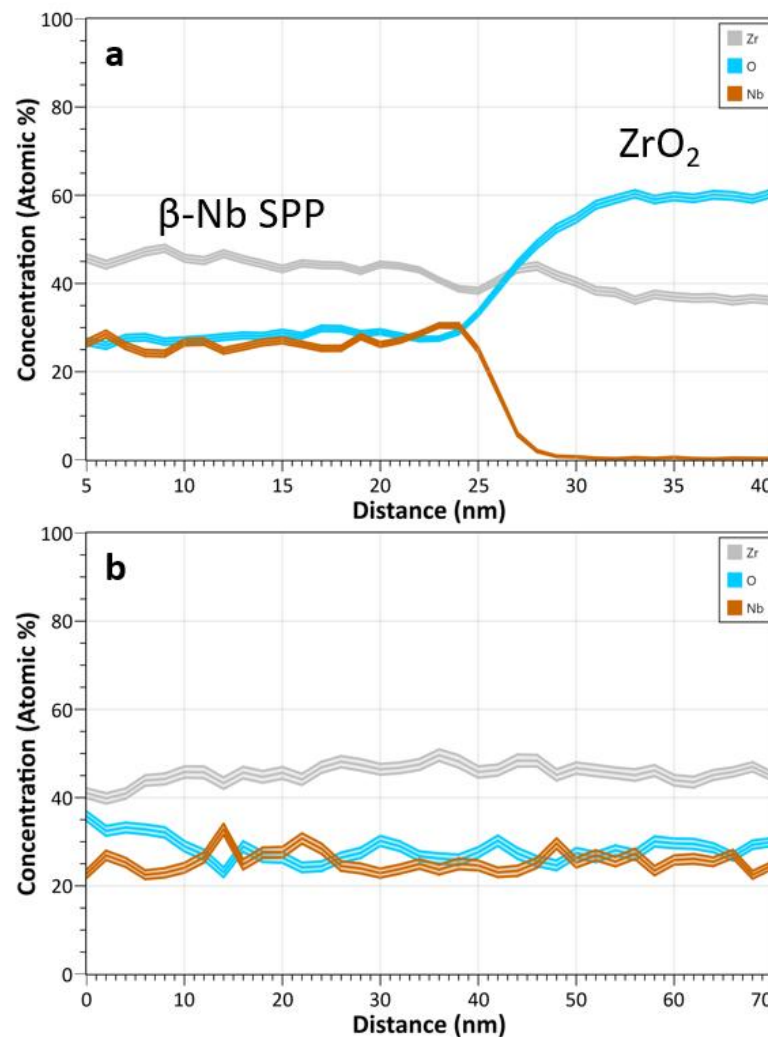


Figure 6-4. Composition profiles of Nb, Zr and O along the (a) black arrow, and (b) yellow arrow in **Figure 6-1(a)**, binning with 2 nm.

Figure 6-5(a and b) show an APT dataset at the O/M interface of a ZIRLO sample with a $\sim 0.8\ \mu\text{m}$ thick oxide. A Nb-rich SPP is located in between the strong O_2 and Zr signals, indicating that the oxide front has just reached this SPP, and oxidation has just started. The composition profile along arrow 1, **Figure 6-5(c)**, shows that the SPP still has more than 80% Nb and thus is a β -Nb SPP, and the matrix underneath has been oxidised to the ZrO composition. The chemical profile along arrow 2, **Figure 6-5(d)**, shows the surrounding matrix has been fully oxidised to ZrO_2 , and at the edge of the β -Nb SPP, the Nb concentration has decreased to $\sim 70\%$ by the incorporation of O to 30%. The β -Nb SPP clearly presents a delayed oxidation behaviour, and the underlying metal is locally protected by the β -Nb SPP, because O cannot directly diffuse across the SPP and needs to bypass it to corrode the underlying metal. This agrees with the previous NanoSIMS results that SPPs block the O in-diffusion process and thus locally delay the corrosion rate [65]. Similar delayed oxidation of SPPs and protection of the underlying metal has been reported by Wang et al [74].

The Nb concentration in the surrounding matrix is not evidently higher, indicating that the decrease of Nb concentration within the SPP is achieved by the intermixing of O and possibly growth of the SPP, similar to that observed in irradiated β -Nb SPPs under irradiation (Section 5.1 and [226]), instead of releasing Nb to the oxide matrix. The expansion of β -Nb SPP during corrosion along the corrosion direction has been reported [37]. This agrees with the Nb/Zr ratio remains the same in metal and in oxide, **Table 6-2**.

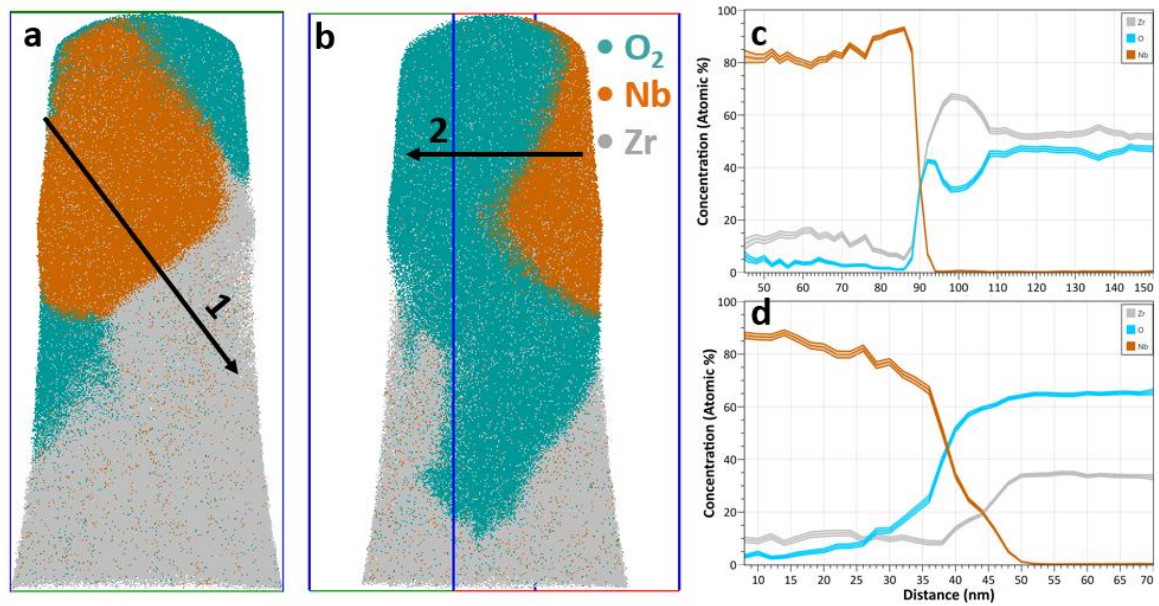


Figure 6-5. APT dataset ‘PZ08_M02’ from the O/M interface of 60-day autoclaved ZIRLO. (a) Ion map of O₂, Nb, Zr. (b) 60° rotation of (a). (c and d) Composition profiles of Nb, Zr and O along the black arrow 1 and 2, respectively, binning with 2 nm.

Grain boundaries

Figure 6-6(a) shows another APT dataset at the O/M interface from a ZIRLO sample, with Fe segregation in the metal substrate in the form of clusters (highlighted by circles). The top view of horizontal slices 1-3 in **Figure 6-6(b-d)** show Fe decoration on linear features that are likely to be dislocations. Although ZIRLO alloy is only stress-relieved annealed, leaving some of remaining dislocations from cold work, this kind of segregation is not seen at such high densities in the baseline ZIRLO alloy (Section 4.4). So the formation of these dislocations may be induced by strain build-up in the metal substrate immediately below the O/M interface.

A GB with Fe decoration is also observed at the left bottom of the dataset, and views from two orthogonal directions are shown in **Figure 6-6(e and f)**. Four dislocations line with Fe decoration at ~15 nm intervals (D) compose this GB. This suggests a pure tilt grain boundary, and the tilt angle (θ) between the two grains can be calculated from

$$\tan\theta = \frac{b}{D},$$

where b is the Burgers vector, and the primary Burgers vector in α -Zr is $1/3\langle 11\text{-}20 \rangle$. So θ is estimated to be $\sim 3^\circ$, indicating a low angle GB (normally GBs with misorientations larger than 15° are defined as high angle GBs [252]). For a high angle tilt GB, the dislocation lines will be very closely spaced and difficult for APT to resolve. The arrangement of dislocation lines in twist GBs or tilt and twist mixed GBs is much more complicated for laser-mode APT (~ 1 nm spatial resolution [196]) to spatially resolve from Fe segregation, which may explain why among all the GBs identified in APT datasets by Fe decoration, very few of them can be observed to contain parallel dislocation lines.

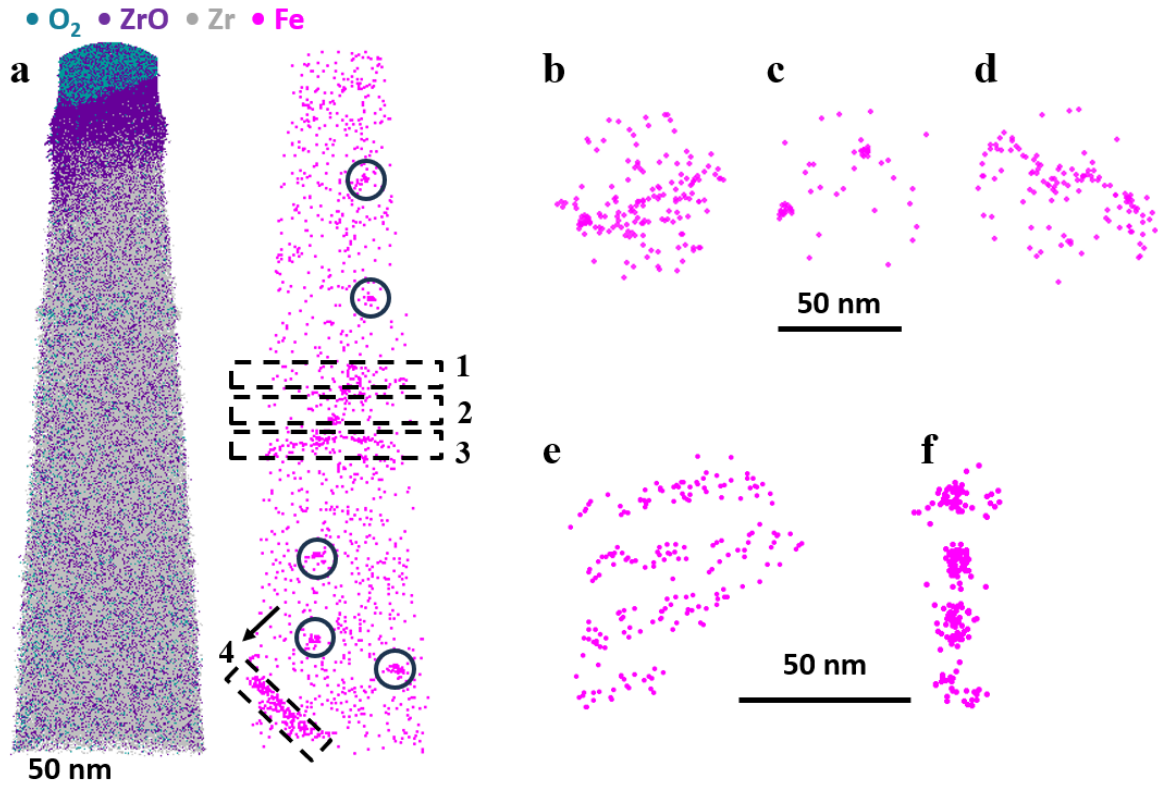


Figure 6-6. APT dataset ‘PZ08_M12’ from the O/M interface of a 30-day autoclaved ZIRLO sample. (a) Ion map of O₂, ZrO, Zr and Fe (⁵⁶Fe²⁺). (b-d) Top view of slices 1-3. (e) Slice 4 viewed from the arrow direction in (a). (f) Side view of (c).

Similarly, Fe shows planar segregation features in the metal below the O/M interface in **Figure 6-7(b)**, that are likely to be GBs. It is interesting to notice that, in the composition profile of Zr, O and Fe in **Figure 6-7(c and d)**, the O concentration, instead of monotonically decreases to trace levels after the Zr(O) region, increases twice to up to $\sim 30\%$, and these O

concentration increases are well correlated with the Fe planar segregations (lines 1 and 2). It is possible that due to the lower evaporation field of GBs compared to the matrix, more O-containing gas from the analysis chamber is adsorbed to the tip and detected. However, it seems unlikely that a ~10% increase in O content could be contributed by this effect, and what is observed here is actual local O enrichment in the metallic matrix on these GBs. Although it cannot be sure whether these are pre-existing metal GBs or newly-formed sub-GBs [141], this correlation between the (sub-)GBs and the localised higher oxygen concentrations indicates that (i) possible preferential diffusion pathways for the O to penetrate into the metal matrix, and (ii) that these GBs might be oxidising faster than the α -Zr.

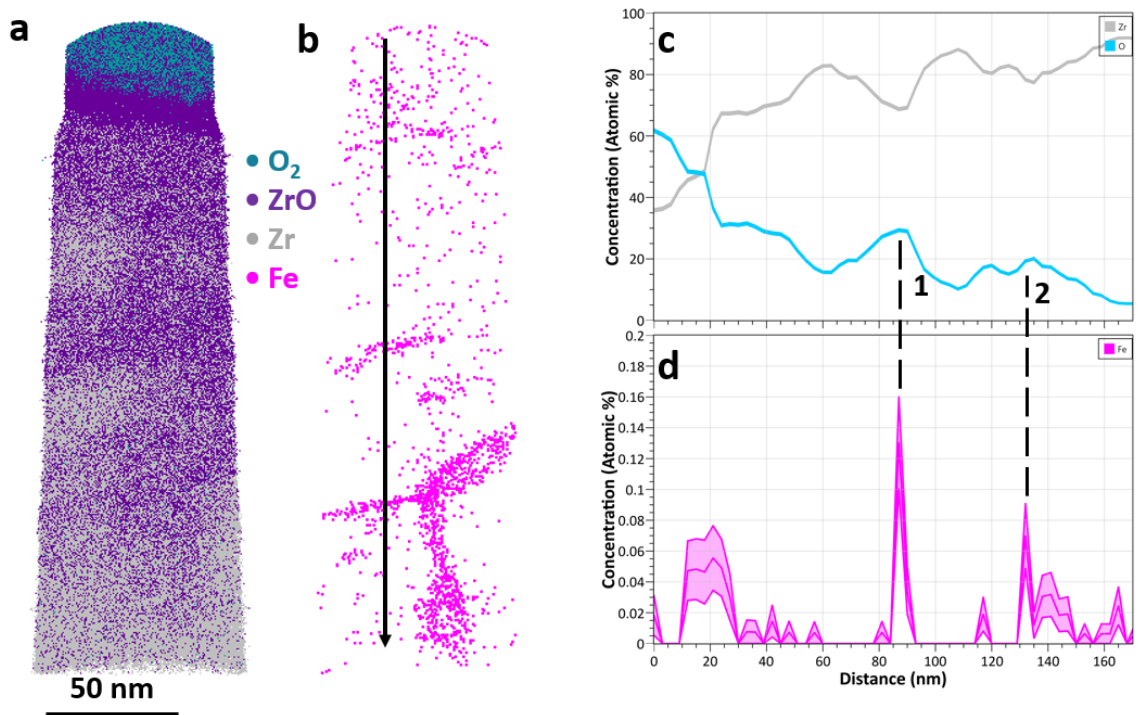


Figure 6-7. APT dataset ‘PZ08_M13_A30Z’ from the O/M interface of a 30-day autoclaved ZIRLO sample. (a and b) Distribution map of O₂, ZrO, Zr, and Fe (⁵⁶Fe²⁺). (c and d) Composition profile of Zr and O, and Fe measured along the arrow in (b).

Planar Fe segregation in the Zr(O) region of a ZIRLO sample are also observed in **Figure 6-8(a)**. These planes are ~50 nm apart, and could be newly formed sub-GBs, given the width of the columnar grains in the ZIRLO metal matrix should be at least 100 nm. This result is

consistent with sub-GBs formation in the Zr(O) region during oxidation, as previously reported [141]. Many linear Fe-segregated features compose the sub-GB 2, as viewed from the red arrow, **Figure 6-8(b)**. As shown in the Zr, O and Fe profile in **Figure 6-8(d and e)**, these sub-GBs with Fe decoration correlate with a local O increase, and that the regions around these sub-GBs have reached $\text{Zr}(\text{O}_{\text{sat}})$ state earlier than the surrounding matrix.

Similar results on Fe segregation to clusters, dislocations and sub GBs have also been reported in [144]. It is reasonable to consider the possibility that the α -Zr lattice is distorted to accommodate interstitial O when forming the Zr(O) phase, and that when such distortion exceeds the yield threshold, dislocation lines form to accommodate the stress. These dislocations gradually pile up and become sub-GBs (**Figure 6-8(b)**), which finally transform into ZrO_2 GBs during further oxidation. GBs seen in the oxide might either originate from propagating metal GBs or be newly formed oxide GBs. Considering the dramatic grain size reduction and thus the GB density increase, when the oxide is formed, most of the GBs in the oxide should be of the latter kind. Due to the limited Fe content in the alloy (~ 0.1 at%), it is reasonable that Fe segregation is only seen on some of the GBs in the oxide.

Figure 6-9(a) presents a ZIRLO oxide dataset containing a GB. In the oxide, Nb is mostly detected as NbO_2^{2+} at 62.5 Da, and Fe is detected as Fe^{2+} at 28 Da and also as FeO^+ at 72 Da. A peak is observed at 44 Da as well, which could be FeO_2^{2+} or CO_2^+ . However, this peak shows random distribution indicating that spurious CO_2^+ from the analysis chamber is dominating this signal, so the 44 Da signal should not be used for Fe analysis. A composition profile measured along the arrow, **Figure 6-9(b)**, shows that both Fe and Nb segregation of up to 0.2% on the GB still exists after oxidation. However, there should be more Fe enriched at this oxide GB because the fraction detected at 56 Da, which overlaps with ZrO^{2+} , is not considered here.

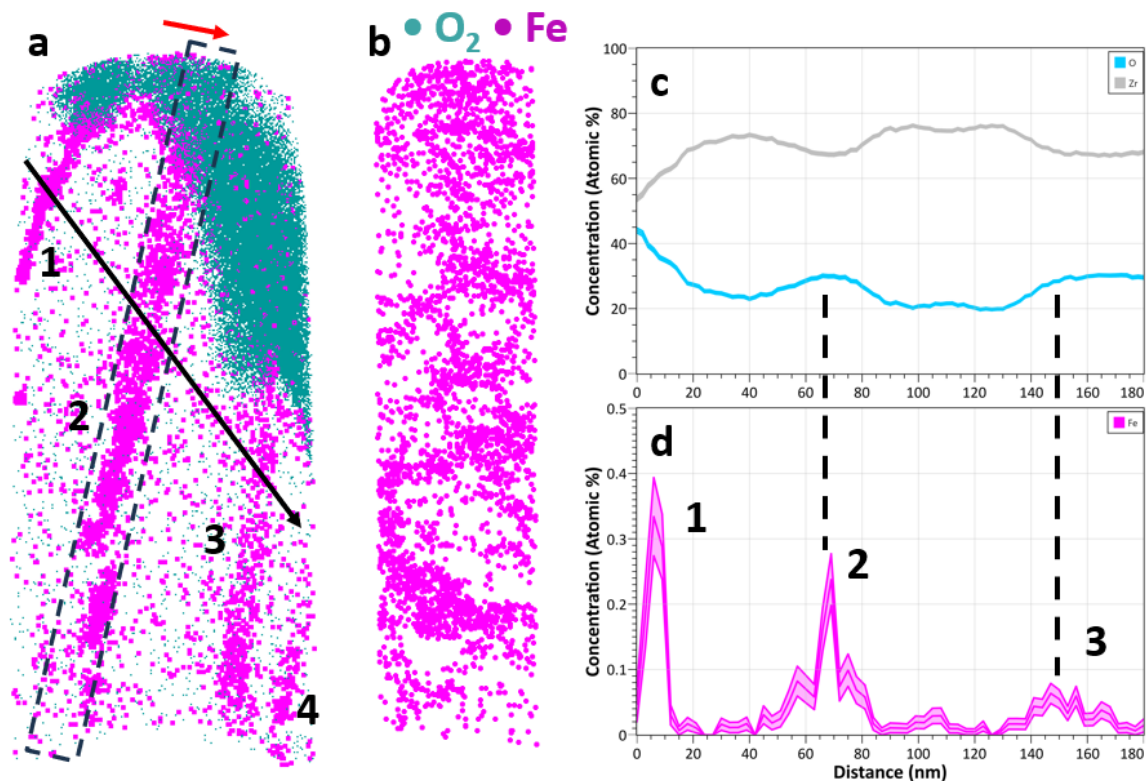


Figure 6-8. APT dataset ‘MCR2_M7’ from the O/M interface of a 30-day autoclaved ZIRLO sample. (a) Spatial distribution of O₂ and Fe (⁵⁶Fe²⁺). (b) Dashed box slice viewed from the red arrow direction. (c and d) Composition profile of Zr, O and Fe along the black arrow in (a). three Fe peaks in (d) correspond with the GBs 1-3 in (a).

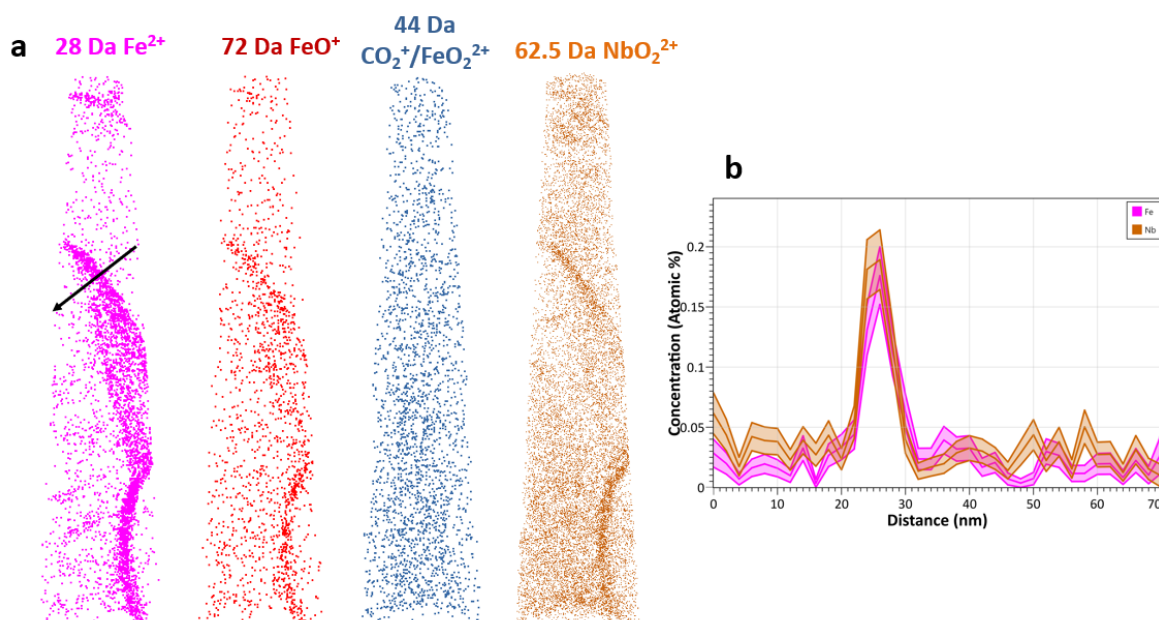


Figure 6-9. APT dataset ‘PZ08_M4’ from a 60-day autoclaved ZIRLO oxide. (a) Spatial distribution maps of selected ions. (b) composition profile across an oxide GB along arrow in (a). binning with 2 nm.

6.2 ^{18}O -spiking

The natural abundance of ^{18}O is 0.205%, so an oxide grown on a Zr-4 alloy (alloyed with 1.5% Sn, 0.2% Fe, 0.1% Cr, 0.1% Ni) in 15% ^{18}O -spiked water should contain a significant stronger ^{18}O signal that can be used to trace the distribution and transport of O species during corrosion.

Interpretation of ^{18}O APT data

However, care must be taken to interpret ^{18}O signal in APT data. 18 Da signal cannot be directly used to analyse $^{18}\text{O}^+$, because $^1\text{H}_2^{16}\text{O}^+$ molecules ions are also detected at 18 Da, especially during laser-pulsing analysis on oxide samples. Although these two ions do not have exactly the same mass, current APT instruments, unlike SIMS, do not have the high enough mass resolution to distinguish this peak overlap, **Table 3-10**.

^{18}O is also evaporated and detected as molecular ions such as $^{18}\text{O}^1\text{H}^+$ at 19 Da, $^{16}\text{O}^{18}\text{O}^+$ at 34 Da, $^{18}\text{O}^{18}\text{O}^+$ at 36 Da. The $^{92}\text{Zr}^{16}\text{O}^{3+}$ peak is one of the main peaks in datasets from oxide on Zr alloys, and $^{18}\text{O}^{18}\text{O}^+$ is buried by this large $^{92}\text{Zr}^{16}\text{O}^{3+}$ peak and cannot be separated. The other two signals are promising in identifying signals containing ^{18}O . The overlaid mass spectra for two oxide layers formed in regular water (red) and ^{18}O -spiked water (black) are shown in **Figure 6-10**. Oxide formed in regular water has a few counts at 34 Da ($^{16}\text{O}_2^1\text{H}_2^+$) but not at 19 Da, because the high electric field required for ion evaporation does not encourage the formation of large poly-ions like $^{16}\text{O}^1\text{H}_3^+$. By contrast, in ^{18}O -spiked oxide, there are a clear peak at 19 Da from $^{18}\text{O}^1\text{H}^+$, and a much stronger peak at 34 Da from $^{16}\text{O}^{18}\text{O}^+$. Therefore, it is concluded that the 19 Da signal contains nearly pure ^{18}O signal, and the 34 Da signal consists of ~90% ^{18}O signal, and thus the 19 and 34 Da signals are most suitable to show the distribution of ^{18}O when analysing datasets from isotopically enhanced oxide.

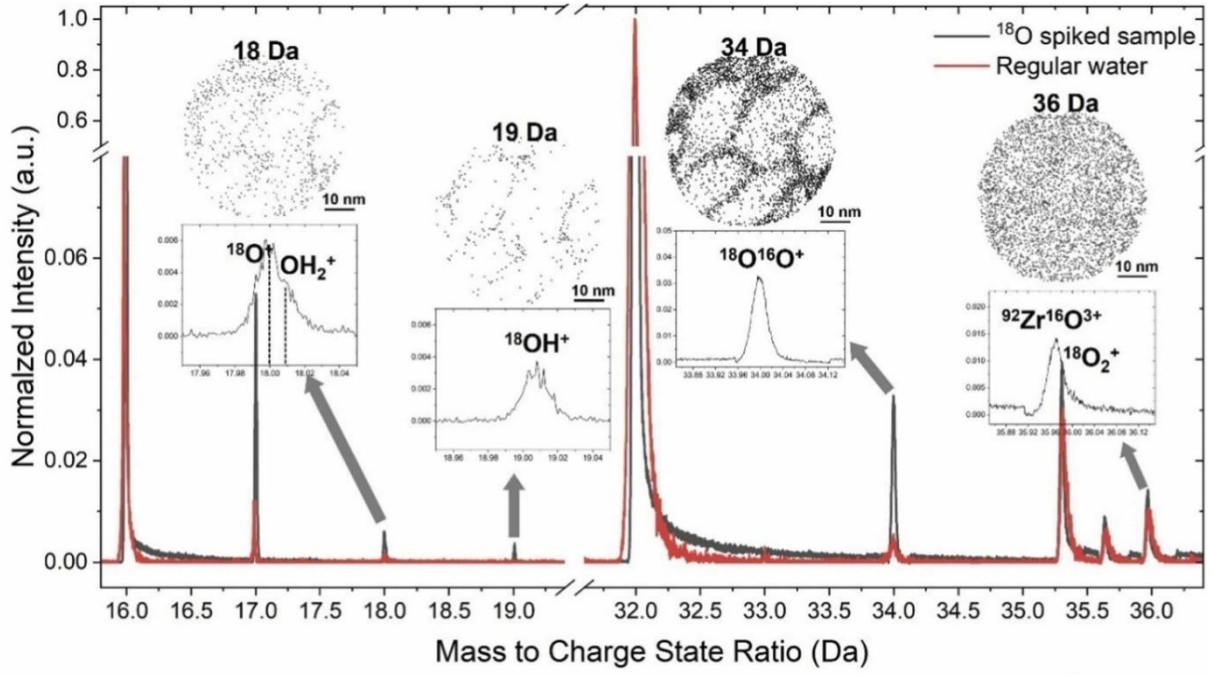


Figure 6-10. APT mass spectra from selected ranges from oxides formed in ^{18}O -spiked water and natural H_2O water. (Figure courtesy of Junliang Liu, University of Oxford)

APT results

These APT tips were made from a ^{18}O -spiked oxide on a pre-sharpened TEM grid, enabling correlated TEM and APT experiments [166]. **Figure 6-11** shows the BF-TEM image and APT ^{18}O distribution (using the 34 Da $^{16}\text{O}^{18}\text{O}^+$ signal) from the same APT specimen. Red arrows in **Figure 6-11(a)** indicate oxide GBs that are shown as dark contrast in the BF-TEM image. ^{18}O segregation at these locations is also observed, as highlighted by the red arrows in **Figure 6-11(b)**, indicating that the ^{18}O segregates to the oxide GBs identified by BF-TEM. However, it must be admitted that due to the surface contamination and the nanocrystalline structure with complex defects [57], TEM imaging on oxide APT tips did not give very clear images. As the diameter of the tip increases going along the z-direction, the tip becomes thicker for TEM analysis, it is also difficult to achieve clear images.

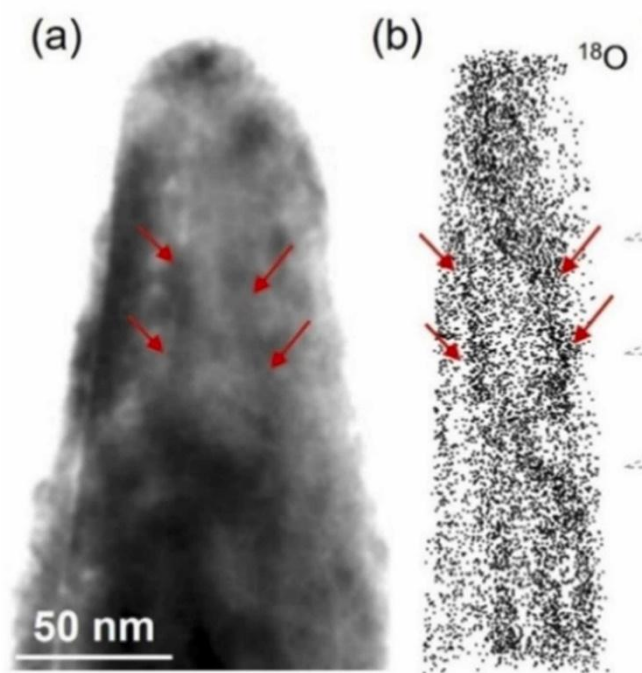


Figure 6-11. Correlative TEM and APT results on APT needle specimen made from ^{18}O -spiked oxide. (a) Bright-field TEM image (courtesy of Junliang Liu, University of Oxford). (b) ^{18}O distribution map using 34 Da signal.

Two 20-nm-thick horizontal slices from the same APT dataset are shown in **Figure 6-12(a and b)**, in both 19 and 34 Da distribution maps. ^{18}O segregation is clearly seen on the correlated GB positions that are also identified with Fe segregation. This correlation is confirmed in the 1D profile along the red arrow in **Figure 6-12(b)** across three GBs in **Figure 6-12(d)**. The 17 Da $^{16}\text{O}^1\text{H}^+$ signal also shows similar segregation as 19 Da because the ^{16}O species should behave the same as ^{18}O . In the oxide, Fe is sometimes also detected as $^{56}\text{Fe}^{16}\text{O}^+$ at 72 Da, but with many fewer counts compared with $^{56}\text{Fe}^{2+}$ at 28 Da. ^{18}O maps in two 10-nm-thick vertical slices, **Figure 6-12(c and d)**, clearly outline the characteristic columnar oxide grain structure as in previous electron microscopy images [57, 81], ~25 nm in width and 150 nm in length, and the long axis running along the z direction of the APT analysis which is also the corrosion direction. This is the first time that the columnar oxide grain structure has been clearly identified in APT analysis.

Interestingly, the H signal at 1 Da is also observed to be enriched on these GBs. H analysis in laser-mode APT datasets can be very difficult, as will be discussed in Section 6.3, and the 1 Da signal can be a combination of actual H from the sample, evaporated as H or H-containing molecular ions that then dissociate, and surface adsorption and evaporation of contaminating H-containing species. Therefore, this higher H concentration at GB locations could be attributed to: (i) O segregates and diffuses along GBs in the form of OH, and is evaporated as OH^+ , which dissociates to O and H during flight so more $^1\text{H}^+$ ions are detected at GBs than the oxide matrix. (ii) GBs have a locally lower evaporation field and slightly different radius during evaporation where the surface-adsorbed H from the analysis chamber collects before evaporation. Given that the 2 Da $^1\text{H}_2^+$ signal is randomly distributed, (ii) can be excluded, because the effect of field difference, if exists, should also induce more 2 Da $^1\text{H}_2^+$ signal to be detected at GB locations.

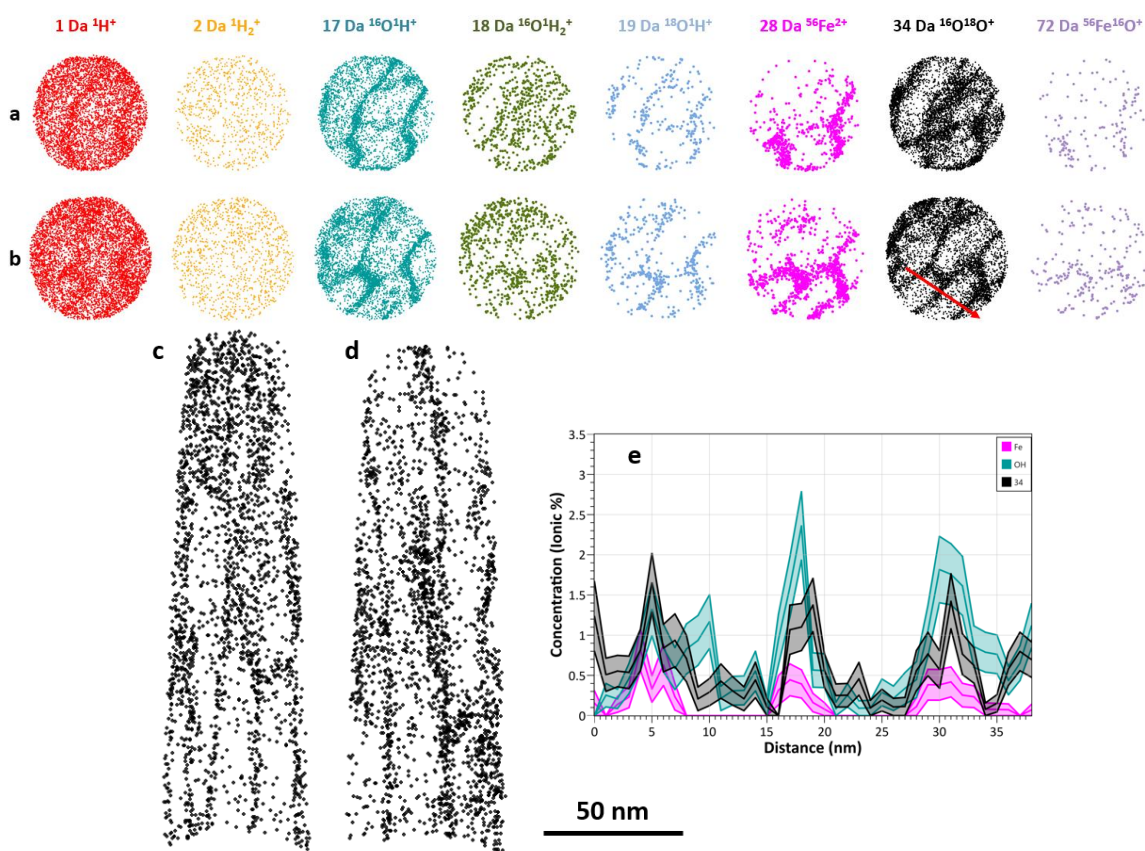


Figure 6-12. (a and b) Top view of selected signals from two 20 nm horizontal slices taken from **Figure 6-11(b)**. (c and d) Side view of the 34 Da signal on two 5 nm vertical slices taken from **Figure 6-11(b)**. (e) Composition profile of $^{28}\text{Fe}^{2+}$, $^{16}\text{O}^1\text{H}^+$, $^{16}\text{O}^{18}\text{O}^+$ signals along the red arrow in (b).

6.3 D-spiking

The nuclear industry has endeavoured for decades to limit H ingress during corrosion, but are still at the first step of understanding the key H in-diffusion mechanisms, partly because mapping H in the oxide layer with enough spatial resolution to resolve the nanoscale grain structure is a prerequisite for developing a model of how H-pickup proceeds. Successful attempts have been made on the detection of hydrogenic in many important engineering materials using APT and deuterium isotopic-tracing. However, this kind of analysis in a nano-structured oxide layers is extremely difficult, because of the smaller grain structure, complex defects, and the insulating nature of the ZrO_2 matrix. Here, by examining ZrO_2 oxide formed by deuterium isotopic spiking corrosion using APT, NanoSIMS and electron microscopy, we present an experimental protocol for unambiguous 3D characterisation of deuterium distributions within the nano-crystalline oxide layers.

A similar autoclave test to that described in Section 6.2 was applied to ZIRLO samples using D-spiked water. Two autoclave corrosions were performed on as-received ZIRLO alloy cladding tubes (**Figure 6-13(a)**), one in 15% D enriched water and the other in normal H_2O water, to give two types of oxide, both with ~ 600 nm thickness, termed **D oxide** and **H oxide**, respectively. **Figure 6-13** illustrates schematically the structures of oxide and metal expected for the two groups, based on the assumption that at this early stage in the corrosion process all the new oxide will be formed only at the oxide/metal interface [84]. A combination of APT, TKD, TEM and NanoSIMS analysis was used to study the D distribution from μm to near-atomic scale in Zr oxides formed during these isotopic spiking corrosion tests, with the aim of exploring the diffusion mechanisms of D through the oxide during aqueous corrosion.

Electron microscopy results

The size of typical areas characterised are indicated by the dashed box in **Figure 6-13(b)**, and covers the entire thickness of the oxide and some underlying metal substrate. The as-received ZIRLO alloy has a starting microstructure with $\sim 3\ \mu\text{m}$ grain size [81]. Upon exposure to the autoclave corrosion, the surface is transformed into a columnar-grained oxide layer, with the grain width decreased to $\sim 50\ \text{nm}$ (TKD map in **Figure 6-14(a)**). Nanopores with diameter of $\sim 3\ \text{nm}$ are observed mostly on the oxide GBs in the TEM Fresnel contrast maps in **Figure 6-14(b-d)**, similar to those previously reported in the oxides on similar cladding Zr alloys [57, 83, 111], and **Figure 6-15**. The typical dimensions of an APT dataset after reconstruction are indicated as a white triangle, and are expected to contain several oxide grains and GBs, with the long axis of the columnar grains aligned with the needle direction.

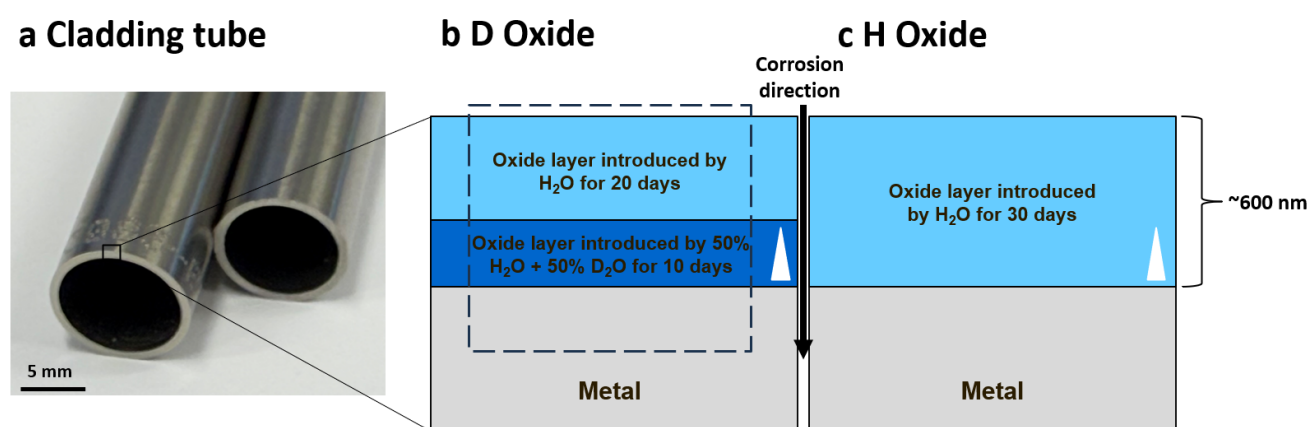


Figure 6-13. Illustration of two types of oxide sample formed during autoclave tests. (a) As-received ZIRLO alloy cladding tubes, with $\sim 1\text{cm}$ diameter and $\sim 600\ \mu\text{m}$ wall thickness. **(b and c)** Schematic diagram showing the **D oxide** (induced by D-enriched water) and **H oxide** (induced by normal water). The black dashed box indicates the characterisation range of TKD, TEM, and NanoSIMS. White triangles indicate the position, orientation, and approximate size of the reconstructed APT datasets, which are normally a conical volume $\sim 80\ \text{nm}$ in diameter and several hundred nm in length.

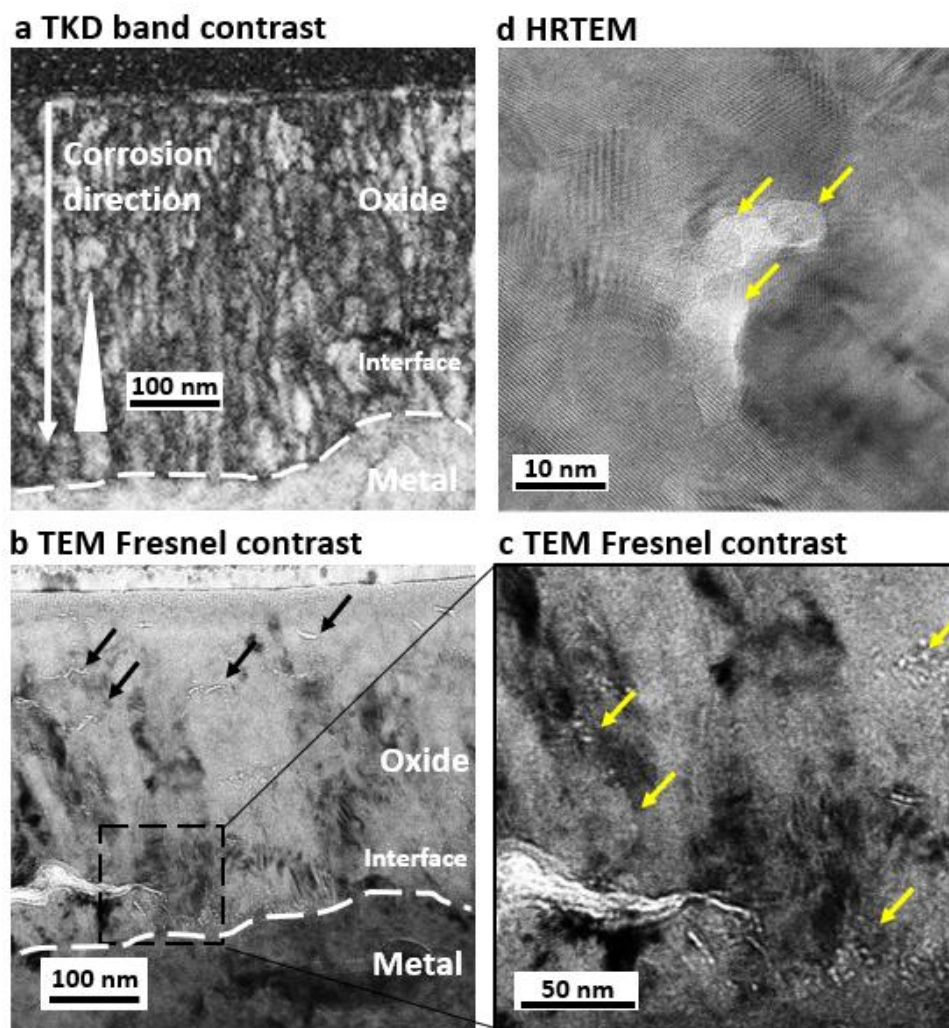


Figure 6-14. D oxide microstructure imaged by electron microscopy. (a) TKD band contrast map at the O/M interface, showing the columnar oxide grain structure, with ~ 50 nm width. The white triangle shows the approximate volume of one reconstructed APT dataset. The white arrow indicates the corrosion direction, and the O/M interface is shown by white dashed lines. (b) Fresnel contrast TEM image from the D oxide, where black arrows indicate lateral cracks in the outer oxide layer. (c) Magnified dashed black box from (b), where yellow arrows indicate nanopores. (d) HRTEM image of interconnected nanopores of ~ 3 nm diameter between two oxide grains. (Courtesy of Rajat Nama, University of Oxford)

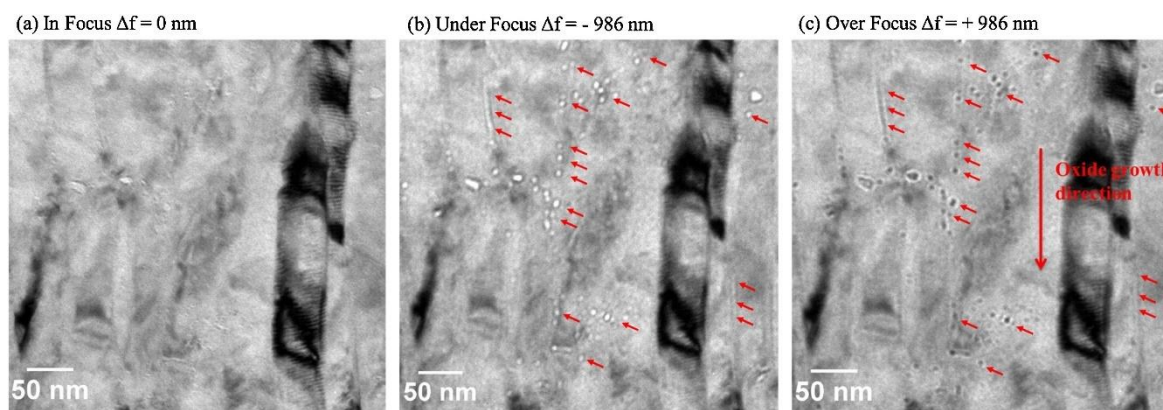


Figure 6-15. Fresnel image of nanopores in columnar oxide in 225-day pre-transition recrystallised Zr-1Nb around 200 nm from the O/M interface. (a) in focus; (b) under focus where nano-porosity is bright; (c) over focus where nano-porosity is dark. (Courtesy of Jing Hu, University of Oxford)

NanoSIMS results

NanoSIMS can unambiguously detect H_2 and D signals thanks to its very high mass resolution, **Table 3-10**. The $^2D^-$ intensity map in **Figure 6-16(a)** shows that the $^2D^-$ signal is higher in the outer **D oxide** and gradually decreases to undetectable levels below the inner oxide layer, as confirmed in the $^2D^-$ intensity profile along the corrosion direction (white arrow) in **Figure 6-16(c)**. There is no $^2D^-$ pile-up observed ahead of the O/M interface, hence the O/M interface does not seem to act as a permeation barrier. These observations align with previous studies [65, 84, 104], and can be explained by the easy permeation of D-rich water through the outer oxide via the interconnected cracks and pores. The inner protective oxide is denser and more protective, and here the D concentrations become undetectable. The inner oxide is thus the rate-limiting barrier to D in-diffusion, and once D reaches the O/M interface, it diffuses rapidly in the underlying metal matrix due to its much higher diffusion coefficient in α -Zr ($10^{-10} \text{ m}^2/\text{s}$ [253], compared with less than $10^{-18} \text{ m}^2/\text{s}$ in ZrO_2 [99]). The $^{16}O^2D^-$ signal shows the same distribution, but at higher intensity than $^2D^-$ signal, in **Figure 6-16(a and b)** and the depth profile in **Figure 6-16(c)**.

An additional visible feature in the NanoSIMS data is the elliptical hotspots in **Figure 6-16(a and b)** that represent regions of strong $^2D^-$ and $^{16}O^2D^-$ enrichment, with more than 4 times higher signal intensity than from the oxide matrix. Hotspots 1 and 2 are also captured as significant peaks in the vertical depth profile in **Figure 6-16(c)**. Such D hotspots have been reported in previous studies [65, 104] and were speculated to be D segregation to defective microstructures, with uncertainty about the real size and nature of these features. There are various microstructural defects in these oxides with approximately corresponding size, including second phase precipitates (SPPs) and the horizontal cracks seen in **Figure 6-14(b)** and commonly observed in Zr oxide layers [57, 254]. However, previous SEM-NanoSIMS results have shown that these lateral cracks actually block D in-diffusion [65, 104], and D-

enrichment at SPPs was also not detected [65]. Thus, these two possibilities can likely be ruled out, and it was suggested that these hotspots could be D trapping at the nanovoids shown in **Figure 6-14**(c and d) [57, 255].

Li et al [104] carried out similar NanoSIMS experiments with the ion sputtering direction both vertical and parallel to the oxide growth direction to investigate whether the observed hotspot morphology is an artefact of NanoSIMS analysis where the spatial resolution is 10 times better along the sputtering direction (z) than in the other two directions (the xy plane, **Table 3-10**). The observation that the long axes of the D hotspots always normal to the direction of incidence of the primary Cs^+ ion beam strongly suggested that the real morphology of the D hotspots is more equiaxed, and that the microstructural features in the oxide are much smaller than shown in the NanoSIMS maps. **Figure 6-16**(d) shows more detail on the three-dimensional (3D) structure of D hotspots 1 and 2, which appear to be interconnected by a vertical pathway, indicating that the region between two hotspots also has a higher D content. Similar NanoSIMS results of vertically interconnected D enriched features in a D-spiked Zr-4 oxide have been previously reported [65, 104]. Based on the observations that nanovoids mostly are present on oxide GBs, and can be arranged as a ‘string-of-pearls’ (**Figure 6-15** [57]), these NanoSIMS results might show D trapping in nanovoids aligned along oxide GBs during the in-diffusion process. APT analysis was used to study this idea.

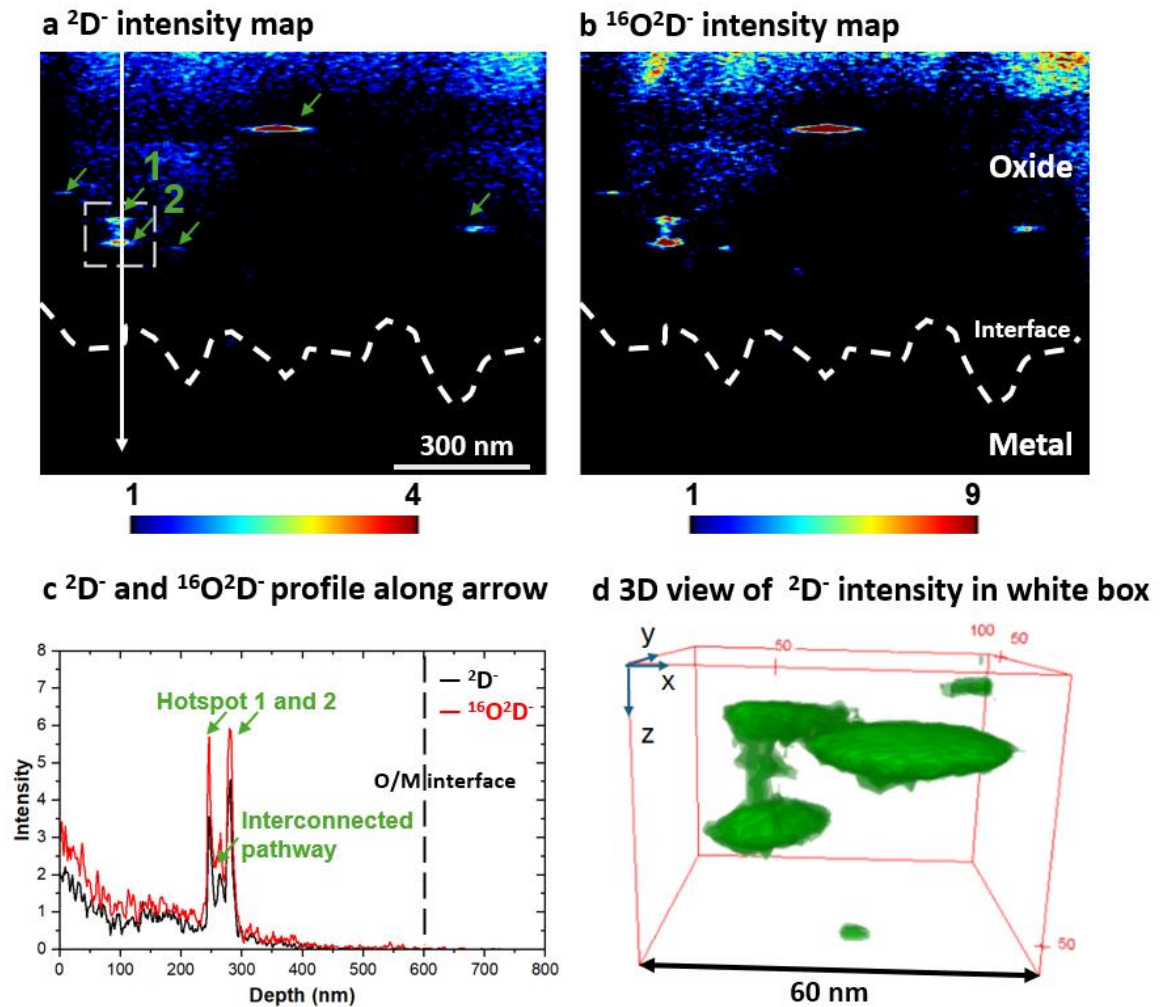


Figure 6-16. NanoSIMS analysis of D oxide. (a) $^2\text{D}^-$ intensity map in xz-plane (coordinates in Figure 3-21), green arrows indicate hotspots of D enrichment, and the dashed white line shows the approximate location of the O/M interface. (b) $^{16}\text{O}^2\text{D}^-$ intensity map in xz-plane, showing the same distribution as the $^2\text{D}^-$ intensity map. The colour legend indicates the count of $^2\text{D}^-$ and $^{16}\text{O}^2\text{D}^-$ signals per pixel. (c) $^2\text{D}^-$ (black) and $^{16}\text{O}^2\text{D}^-$ (red) intensity profiles along the white arrow in (a), the dashed black line indicates the approximate depth of the O/M interface. Hotspots 1 and 2 in (a) correspond to two intense spikes in both signals. (d) 3D map of $^2\text{D}^-$ intensity from the dashed white box in (a). (Courtesy of Kexue Li, University of Manchester)

H/D interpretation in APT data

The main challenge with APT analysis in this study is being confident about the source of the H or D signals detected. There are three main sources of H in APT data [256]:

- (i) H incorporation during FIB milling,
- (ii) contamination of a cooled sample by H-containing gas in the APT analysis chamber, and
- (iii) inherent H in the materials, i.e. H ingress during corrosion.

FIB milling at cryogenic temperatures can minimise (i) [257]. In comparison, (ii) is extremely difficult to avoid even when the base pressure during the experiment is below 10^{-10} Torr, especially in laser-mode APT analysis on oxide materials, so there will almost certainly be adventitious H signals detected as $^1\text{H}^+$ at 1 Da, $^1\text{H}_2^+$ at 2 Da and potentially even $^1\text{H}_3^+$ at 3 Da [256]. As previously reported, the concentration of adventitious H that is detected as singular and complex molecular ions can be affected by the pulse frequency [258, 259], laser incidence [195], and even APT needle shape [110]. These spurious contributions to the APT mass spectra add uncertainty when trying to extract the distribution and content of (iii) the real incorporated H in the sample. D spiking cannot readily solve this problem as in the NanoSIMS, because APT instruments do not have a high enough mass resolution to distinguish $^2\text{D}^+$ and $^1\text{H}_2^+$ at 2 Da in the mass spectrum [260, 261].

In this study, the interpretation of the D data is based on the comparison of the APT datasets extracted from **H oxide** and **D oxide**. Mass spectrum peak-to-peak ratios are known to vary with the specific evaporation field applied during APT analysis [175, 262]. The formation of Zr^{3+} ions requires higher fields (35 V/nm) than Zr^{2+} ions (28 V/nm), hence the $\text{Zr}^{3+}/\text{Zr}^{2+}$ ratio depends on the evaporation field applied during a given experiment, and a higher ratio indicates a higher applied electric field. This ratio is measured to be 1.59 and 1.60 for the **H oxide** and **D oxide** datasets, respectively. Thus, these two APT needles are expected to experience similar evaporation conditions, and the results from the two datasets should be directly comparable.

Figure 6-17 displays the mass spectrum ranges between 0-4 Da and 15-19 Da for two typical APT datasets, (a, c) from **H oxide** and (b, d) from **D oxide**. Because of the introduction of D, higher peaks at 2, 3 and 4 Da are expected in the **D oxide** dataset than in **H oxide** from the extra contribution of the D-containing ions, D^+ , $^1\text{H}^2\text{D}^+$ and $^2\text{D}_2^+$. However, there is no 4 Da peak in either dataset, and the intensity of the 1, 2 and 3 Da peaks are similar in both,

indicating these peaks cannot be used to map reliably the D distribution in the oxide layers. In the **H oxide** dataset, the small 18 Da peak arises mostly from adventitious H₂O gas in the APT analysis chamber ($^{16}\text{O}^1\text{H}_2^+$ molecular ions) [263], and is only just visible above the background level in the mass spectrum in **Figure 6-17(c)**. By contrast, in the analysis of the **D oxide**, the 18 Da peak consists of both $^{16}\text{O}^1\text{H}_2^+$ and $^{16}\text{O}^2\text{D}^+$ ions and is much more prominent due to the extra contribution of $^{16}\text{O}^2\text{D}^+$ ions originating from the sample. As shown in **Table 6-3**, the 18/16 count ratio in the data from the **D oxide** is almost 7 times higher than that from the **H oxide**, hence we can be sure that the majority of the detected 18 Da ions in **D oxide** dataset originate from $^{16}\text{O}^2\text{D}^+$ molecular ions. Furthermore, when the spatial distribution of ions contributing to the 18 Da signal from the **H oxide** is plotted (**Figure 6-18**), a random scatter of ions is seen, as expected from $^{16}\text{O}^1\text{H}_2^+$ arising from the adsorption of gas in the analysis chamber onto the needle surface. The 18 Da signal from **D oxide** consists of both spurious $^{16}\text{O}^1\text{H}_2^+$ and the $^{16}\text{O}^2\text{D}^+$ signal, and the ion distribution significantly deviates from a random pattern. These analyses provide the basis for using the 18 Da signal to trace the distribution of D in the oxide from **D oxide** APT datasets.

Table 6-3. Detected 16, 17 and 18 Da signals in exemplar H oxide and D oxide APT datasets.

Dataset	Dataset size (ion counts)	16 Da counts	17 Da counts	18 Da counts	18/16 ratio ($\times 10^{-3}$)
H oxide	15 million	434514	11614	807	1.9
D oxide	12 million	475535	24382	7119	15

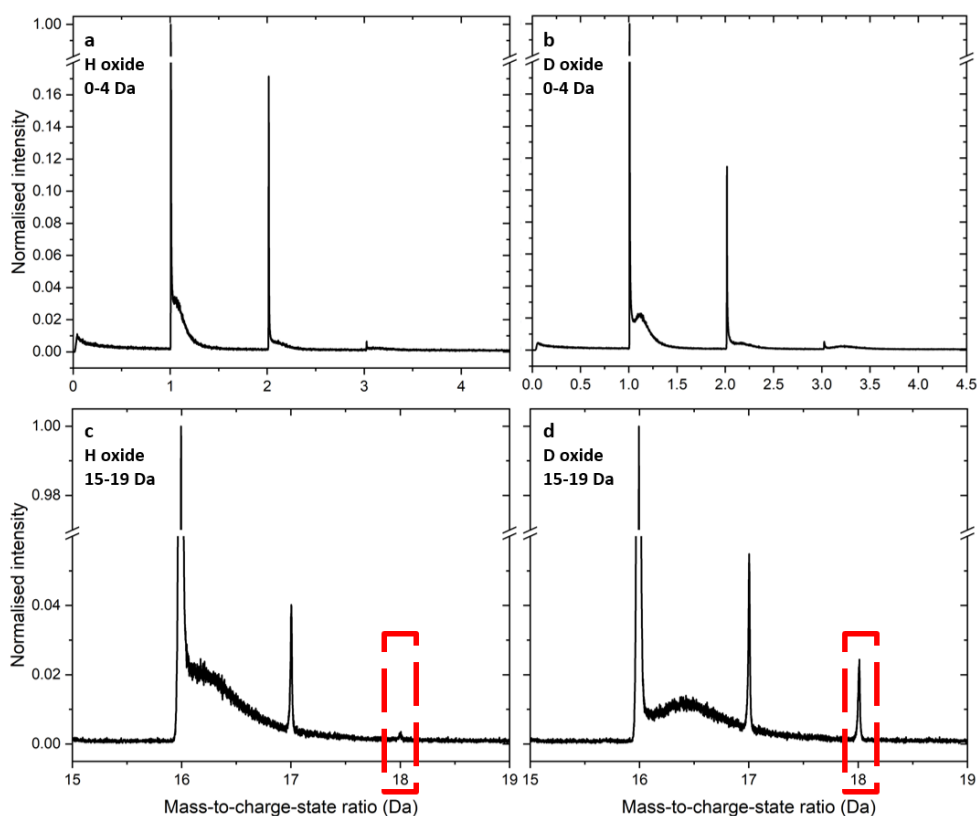


Figure 6-17. APT mass spectra over the ranges of (a) 0-4 Da, and (c) 15-19 Da from a typical **H oxide** dataset, and (b) 0-4 Da, and (d) 15-19 Da from a typical **D oxide** dataset. Peak height is normalised to the 1 and 16 Da peaks respectively, and the red dashed boxes highlight the 18 Da peaks.

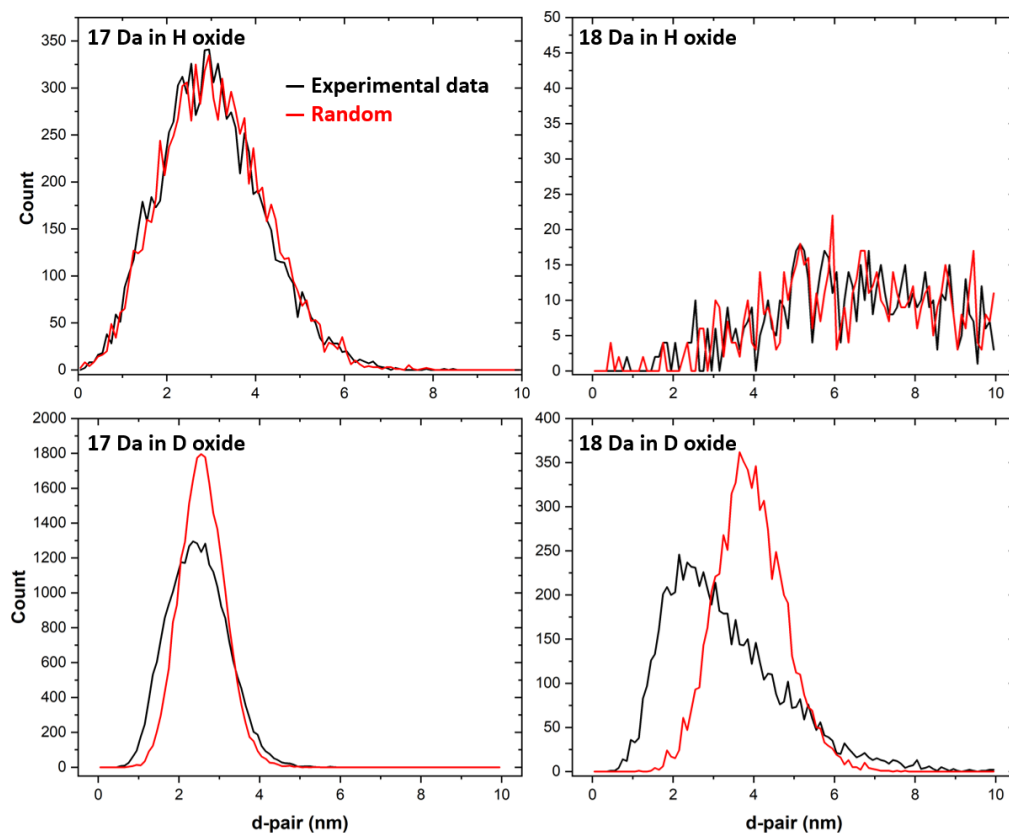


Figure 6-18. Nearest neighbour distribution of 17 and 18 Da signals in D and H oxide APT datasets. Experimentally observed data (black) and random (red) nearest neighbour distribution of 17 Da and 18 Da from H oxide, and D oxide, respectively. Note the different scale in the y-axis.

APT results

The 17 and 18 Da APT signals are utilised to map the distribution of H and D in the oxide to eliminate the influence of spurious H as elaborated above. **Figure 6-19(a)** shows a 3D map of the $^{56}\text{Fe}^{2+}$ ions detected from a typical reconstructed dataset from the **H oxide** sample, where the planar segregation of Fe to oxide GBs is clearly seen. **Figure 6-19(b)** displays the side views of a 5-nm-thick vertical slice 1 (vs1) from the same dataset. The higher density regions shown as darker lines in the density map outline the columnar grain structure in the oxide, in agreement with the columnar oxide grain structure in images in **Figure 6-14(a)**, and previous studies [14, 166]. Ions from the 17 Da signal are also observed to be spatially segregated to some of these GBs, suggesting that H is enriched at the oxide GBs, and detected as $^{16}\text{O}^1\text{H}^+$, as in previous APT work [103]. The weak 18 Da signal (**Figure 6-17a**) is distributed randomly, as very dilute background noise, and not observed to segregate to any particular feature. A similar observation of the correlated segregation of $^{56}\text{Fe}^{2+}$ and $^{16}\text{O}^1\text{H}^+$ signals to oxide GBs in another vertical slice (vs2) in this dataset is displayed in **Figure 6-19(c)**.

It is notable that a characteristic pattern of columnar oxide GBs is readily identified within the dataset, regardless of Fe enrichment or not, using the higher density regions (**Figure 6-19(c)**). The areal density of GBs greatly increases when the α -Zr metal matrix is consumed and transformed into ZrO_2 oxide, and the low overall concentration of Fe (0.1 wt%) in the alloy is not sufficient to encourage Fe segregation at all the oxide GBs. Therefore, it is concluded that the density maps are more reliable than Fe decoration in determining the positions of oxide GBs.

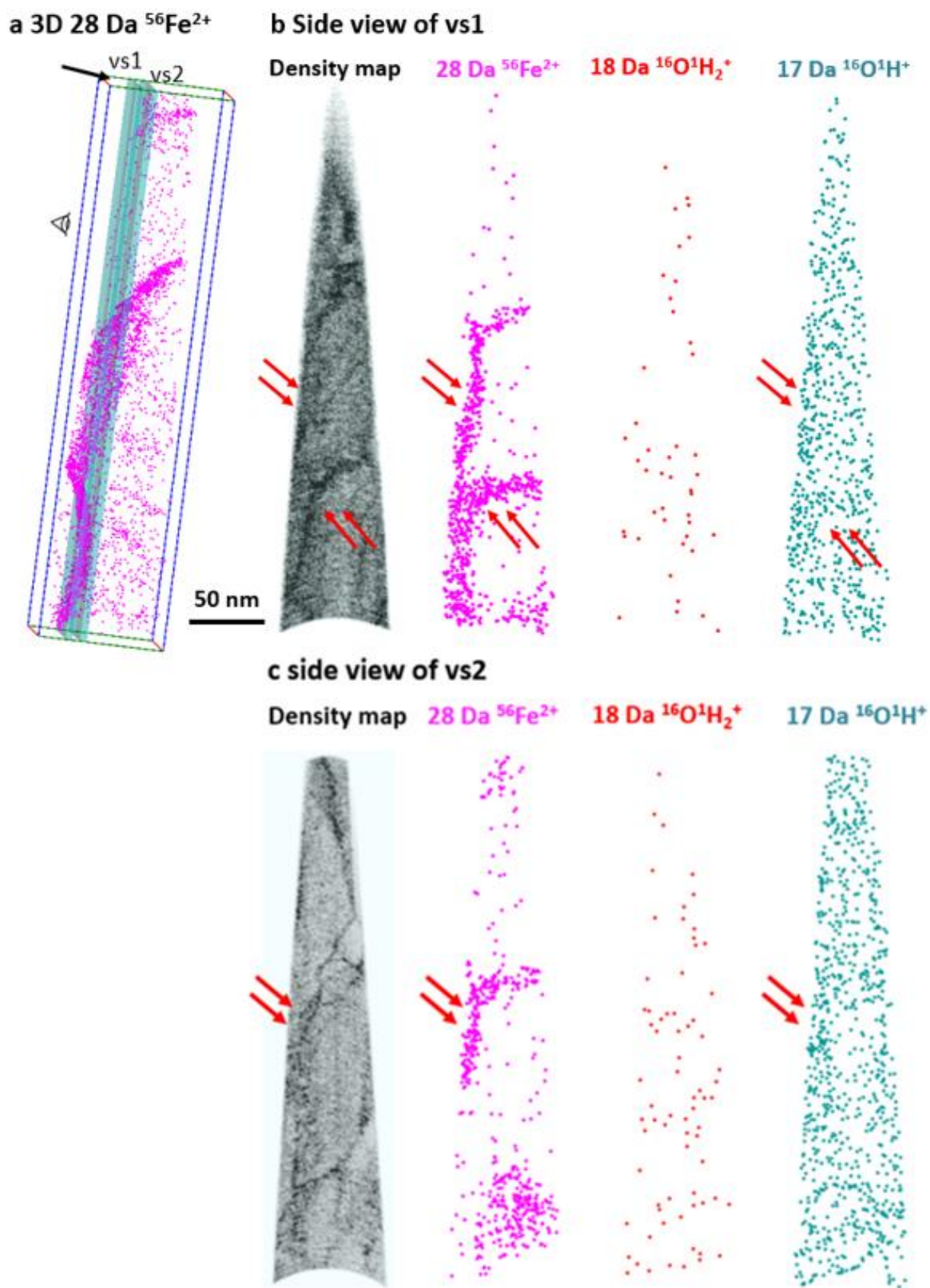


Figure 6-19. Analysis of a typical H oxide APT dataset. (a) 3D distribution of the detected 28 Da $^{56}\text{Fe}^{2+}$ signal. The black arrow indicates the laser incidence direction. Two 5-nm-thick vertical slices (vs1-2) are selected for detailed investigation. (b and c) Density map and selected species maps from vs1 and vs2 viewed from the eye symbol direction in (a), red arrows highlight the co-segregation of $^{56}\text{Fe}^{2+}$ and $^{16}\text{O}^1\text{H}^+$ at GBs.

Figure 6-20 presents analysis of a typical APT dataset from the **D oxide** sample. The 18 Da ions in **Figure 6-20(a)** now show strong planar segregation on oxide GBs. The side view of vertical slice 3 (vs3) in **Figure 6-20(b)** shows lines of higher density that reveal the location of GBs. In contrast to **Figure 6-19(b)**, many more 18 Da ions are detected, and these are strongly spatially correlated with GBs identified in the density map. Here the 18 Da signal originates from both $^{16}\text{O}^1\text{H}_2^+$ and $^{16}\text{O}^2\text{D}^+$ ions, but the $^{16}\text{O}^1\text{H}_2^+$ fraction would be expected to be much less intense and to occur as an approximately random spatial distribution of ions, like the 18 Da ion map from **H oxide** in **Figure 6-19(b)**. Hence, the $^{16}\text{O}^2\text{D}^+$ ions dominate the 18 Da signal, and these ions are strongly segregated to the GBs in **D oxide**. The 17 Da $^{16}\text{O}^1\text{H}^+$ signal also shows the same localisation behaviour to GBs as the 18 Da signal. This is as expected, because, given the 50% D₂O/50% H₂O mixture in the corroding water, the 17 Da $^{16}\text{O}^1\text{H}^+$ ions originating from H₂O water should behave exactly as the 18 Da $^{16}\text{O}^2\text{D}^+$ ions originating from D₂O water. These observations provide direct evidence that H/D is enriched at and possibly preferentially diffusing along the oxide GBs during the corrosion process.

Nanovoids in APT specimens lead, due to trajectory aberrations, to regions of high apparent ions/nm³ in the reconstructed volumes, as previously reported in tungsten alloys [29] and Zr oxides [57]. The darker regions in the density map in **Figure 6-20(b)** identify exactly this kind of feature in the **D oxide** samples. The total ion count profile around the nanovoid (**Figure 6-21(c)**) is similar to the ‘λ’ type nanovoids proposed by Wang et al [264]. The composition profiles across both nanovoid and GBs in **Figure 6-21(a and b)** show abrupt concentration increases in the 17 Da and 18 Da signals, confirming that the H and D species segregate to these microstructural features. We conclude that the higher density spots in the APT data and the D-rich hotspots in the NanoSIMS data are very likely both from D-segregated nanopores, which are detected as having different dimensions by two techniques

due to the different spatial resolutions (**Table 3-10**). The interconnected pathways in the NanoSIMS data can be identified as the columnar oxide GBs on which the nanopores are present [57], **Figure 6-15**, contributing to the concept that during the preferential diffusion of hydrogenic species along oxide GBs that the nanopores act as strong trapping sites.

Diffusion species

The remaining question is whether the detection of 17 Da $^{16}\text{O}^1\text{H}^+$ and 18 Da $^{16}\text{O}^2\text{D}^+$ ions in the **D oxide** dataset is an indication that H/D exists as mobile hydroxyl species in the oxide. The APT evaporation process is complicated, especially during laser-mode analysis of an insulating oxide material [265]. Top views of 3 horizontal slices (hs1-3) from the same **D oxide** APT dataset are displayed in **Figure 6-20(c-e)**, showing clear spatial correlation between the density map and 17 Da and 18 Da signals. By contrast the 1, 2, and 3 Da signals from $^1\text{H}^+$, $^1\text{H}_2^+/^2\text{D}^+$ and $^1\text{H}_3^+/^1\text{H}_2^2\text{D}^+$ are homogeneously distributed, probably because some H-containing gas from the analysis chamber adsorbs onto the surface of the APT needles during analysis, which on evaporation generate the adventitious $^1\text{H}_2^+$ and $^1\text{H}_3^+$ signals that overwhelm the signals from D species that might be segregated to GBs. However, the very different distribution of these ions at 1, 2 and 3 Da to those at 17 and 18 Da that contain oxygen, could also indicate that D from the isotopically spiked corrosion environment exists in the oxide mostly in the form of OD species, and these are subsequently field evaporated as $^{16}\text{O}^2\text{D}^+$ ions during the APT experiments. The stronger intensity of $^{16}\text{O}^2\text{D}^+$ signal compared to $^2\text{D}^+$ signal in NanoSIMS results (**Figure 6-16**) may also imply that the O and D are co-located in the **D oxide** sample.

Infra-red spectroscopy has been a valuable tool to confirm the incorporation of hydroxyl species in Zr oxides during water corrosion. It is agreed that for zirconia under water exposure, H_2O reacts with the surface of ZrO_2 forming hydroxyl groups which penetrate into the oxide by GB diffusion [160-162, 266]. The presence of O-H bond has been shown

in oxides formed on Zr-1Nb in autoclave conditions up to 773 K [161], and reversibility of such sorption is 100% at 373 K on a hydroxylated surface but decreases to only 60% at 823 K on a dehydroxylated surface across a pressure range. These results confirm that hydroxyl species are stable in ZrO_2 , and a strong chemisorption reaction of water with the ZrO_2 layer. Additionally, the O-H bonds detected in ZrO_2 in a H_2O environment were completely replaced by O-D bonds after changing into a D_2O environment [267], supporting the concept that hydrogenic permeation through Zr oxides occurs in the form of hydroxyl species on the oxide GBs.

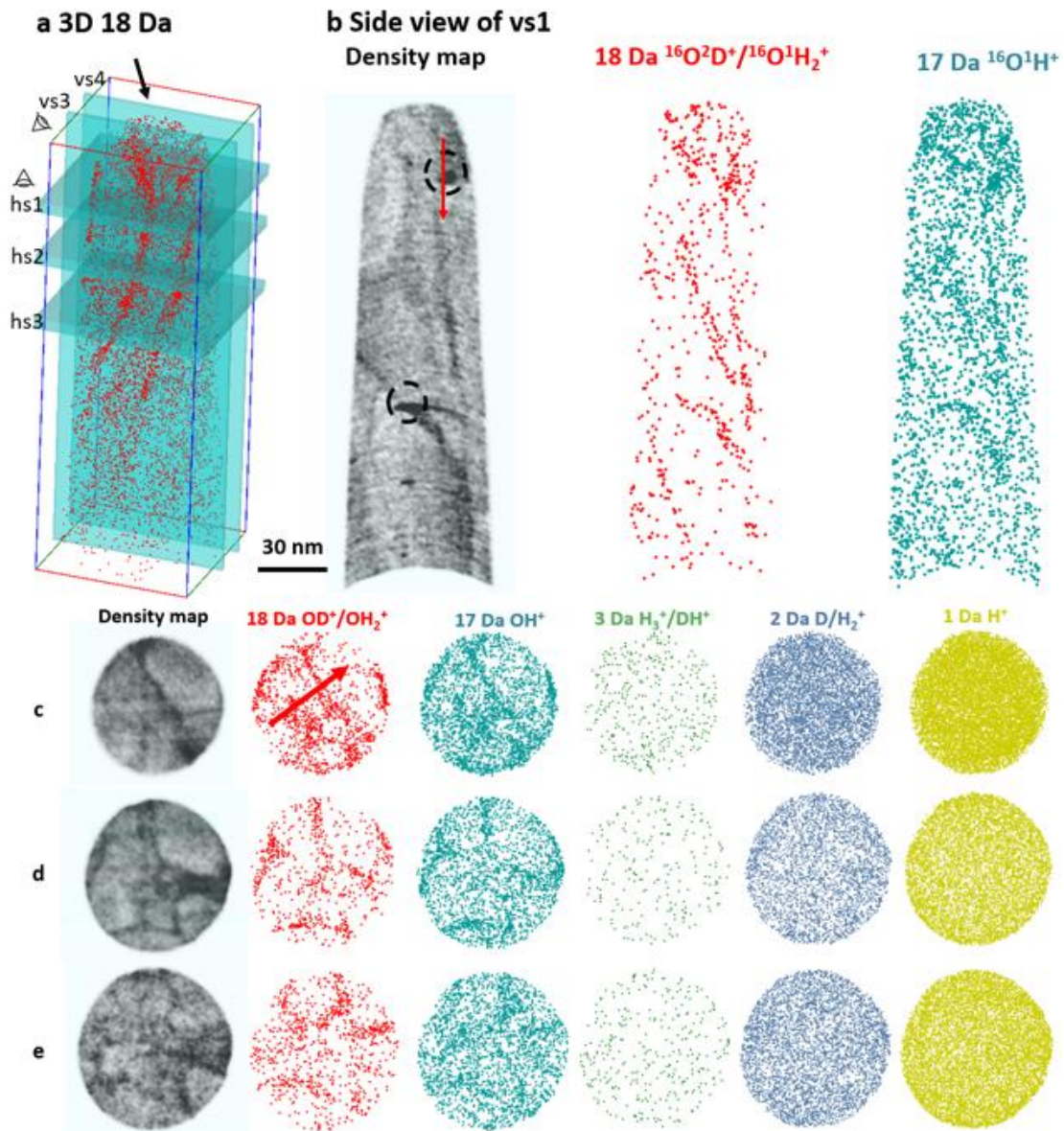


Figure 6-20. Analysis of a typical D oxide APT dataset. (a) 3D distribution of the detected 18 Da signal, with two 5-nm-thick vertical slices (vs3-4) and three 10-nm-thick horizontal slices (hs1-3)

selected for detailed investigation. The black arrow indicates the laser incidence direction. (b) Density map and selected ion maps from vs3 viewed along the eye symbol direction in (a). Dashed black circles highlight nanopores, and the red arrow indicates the position of the 1D profile measurement across a nanopore shown in **Figure 6-21(a and b)**. (c-e), density map and selected ion maps from hs1-3 viewed along the eye symbol direction in (a). The red arrow indicates the position of the 1D profile measurement across two oxide GBs shown in **Figure 6-21(c and d)**.

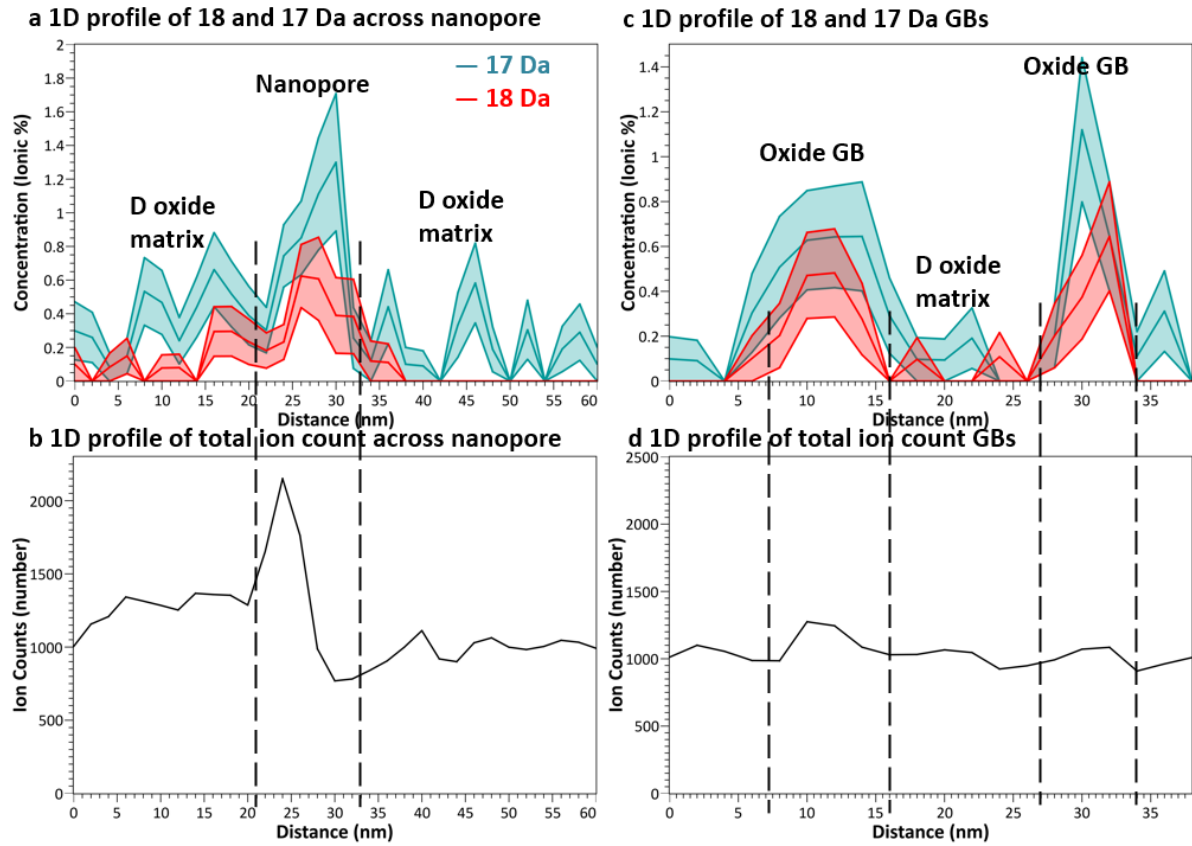


Figure 6-21. 17 and 18 Da signal compositions at nanopore and oxide GBs in the D oxide dataset. (a) 1D composition profile of 17 and 18 Da signals across the nanopore along the red arrow in **Figure 6-20(a)**. (b) Total ion count profile of (a), vertical black lines indicate approximate width of the nanopore. (c) 1D composition profile across two oxide GBs along the red arrow in **Figure 6-20(c)**. (d) Total ion count profile of (c), vertical black dashed lines indicate the approximate widths of the two oxide GBs.

Summary

This work demonstrates that with careful experimental design the distribution of hydrogenic species can be studied even in non-metallic materials containing nanoscale and complicated defect microstructures. A workflow has been developed for the direct observation of how D, used as a surrogate for H, behaves during the aqueous corrosion of ZIRLO alloy cladding in D-spiked water. **Figure 6-22** summarises the key H/D ingress mechanisms. Coolant water dissociates into protons and hydroxyl species around the water/oxide interface. Protons may

recombine as H_2 and escape to the coolant water, while hydroxyl species penetrate to the inner oxide layer through the interconnected cracks in the outer oxide. Thereafter, because of the very low intragranular diffusivity, hydroxyl species preferentially segregate to, and diffuse along, GBs in the inner protective oxide. These species can also be trapped at nanopores on GBs, and thus isolated nanopores actually delay the diffusion kinetics. Only when the pores become interconnected at a later stage of corrosion [199] will they offer rapid penetration paths down to the metal matrix, and this has been proposed as a key microstructural factor explaining the abrupt periodic accelerations in corrosion rate observed in these materials in service [83, 249]. Once they reach the O/M interface, these OH species further disassociate into O^{2-} ions and protons, with the O contributing to the thickening of the ZrO_2 layer, and the H diffuses freely into the metal matrix, contributing to the degradation mechanisms like delayed hydride cracking that limit the in-service lifetime of the fuel cladding components.

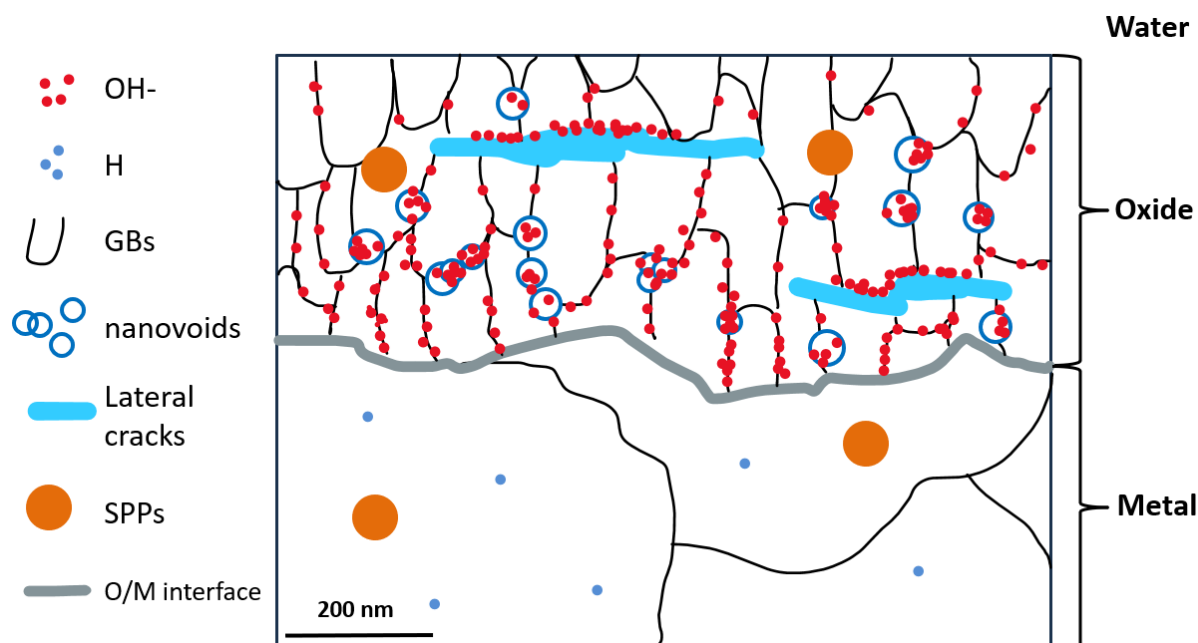


Figure 6-22. Schematic diagram summarising the H ingress mechanisms from water to the Zr cladding.

6.4 Discussion and conclusions

The chemistry around the O/M interface of oxides formed by autoclave corrosion in **Section 6.1** shows a region ~ 100 nm thick, containing ZrO_2 , ZrO suboxide, $\alpha\text{-Zr}(\text{O}_{\text{sat}})$, $\alpha\text{-Zr}(\text{O})$, and $\alpha\text{-Zr}$. Sn is continuously pushed out from the oxide into the metal, while Nb remains at a similar content after oxidation, showing little redistribution. Both the Laves phase SPPs and $\beta\text{-Nb}$ SPPs show delayed oxidation by maintaining metallic compositions for much longer time than the surrounding $\alpha\text{-Zr}$ matrix, and can protect the underlying metal locally by blocking the in-diffusion of O. Dislocations can form in the $\alpha\text{-Zr}(\text{O})$ region to accommodate the stress induced by the Pilling-Bedworth expansion or from the interstitial O, and some of these dislocations gradually pile up forming oxide sub-GBs, which finally become oxide GBs. The Fe and Nb segregation on GBs can still remain after oxidation.

Delicate APT results on ^{18}O - and D-spiked oxide layers with careful data analysis are presented in **Sections 6.2** and **6.3**. The results have shown that in the inner oxide layer, both O and H are enriched on the oxide GBs in the form of OH, suggesting that their in-diffusion process preferentially occurs along GBs in the form of hydroxyl species. This mechanism can be the basis for more experimental and modelling investigations focussing on understanding how to increase oxide grain width, since the columnar oxide GBs are proven to act as an easy path for corrosion species, or to modify the interactions between GBs and hydroxyl species, possibly by changes to the alloy composition and the introduction of more isolated nanovoids. Either of these microstructural changes can potentially prolong the lifespan of cladding, and increase fuel burnup. These insights are equally important for understanding and mitigating the environment degradation of zirconia and other similar ceramics materials when exposed to water at elevated temperatures. The APT and NanoSIMS results on D signal hotspots are carefully interpreted and concluded that

nanovoids aligned on the oxide GBs act as strong traps for H species, which, before become interconnected at later-stage corrosion, actually delay the in-diffusion process.

However, these results are acquired from oxides formed during autoclave corrosion, which is often used as a proxy for the in-pile corrosion. The real in-service corrosion of Zr cladding alloys occurs under the combined effects of neutron irradiation and aqueous corrosion, where there can be more hydroxyl groups due to the radiolysis of H_2O , and the high density of microstructural defects induced by irradiation damage can accelerate in-diffusion processes. The techniques developed in this study based on this understanding from proxy autoclave corrosion tests now need to be applied to the much more complicated situation of ex-reactor materials where, particularly when the concentration of hydroxyl species is a significant parameter, understanding the rate of hydrolysis reactions will become much more important.

7. In-pile corrosion of Zr alloys

Finally, ex-reactor RXA X2 and SRA ZIRLO samples from the Vogtle reactor provided by Westinghouse were studied using mainly APT to understand the in-service degradation mechanisms of cladding materials. The APT tips were made in the inner oxide or around the O/M interface. With the separate understanding on both irradiation and corrosion processes presented in **Chapters 5** and **6**, this chapter focuses on mechanisms of the accelerated corrosion induced by in-situ irradiation. The major factors considered are (i) the irradiated corrosion environment, (ii) the irradiated metal substrate, and (iii) the effect of in-situ irradiation on the phase transformations and in-diffusion of corrosion species. Section **7.1** presents the Li ingress observed in these samples and involves part of (i). Sections **7.2** and **7.3** provide detailed investigation of the microchemistry of in-pile corroded X2 and ZIRLO alloys around the O/M interface, focussing on (ii). There is currently limited understanding of (iii), and since APT may not be the most suitable technique to study it, (iii) is not extensively discussed in this work.

7.1 Li ingress

As reviewed in Section **2.3.4 Li accelerated corrosion**, it was known before the work in this thesis was undertaken that Li segregates and diffuses along the oxide GBs, and it is considered that Li accelerates the corrosion rate by promoting O diffusing through oxide, or plays a role at the O/M interface that affects the metal to oxide phase transformation or the nucleation of new oxide grains. This section focuses on the precise mapping of the Li distribution around the O/M interface and in the underlying metal after exposure to actual in-service conditions.

Li distribution in the metal

Figure 7-1 shows a detail of typical APT mass spectra from the X2 alloy samples over the range of 5-12.5 Da where the APT needles are extracted from: the bulk metal matrix of a pristine sample (**Figure 7-1(a)**, unirradiated and uncorroded), the bulk metal matrix of an ex-reactor sample (**Figure 7-1(b)**, irradiated-only), and from the O/M interface of an ex-reactor sample (**Figure 7-1(c)**, irradiated and corroded) after 5.2 years in-pile corrosion and ~32 dpa irradiation damage. The 7 Da signal is from the isotopically pure ^7Li used in the cooling water, and is only detected around the O/M interface in the in-pile corroded sample. To avoid the formation of ^3H from ^6Li during irradiation [268], only isotopically pure ^7Li is added into the primary water, explaining why no ^6Li signal is found in **Figure 7-1(c)**.

This is surprising given the concentration of Li in the coolant water is only a few wtppm. Li ingress has not been reported in autoclave corroded Zr alloys, with similar corrosion times (1-cycle) and water chemistry (Li content) [57]. However, we must remember that ^{10}B in the primary water can produce ^7Li under irradiation ($^{10}\text{B} + ^1_0\text{n} \rightarrow ^4_2\text{He} + ^7_3\text{Li} + 2.79 \text{ MeV}$ [158]), so during in-pile corrosion, the cladding has been actually subjected to a water with higher Li concentration than the starting nominal value or than in autoclave water. And presumably, the concentration of ^7Li in the primary water keeps increasing until the change of primary water at the end of a cycle when B is depleted.

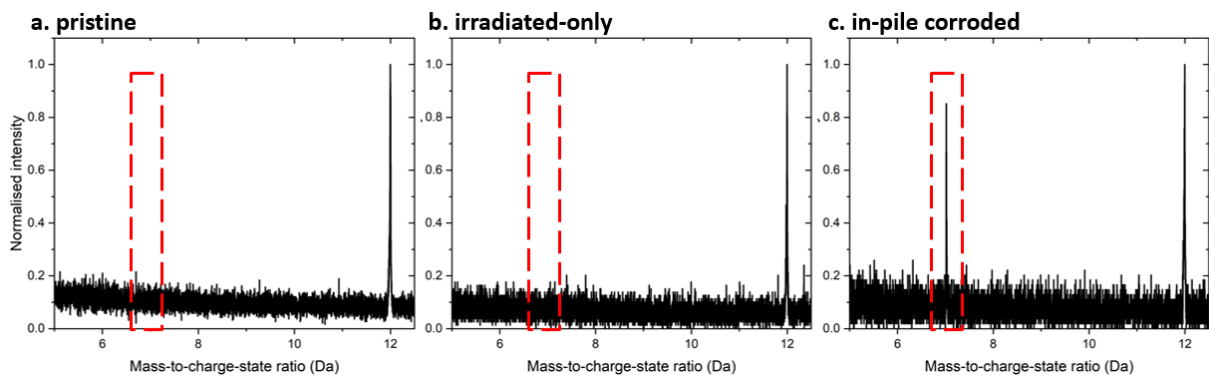


Figure 7-1. Detail of mass spectra from typical APT datasets from X2 alloys in (a) pristine state, (b) irradiated-only state, (c) in-pile corroded state, respectively. Signal intensity is normalised to the 12 Da $^{12}\text{C}^+$ peak.

Previous studies have shown that Li can penetrate through the ZrO_2 oxide layer formed on the cladding Zr outer surface during corrosion, by preferentially diffusing along the oxide GBs [114, 119, 127], **Figure 2-22**. So it is expected that some Li atoms will eventually diffuse through the whole oxide layer and reach the metal matrix, but there is currently no evidence to confirm this. **Figure 7-2** displays a typical APT dataset at the O/M interface from a 4-cycle ex-reactor X2 sample. The spatial distributions of O_2^+ , ZrO^{2+} and Zr^{2+} signals are shown in the atom map **Figure 7-2(a)**, and a Zr and O chemical composition profile measured from the top to the bottom of the dataset is shown in **Figure 7-2(b)**.

The characteristic Zr-O ratio change at the O/M interface is observed, with the progression of ZrO_2 , ZrO , $\text{Zr}(\text{O}_{\text{sat}})$, $\text{Zr}(\text{O})$ and finally to $\alpha\text{-Zr}$. The Zr-O chemistry at the O/M interface is similar to that found in oxides formed by autoclave and in-pile corrosion environments. It is, however, surprising to notice that here the O/M interface is ~ 200 nm and that the O/M interface thickness formed in an autoclave (**Figure 6-1**) is only 100 nm thick. An oxide growing faster might be expected to have a thinner O/M interface due to the faster consumption of the suboxide and $\text{Zr}(\text{O})$ regions [141]. The discrepancy is possibly because the composition of the O/M interface is not uniform, and these two profiles are based on the analysis of very limited volumes of materials and thus are not representative. It would be interesting to see if mapping the interface with EDX or EELS [137] over larger areas would show the same trend.

From this same dataset, **Figure 7-2(c)** shows that the detected $^7\text{Li}^+$ signals are spatially distributed very inhomogeneously, forming a number of well-defined clusters labelled 1-3 in the metal and 4-6 around the O/M interface. In the same image, the green isosurfaces define volumes of the reconstruction measured to have a significantly higher atom density ($40/\text{nm}^3$) than the average from the rest of the analysed volume ($\sim 30/\text{nm}^3$). All 6 Li-rich clusters are perfectly spatially correlated with these regions of higher atom density. The two

enlarged insets show that Li cluster 3 in the metal has a planar shape (as do clusters 1 and 2), whereas cluster 6 at the O/M interface, although still well-correlated with a region of higher atom density, seems much more diffuse.

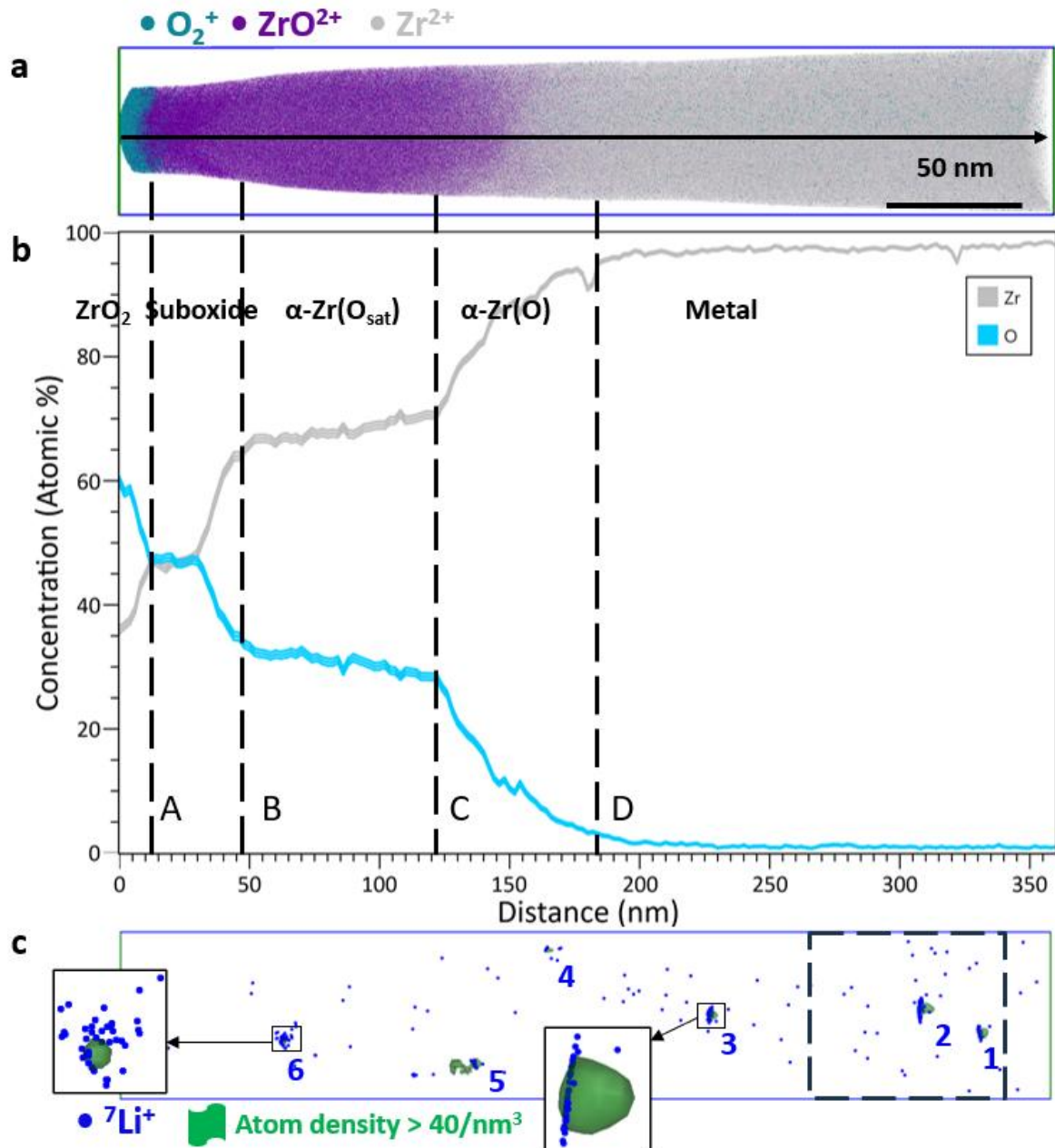


Figure 7-2. Typical APT dataset at the O/M interface from a 4-cycle ex-reactor X2 alloy (5.2 years in-pile corrosion and 32 dpa irradiation damage). (a) Overlaid spatial distribution maps of O_2^+ , ZrO^{2+} , and Zr^{2+} . (b) 1D composition profile of Zr and O along the arrow in (a), showing several changes in stoichiometry around the O/M interface. (c) Spatial distribution map of $^7\text{Li}^+$ in the same region of material as (a), green surfaces indicate regions with atom density higher than $40/\text{nm}^3$. Li clusters are labelled as 1-6. Two insets show magnified images of Li clusters 3 and 6. 340 Li ions are detected in the dataset.

The regions within the dashed box in **Figure 7-2(c)** were investigated in more detail. **Figure 7-3(a)** shows the overlaid spatial distribution of Li^+ , Fe^{2+} and Nb^{3+} signals. The Nb and Fe alloying elements are randomly distributed in the matrix in the pristine state, but as previously reported ([43, 44, 269] and **Chapter 5**), they redistribute during irradiation to form nanoscale regions of high solute concentration (irradiation-induced clusters). From this particular sampled region, it is clear that the Fe and Nb are forming clusters independently, similar as in **Figure 5-16(d)**, so likely with different mechanisms during irradiation. By contrast, both Li clusters 1 and 2 are reconstructed in the APT data as planar features and are located immediately above the denser regions indicated with green isosurfaces. Neither of the Li clusters appears to co-segregate with Fe or Nb. As observed along the APT z-axis (eye symbol in **Figure 7-3(a)**), these two Li clusters are present in the reconstruction as a disk apparently only one atom layer thick (**Figure 7-3(c and d)**).

The detected atom density during analysis of a dense metal matrix should be uniform, and the detection of localised regions with higher than average density (atoms/nm^3) are very likely due to the trajectory aberrations and can be used to locate the nanovoids, as has been used in **Section 6.3** to locate oxide GBs and oxide nanovoids. **Figure 7-3(b)** shows the atom density map from the same volume as **Figure 7-3(a)**, where the two denser isosurfaces are now identified as regions of black contrast (higher ion densities) of similar size and morphology in **Figure 7-3(b)**. **Figure 7-4** displays the variation in atom count measured within a region-of-interest spanning Li clusters 1 and 2 along the z-direction, respectively. These plots show a sudden increase in detected ion counts (atom density) by up to a factor of four compared to the matrix over a distance of 5-10 nm. These are very similar to the density profiles of ‘ λ ’ type nanovoids proposed in [264, 270], where experimental and modelling evidence is given for these artificial density fluctuations in APT reconstructions. It is well-known that condensation of the excess point defect concentrations generated by

neutron irradiation can produce nanovoids in irradiated steels [271], and in Zr alloys [272, 273], and it is thus not unexpected to observe nanovoids in these heavily-irradiated samples. TEM Fresnel contrast has been a valuable tool to identify nanovoids [57, 73], and **Figure 7-4(c)** shows a TEM Fresnel contrast image around the O/M interface on the same bulk sample, confirming the presence of the nanovoids in the region from which this APT sample was taken.

By contrast with these low-field nanofeatures, those requiring a higher-field to be evaporated during the APT experiment will induce smaller local radii of curvature and be reconstructed as localised lower-density regions [173]. For instance, Nb atoms requires a higher electric field for evaporation (37 V/nm) than Zr (28 V/nm), so Nb clusters are expected to be spatially correlated with localised regions of low reconstructed atom density, as highlighted by the red dashed circles in **Figure 7-3(a and b)**.

Figure 7-5 presents a typical APT dataset from a 2-cycle ex-reactor ZIRLO[®] at the O/M interface. The O₂⁺ signal detected at the left-hand side of **Figure 7-5(a)** and decreasing content of ZrO₂⁺ along the needle-shaped analysed volume indicate that this dataset is also located at the O/M interface. The spatial distribution of Nb³⁺, Fe²⁺ and Li⁺ signals taken from a region of the metal substrate immediately below the O/M interface defined by the dashed box in **Figure 7-5(a)** is displayed in **Figure 7-5(b)**. Again, several well-defined Li clusters are observed, labelled 7-10. As in **Figure 7-2** and **Figure 7-3** for the X2 alloy sample, these Li clusters are 2D disk-shaped features, and they are all spatially correlated with nanovoids but not with Fe or Nb clusters (which at this lower irradiation dose are less well developed than in the 4 cycle X2 sample). As is highlighted by the dashed circles, some of the solute clusters are also correlated with nanovoids detected by the increased atom density in the reconstruction, indicating that nanovoids can also be precipitation site for these solute clusters during irradiation. However, we cannot rule out the possibility that these denser

regions could be vacancy <a>-type dislocation loops, since it has been confirmed that these loops (or the strain field surrounding them) can be effective precipitation sites for solute clusters [48, 142, 269].

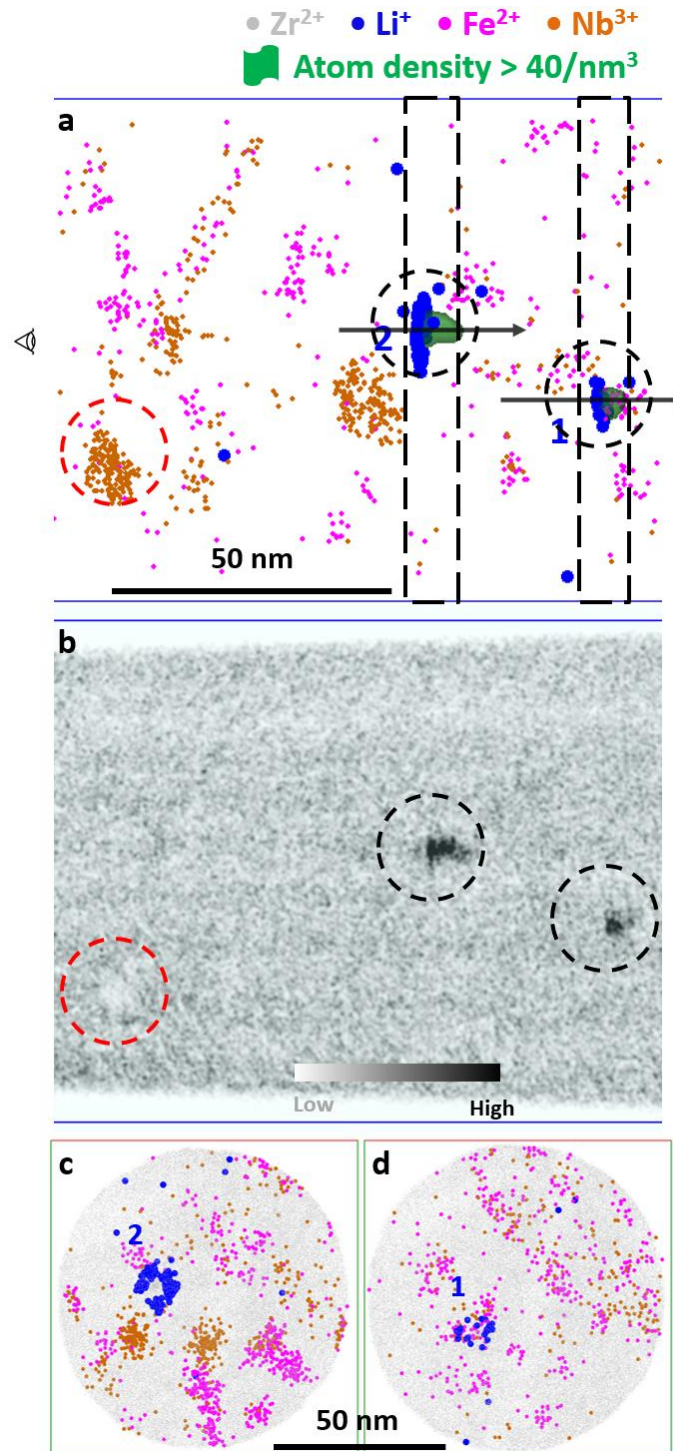


Figure 7-3. Typical APT dataset from 4-cycle in-pile corroded X2 alloy, region inside the dashed box in **Figure 7-2(c)**. (a) Overlaid spatial distribution maps of Li^+ , Fe^{2+} and Nb^{3+} . (b) Atom density map from the same region with (a). Black and white contrast indicates higher and lower atom density, respectively. (c, d) Vertical view of the two dashed boxes in (a) along the eye symbol direction, showing the disk shape of Li clusters 2 and 1, respectively.

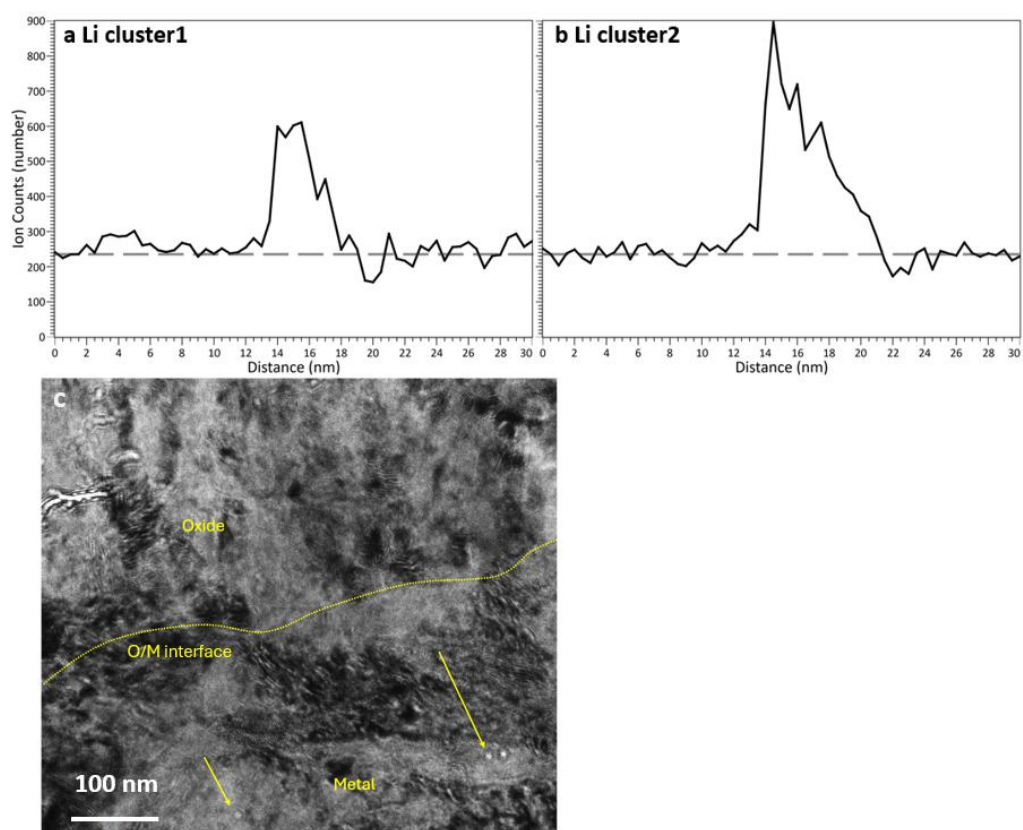


Figure 7-4. Atom counts across Li cluster 1 (a) and 2 (b) measured along a $5\text{ nm} \times 5\text{ nm} \times 20\text{ nm}$ region-of-interest (grey arrows in **Figure 7-3(a)**) with 0.5 nm binning width. The horizontal dashed line indicates the matrix level of atom counts. (c) TEM Fresnel contrast at $-1\text{ }\mu\text{m}$ defocus at the O/M interface in 4-cycle X2, the bright dots (indicated by the yellow arrows) show the presence of irradiation-induced nanovoids (image by courtesy of Rajat Nama, University of Oxford).

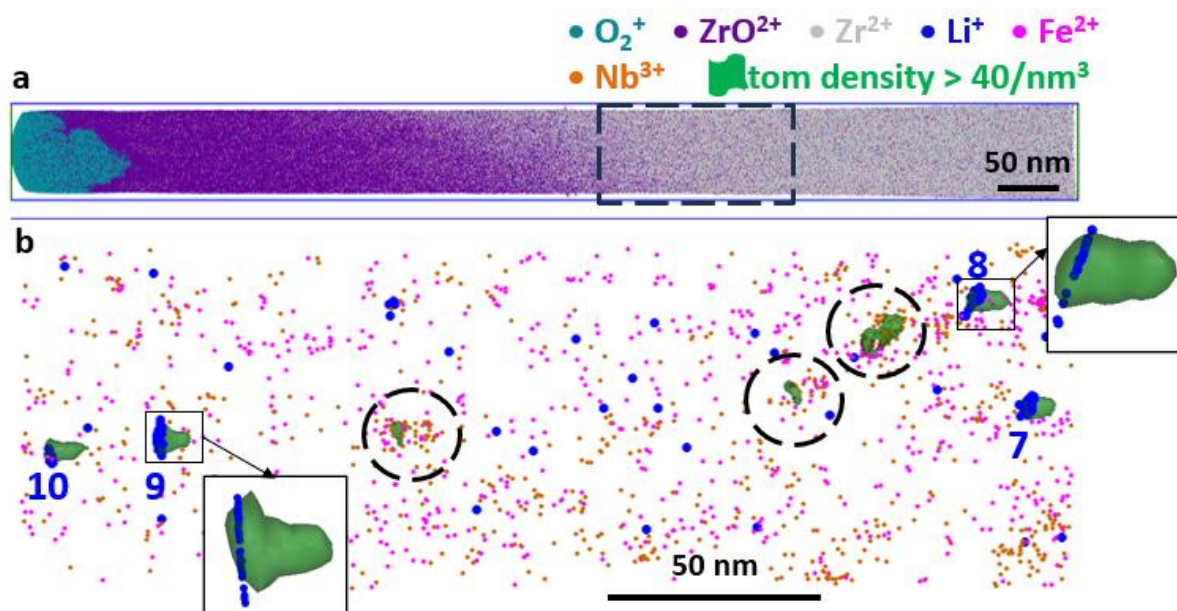


Figure 7-5. Typical APT dataset at the O/M interface from 2-cycle ex-reactor ZIRLO[®] alloy sample (2.6 years in-pile corrosion and 16 dpa irradiation damage). (a) Overlaid spatial distribution maps of O_2^+ , ZrO^{2+} , and Zr^{2+} . (b) Overlaid spatial distribution map of Nb^{3+} , Fe^{2+} and Li^+ in the region of the dashed box in (a) with 20 nm thickness. Green surfaces indicate regions with atom density higher than $40/\text{nm}^3$. Li clusters are labelled as 7-10 going from right to left. The two insets show magnified views of Li clusters 8 and 9.

The apparent planar morphology of the Li clusters in both these materials is likely also to be an APT artefact because the electric field required to evaporate for Li (14 V/nm) is much lower than that for Zr (28 V/nm), and so a substantially different evaporation behaviour is expected [274]. This can be explained using the schematic diagram shown in **Figure 7-6**. We suggest that in the alloy matrix, Li atoms are segregated to the irradiation-induced nanovoids, likely attached to the inner surface (**Figure 7-6(a)**). During APT analysis, when an individual nanovoid enriched with Li reaches the top surface of the evaporating APT sample, the nanovoid is opened up (**Figure 7-6(b)**), releasing all the Li atoms immediately. These Li atoms are then all evaporated and arrive at detector at the same time, and the reconstruction algorithm positions them at the same z location but with over a range of x and y locations, giving the apparent disk-shaped arrangement of Li seen in the experimental data and shown schematically in **Figure 7-6(c)**. Li clusters with similar morphologies, well correlated with nanovoids induced by high-dose irradiation, are also detected by APT around the O/M interface in reactor pressure vessel steels after more than 20-years of in-pile corrosion [275].

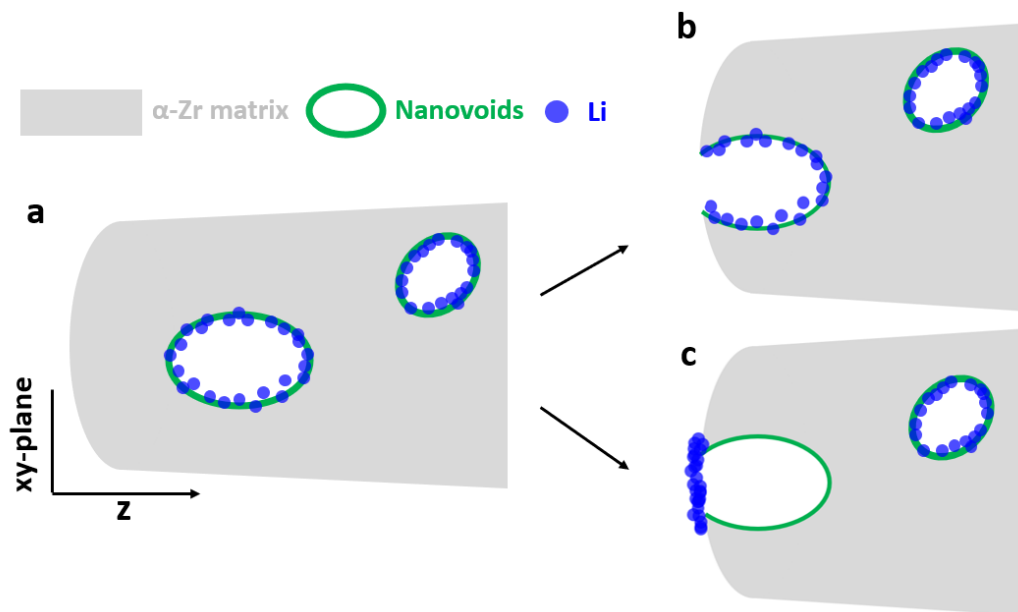


Figure 7-6. Schematic diagrams showing (a) the actual Li distributions within nanovoids in α -Zr matrix, (b) the suggested Li distribution as the nanovoid reaches the sample surface during APT analysis, and (c) The actual Li distribution of low-field Li as the nanovoid reaches the sample surface during APT analysis.

Figure 7-7(a) shows an APT dataset from 4-cycle X2 sample in the metal substrate within 1 μm of the O/M interface. After ~ 32 dpa neutron irradiation, it is not surprising to see well-defined Nb clusters with ~ 10 nm diameter form in the matrix lying on clear bands aligned on the c-plane with ~ 80 nm separation as previously reported ([49, 276] and **Section 5.2.2**). Interestingly, **Figure 7-7(b and c)** also shows strong Li segregation at the interface between the β -Nb SPP and the metal matrix.

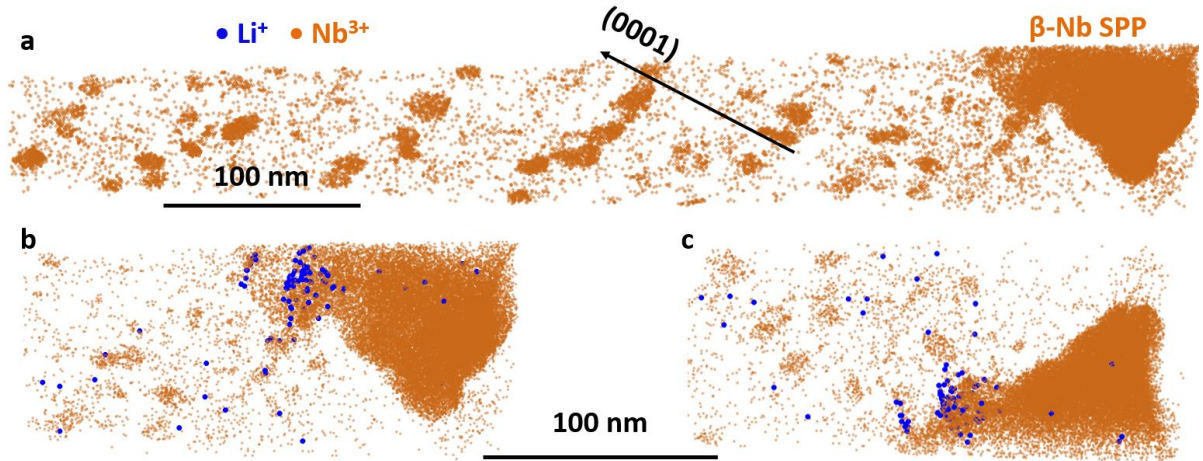


Figure 7-7. APT dataset in the metal below the O/M interface from 4-cycle ex-reactor X2 sample. (a) Nb³⁺ spatial distribution map showing a β -Nb SPP and bands of Nb clusters. (b) overlaid Nb³⁺ and Li⁺ map showing Li segregation at the β -Nb SPP interface. (c) is a 180° rotation of (b).

Penetration depth of Li

Figure 7-8 shows a large APT dataset from 1-cycle ZIRLO sample around the O/M interface, enabling analysis of a significant volume of material, and giving a chance to study the range of Li diffusion. Despite some background noise, several Li clusters around the O/M interface and in the metal are observed, and are identified by peaks in the Li concentration profile in **Figure 7-8(c)**. The deepest segregation is ~ 400 nm below the O/M interface and places a lower bound on the diffusion distance of Li into the ZIRLO metal substrate after one cycle, i.e. 2.7 μm (2.3 μm oxide thickness plus 400 nm penetration depth in α -Zr).

From $x = \sqrt{2Dt}$,

where x , D and t denotes Li diffusion distance in the α -Zr, diffusion coefficient of Li in the α -Zr at ~ 302 °C, and the diffusion time (1-cycle time, 1.3 years), in this dataset D is

estimated to be $8.89 \times 10^{-20} \text{ m}^2/\text{s}$. Based on the observation that Li penetrates faster than the oxide front grows downward consuming the underlying metal, we expect the limit of Li diffusion to be deeper into the metal in the higher-cycle samples. This distribution of Li atoms well below the O/M interface may have influence on the mechanical and corrosion performance of the metal matrix, but is beyond the scope of this thesis to study further.

The results presented above on both X2 and ZIRLO samples suggest that during in-pile corrosion Li can penetrate from the coolant water through the entire thickness of the oxide layer (2-10 μm) and dissolve hundreds of nm into the metal substrate. Because Li is almost insoluble in the $\alpha\text{-Zr}$ matrix [133], once in solution in the metal substrate, it segregates strongly to any lattice defects, i.e., irradiation-induced nanovoids and the SPP interfaces.

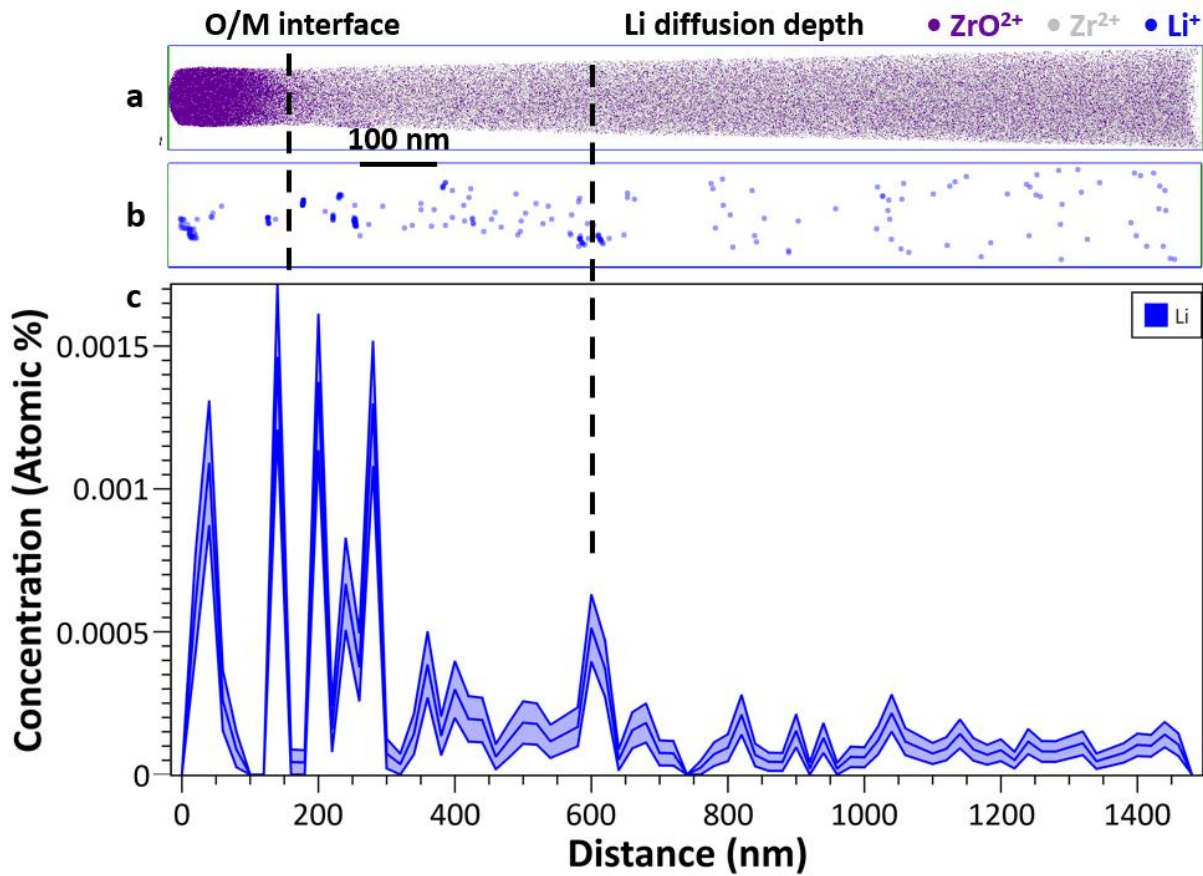


Figure 7-8. APT dataset showing 1-cycle ZIRLO O/M interface and substrate metal. (a) ZrO²⁺ and Zr²⁺ overlaid spatial map. (b) Li spatial map showing some Li clusters in the same volume of material. (c) Composition profile of Li from the top to bottom of the dataset. Left and right dashed lines indicate the position of the O/M interface and the limit of Li diffusion into the metal, respectively.

Redistribution of Li clusters during oxidation

The next question is how do these Li clusters at irradiation-induced nanovoids behave during oxidation. **Figure 7-9**(a and b) shows that diffuse Li clusters spatially correlated with nanovoids can still be observed in the oxide of the 1-cycle X2 alloy, although the distance to the O/M interface and thus the oxidation time are unknown. **Figure 7-9**(c) shows the well-defined planar Li clusters in the underlying metal that is in the same APT tip of (a). These indicate that the oxide advances into the metal substrate containing Li clusters, and while they become diffuse once incorporated into the oxide they can remain as identifiable clusters for some time in the oxide.

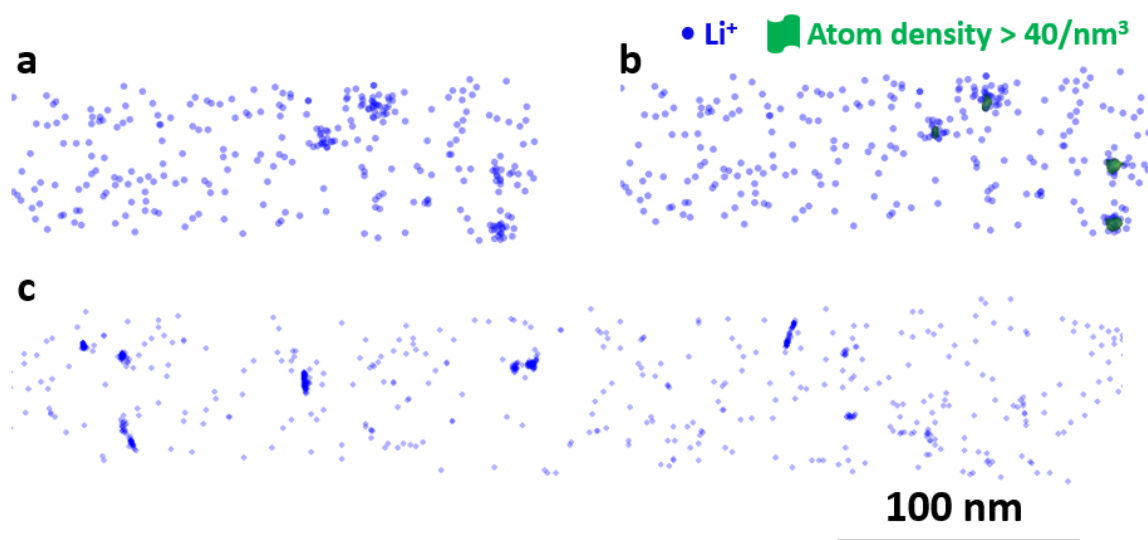


Figure 7-9. APT dataset from 1-cycle X2 sample around the O/M interface. (a) Li⁺ spatial map in oxide. (b) overlaid map of nanovoids (green isosurface with atomic density larger than 40/nm³) on (a). (c) Li⁺ spatial map in the underlying metal substrate from the same APT needle (but another run started on the fractured needle).

Finally, **Figure 7-10**(a) shows an APT dataset taken from the ZrO₂ oxide of 2-cycle ZIRLO sample. **Figure 7-10**(b and c) show respectively the distributions of Fe²⁺ and Li⁺ from the same oxide region. The irradiation-induced Fe clusters observed in the metal matrix in **Figure 7-3** and **Figure 7-5**, have mostly disappeared after incorporation into the growing oxide. In contrast, Fe segregation to oxide GBs as **Figure 6-9** and reported in [26, 111], is

still present. Although the 7 Da peak can still be observed in the dataset, the $^7\text{Li}^+$ signal becomes randomly distributed in the oxide matrix. This suggests that the diffuse Li clusters seen in the early-stage oxide (**Figure 7-9(a)**) finally become randomly distributed after a longer period time of incorporation in the oxide. An overall concentration of Li in the ZrO_2 is estimated to be $\sim 0.002\%$, whereas the concentration of Li in the metal matrix close to the O/M interface is below the APT detection limit in this study ($\sim 0.001\%$).

Nanovoids are shown as green isosurfaces in the insets in **Figure 7-10(c)**. The evaporation process of oxide materials is more complex during APT analysis due to their insulating nature. **Figure 7-11** uses a series of isosurface thresholds of atom density to be confident about identifying the nanovoids shown in **Figure 7-10**. Indeed, some of the denser regions are density fluctuations (black boxes), which normally align along the z-axis and disappear with higher isosurface values, but there are at least some denser regions that are morphologically-stable with higher isosurface values. The ion count is measured along one feature identified as a nanovoid as an example, **Figure 7-11(d)**, and it shows a similar atom count profile to the ‘ λ ’ type nanovoids, **Figure 7-4**. Therefore, this analysis confirms the presence of nanovoids in the oxide.

However, the oxidation process is known to introduce new nanovoids into the oxide matrix [57, 166], so it is not possible to know whether these are the remaining irradiation-induced nanovoids from the metal or newly-formed ones induced by oxidation. From the observation that Li segregation at nanovoids becomes diffuse during oxidation (**Figure 7-2(c)**, **Figure 7-9(a)**) and becomes completely random after longer times (**Figure 7-10(c)**), and that there is a substantial expansion on the formation of ZrO_2 from Zr metal [83], it seems reasonable to suggest that irradiation-induced metal nanovoids are lost during oxidation, together with the Li segregation they contained. And the nanovoids observed in the oxide are likely oxidation-induced ones. Li segregation at oxide GBs is not seen in this study, but the previous studies

[114, 127] showing this segregation was when the sample was corroded with water doped with hundreds of wtppm of Li. The ~ 3 wtppm content of Li in the coolant water in this study is apparently not high enough to see a clear segregation to the oxide GBs in these APT analyses.

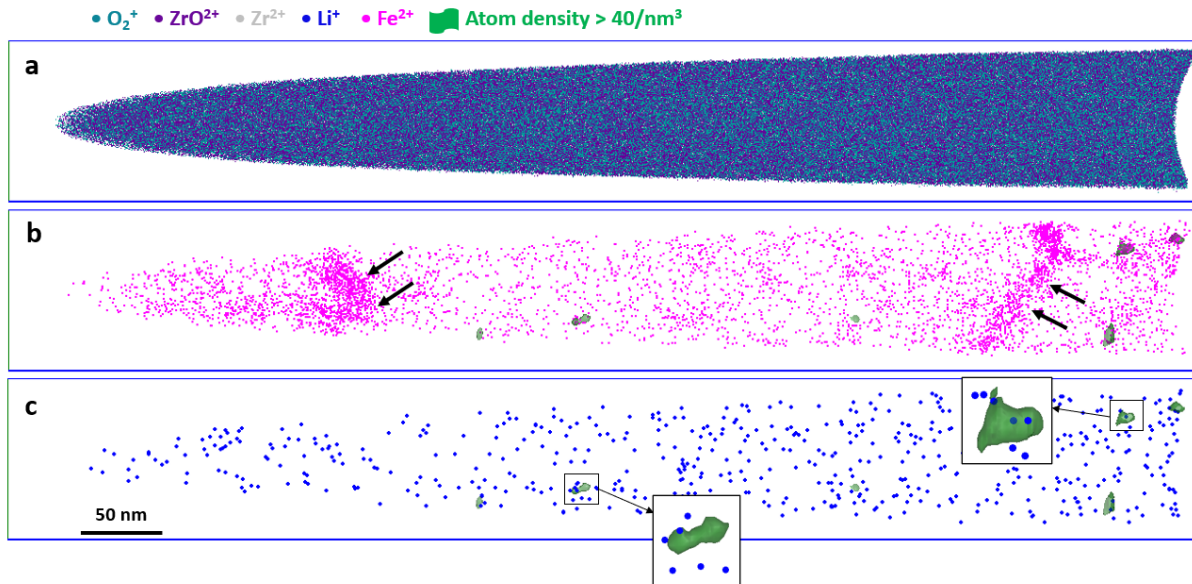


Figure 7-10. APT dataset in the oxide $\sim 1 \mu m$ above the O/M interface from a 2-cycle ex-reactor ZIRLO sample. (a) Overlaid spatial distribution maps of O_2^+ , ZrO_2^+ , and Zr^{2+} . (b) Fe distribution map showing Fe segregation to oxide GBs (indicated by the black arrows). (c) Li distribution map. Green isosurfaces indicate regions with atom density larger than $40/nm^3$. Two insets show magnified images of selected nanovoids, with further images in **Figure 7-11**.

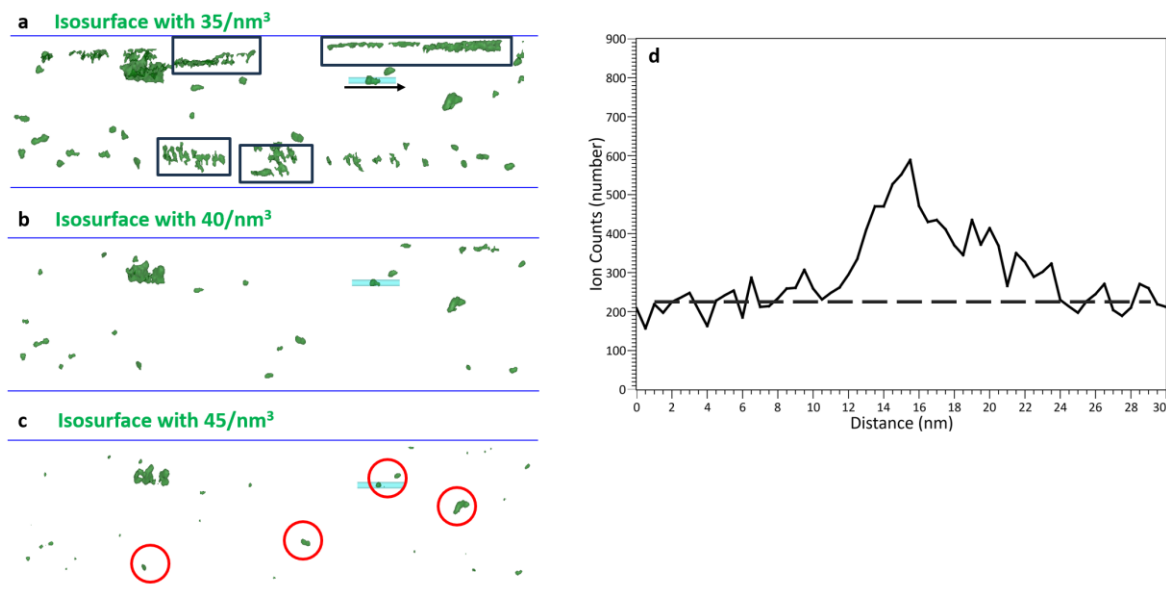


Figure 7-11. Nanovoid check in the APT dataset in **Figure 7-10** using different iso-density values (a-c), and a 1D atom count profile across a selected nanovoid along the arrow (d). Examples of artificial denser regions and actual nanovoids are indicated by black boxes and red circles, respectively.

Summary

This section has used APT analysis to investigate the atom-scale chemistry of X2 and ZIRLO cladding alloys that have been neutron irradiated, and in-pile corroded for 1-4 reactor cycles. Almost every dataset taken around the O/M interface with different in-pile times contains a significant 7 Da Li signal. Li diffuses faster than the growth of oxide, and it can diffuse through the entire thickness of the oxide layer (2-10 μm) and penetrate at least several hundreds of nm into the metal substrate. The mechanisms of Li in-diffusion from the primary water to the underlying metal are summarised in a schematic diagram in **Figure 7-12(a)**. Excess ^7Li is induced in the primary water by the transmutation of B, and this Li diffuses through the oxide layer via GBs. The observation of Li deep into the underlying metal shows that the O/M interface does not act as a barrier for the in-diffusion Li. Li has very low solubility in $\alpha\text{-Zr}$, so once into the underlying metal Li redistributes to microstructural defects, as shown by the strong Li segregation to the inner wall of irradiation-induced nanovoids (black circles) and at SPP interfaces. During further oxidation, **Figure 7-12(b)**, these metal regions will be incorporated into the oxide layer. The irradiation-induced nanovoids in the metal are removed during the phase transformation from metal to oxide at the O/M interface, and the Li clusters within these nanovoids become diffuse once in the Zr(O) region and finally randomly distributed in the oxide after a certain period of time following oxidation. The nanovoids observed in the oxide are mostly newly-formed corrosion-induced nanovoids (red circles, mostly on the oxide GBs [57]) on which there are no Li clusters.

The irradiation-induced Nb and Fe clusters are not spatially correlated with each other, but partially correlated with nanovoids or vacancy <a>-type loops, and are mostly redistributed after oxidation. Thus, the atomic scale details of the corrosion mechanism at the O/M interface involve the local redistribution of Fe, Nb and Li, all of which can contribute to the

rate determining processes. The solute redistribution during oxidation will be studied in details in **Sections 7.2** and **7.3**.

This is the first time that the presence of Li from the water has been detected in the underlying Zr cladding alloy, and since it is this metal at the O/M interface that is being consumed as corrosion proceeds, it is interesting to speculate how the redistributed Li could be playing a role in controlling the local corrosion rate. It has been shown that the Li concentration near the O/M interface will be controlled both by penetration through the oxide and by re-accumulation of Li from the metal as the oxide growth front proceeds. This dual process will determine the Li concentration locally, and hence the pH of water penetrating through the fossil oxide on top of the thin electrochemical barrier layer at the O/M interface could be higher than that of the external water. Such change in pH can significantly alter corrosion mechanisms on water dissociation [277], ZrO_2 phase transformation [278] and the formation of porosity [279].

However, even with the extremely high sensitivity and spatial resolution offered by APT analysis, the low Li content in the samples limits the detailed investigation of how Li interacts with nanofeatures in the oxide formed. This study provides valuable data on how deep the Li penetrates and the distribution of Li in materials that underwent real in-service degradation. Further APT and TEM studies on autoclave corroded sample with hundreds of wtpm of Li in the water [114] would be interesting, with the aim of further understanding how the Li distribution around the O/M interface can affect features like the oxide grain structure and local porosity that may help explain the phenomenon of Li-accelerated corrosion.

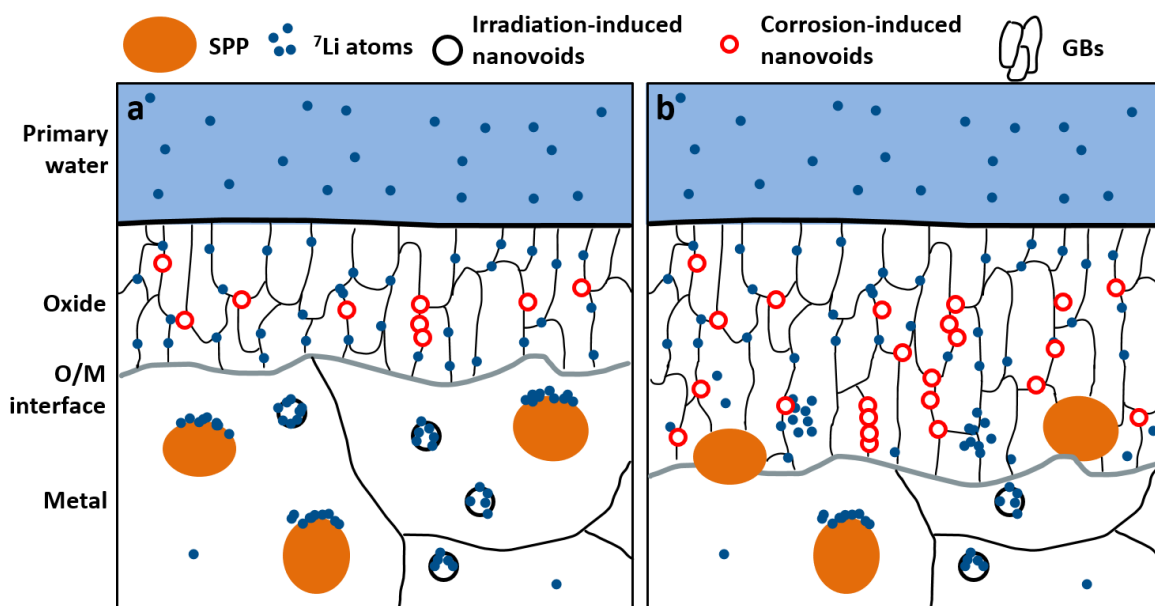


Figure 7-12. Schematic diagrams of (a) Li ingress from the primary water to the underlying metal substrate, and (b) redistribution of Li clusters during further in-pile corrosion.

7.2 Vogtle X2 alloy

Datasets from samples that have been in-pile corroded for different cycles are discussed together, because the effect of different corrosion times when considering APT datasets right at the O/M interface is considered to be limited, and the effect of different irradiation times has already been discussed in **Chapter 5**.

Oxide analysis

Figure 7-13 shows the distribution of Fe and Nb from a typical APT dataset from the 1-cycle X2 oxide. Nb clusters induced by irradiation are still present in the oxide, whereas Fe either segregates at oxide GBs or is randomly distributed in the oxide matrix. This indicates that after the irradiated metal is incorporated into the growing oxide, Fe clusters dissolve faster than Nb clusters. This APT dataset is ~700 nm long along the corrosion direction, and the analysis stopped before reaching the O/M interface, so we can assume that Nb clusters can persist in the oxide for at least ~700 nm deep into the oxide (which is approximately 150 days of exposure in reactor). It is interesting to know the limit of how long Nb clusters can persist in the oxide (or how far away to the O/M interface), but this analysis is difficult for

APT because most of the datasets extend for less than 1 μm in the z-direction. It has been reported that the bright contrast of Nb clusters in STEM-EDS images disappears at around 2.5 μm into the oxide in the same ex-reactor X2 sample [227]. However, this also depends on the irradiation dose at the point that the corrosion reaches a particular cluster, because those in the metal after higher doses are more enriched with Nb and should persist for longer after incorporation into the oxide.

The Fe signal is presented only by $^{56}\text{Fe}^{2+}$, because in oxide datasets $^{56}\text{Fe}^+$ is buried by $^{96}\text{Zr}^{16}\text{O}^{2+}$ and cannot be used to map Fe. Although using the $^{56}\text{Fe}^{2+}$ alone cannot show all the Fe ions in the dataset, it should be representative of the Fe distribution in the oxide, and reveal if Fe segregates only at GBs or whether clusters are still present. The detection of Zr^{3+} ions indicates an electric field of 20-30 V/nm during evaporation, where Fe should be mostly detected as Fe^{2+} .

The Nb signals in this oxide dataset have also been carefully checked. Four selected ranges of the mass spectrum related with Nb is shown in **Figure 7-14**. The normal Nb peaks at 31 Da ($^{93}\text{Nb}^{3+}$) and 46.5 Da ($^{93}\text{Nb}^{2+}$) in a metal dataset are not observed, **Figure 7-14(a and b)**, and Nb is detected as NbO_2^{2+} at 62.5 Da and NbO_2^+ at 125 Da, **Figure 7-14(c and d)**. Nb is detected as oxidized ions in the oxide is possibly due to the combined effect of the different evaporation field and composition in the oxide as well as that Nb atoms in the oxide matrix have been oxidised to Nb^{2+} , Nb^{3+} , or Nb^{5+} states. Both of the two NbO_2 peaks are affected by the thermal tails of $^{92}\text{Zr}^{16}\text{O}$ peaks, especially the $^{93}\text{Nb}^{16}\text{O}_2^{2+}$ peak. The arrow in **Figure 7-14(d)** indicates the level of the static background noise, and the thermal tails from the ZrO peaks are much higher than that, therefore these two Nb peaks are significantly affected by these tails and this influence cannot be mitigated. The $^{93}\text{Nb}^{16}\text{O}_2^{2+}$ ion is ranged very narrowly to minimise the incorporation of thermal tails from previous peaks. It is also possible that some Nb signals of $^{93}\text{Nb}^{3+}$, $^{93}\text{Nb}^{2+}$, $^{93}\text{Nb}^{16}\text{O}^{2+}$ and $^{93}\text{Nb}^{16}\text{O}^+$ are buried in background noise

or thermal tails, but it should contribute only limited numbers of counts. Most of the Nb atoms in the dataset should have been taken into account using the ranging strategy for Nb in **Figure 7-14**.

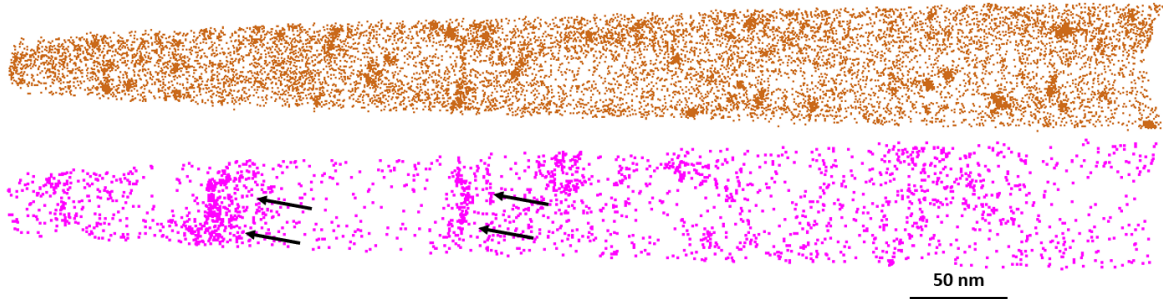


Figure 7-13. APT dataset ‘PZ16_M13_1cXR’ from the oxide of a 1-cycle Vogtle X2 alloy. Spatial distribution of Fe ($^{28}\text{Fe}^{2+}$) and Nb ($^{93}\text{Nb}^{16}\text{O}_2^{2+}$) in a 20-nm slice. Fe segregation at oxide GBs is indicated by arrows.

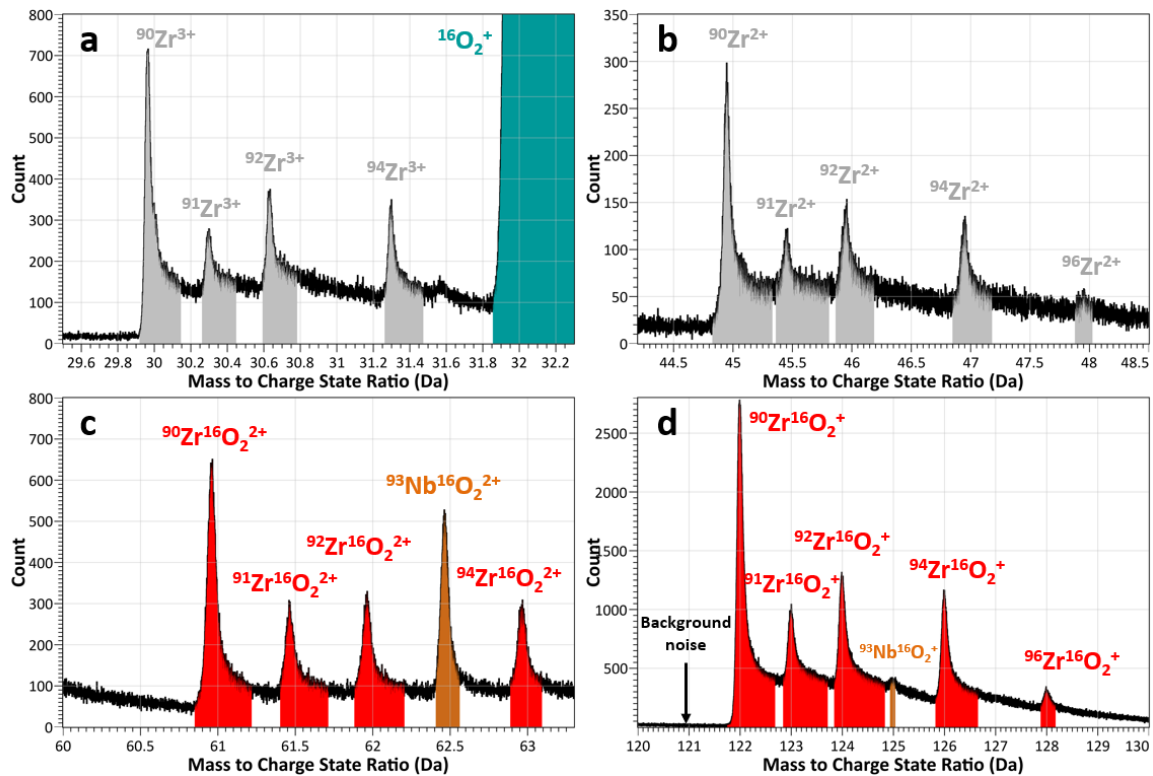


Figure 7-14. Mass spectra of dataset in **Figure 7-13** from selected ranges, (a) 29.5-32.3 Da, (b) 44.4-48.6 Da, (c) 60-63.3 Da, and (d) 120-130 Da. Peaks are labelled with ion types. Note the different vertical axes.

A similar Nb cluster analysis using the isosurface method as in the metal (**Chapter 5**) is applied to these NbO_2 signals. Given the Nb clusters are observed to be smaller than in the irradiated metal (**Figure 7-13**), lower thresholds, $c_{\text{iso}}=0.8\%$, $v_{\text{iso}}=20 \text{ nm}^3$, are used to identify

Nb clusters, **Figure 7-15(a)**. The proxigrams of Zr, O and Nb concentrations for these Nb clusters are shown in **Figure 7-15(b)**. There is ~3% Nb, 33% Zr and 65% O in the cluster core, giving a lower than 0.1 Nb/Zr ratio. Unlike the delayed oxidation seen in SPPs with lower O content than the surrounding oxide matrix, these clusters have been fully oxidised to a (Zr,Nb)O₂ composition. Before corrosion, there is ~30% Nb and 60% Zr at the Nb cluster core in the 1-cycle irradiated metal, **Figure 5-9(a)**, giving a ~0.5 Nb/Zr ratio. Although the Nb content may be slightly underestimated because of the complicated mass spectrum in the oxide dataset, the Nb/Zr ratio at the core of oxide Nb cluster is still far below the 0.5 Nb/Zr ratio in the initial metal Nb clusters. This suggests that at least some of the Nb originally enriched in the metal Nb clusters is released to the bulk oxide during oxidation, and the cluster radius, determined from the proxigram horizontal axis, decreases from 3 nm to 2 nm.

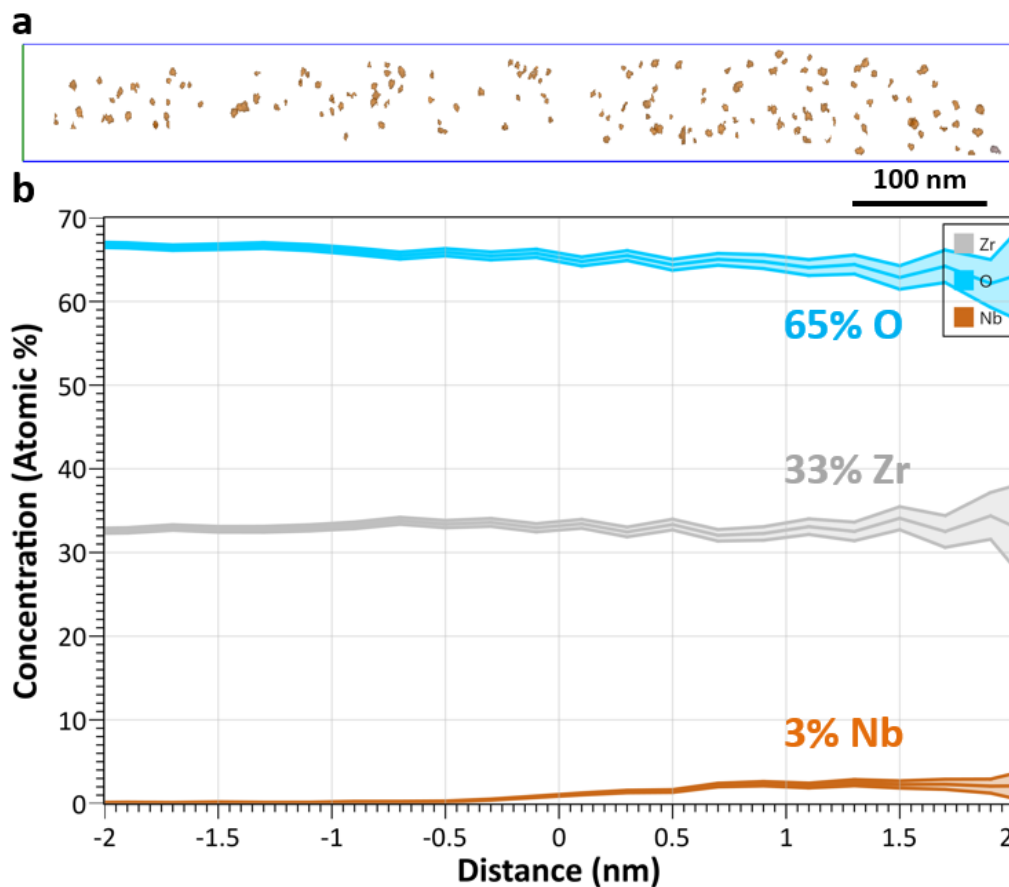


Figure 7-15. (a) Nb clusters identified in APT dataset in **Figure 7-13** using isosurface method with $c_{iso}=0.8\%$, $v_{iso}=20 \text{ nm}^3$. (b) Proxigram of Nb clusters, binning with 0.2 nm.

Chemistry of the O/M interface

A typical APT dataset from the O/M interface of a 4-cycle in-pile corroded X2 sample is shown in **Figure 7-16**. The oxide, interface and underlying metal are divided by the dashed lines according to the Zr-O ratio. Zr and O concentrations throughout the dataset along the corrosion direction are shown in **Figure 7-17(a)**, similar to **Figure 7-2**, the interface thickness is ~250 nm. This could be biased by the limited sampled volume in APT analysis, but in this work the O/M interfaces formed during in-pile corrosion seem to be thicker than those formed during autoclave corrosion, which is opposed to the theory that oxide formed at a higher corrosion rate should have a thinner interface.

Nb, Cr, Al and Fe show clustering and banding on the basal plane in the underlying metal substrate, clearly showing that the oxide front is advancing into an irradiated metal substrate. The $\langle 0001 \rangle$ direction in the metal region can be determined by the hit map in **Figure 7-17(b)**. Due to trajectory aberrations and surface diffusion, fewer ions are detected around the crystal poles, and this is often seen most intensively in the $\langle 0001 \rangle$ pole in the HCP α -Zr matrix. Four out of the six major zone axes of the HCP crystal structure can also be seen with lower densities of ion hits.

A similar Li distribution at the interface to that discussed in the last section is observed. Li clusters are well-defined in the metal, become diffuse in the Zr(O) region, and finally dissolve in the oxide. I have attributed this trend of Li distribution as the disappearance of irradiation-induced nanovoids during oxidation.

During oxidation most of the solute clusters formed in the irradiated metal also redistribute. Fe clusters dissolve once incorporated in the Zr(O) region, Al, Cr and Mo clusters become diffuse in the Zr(O) region and dissolve once in the ZrO₂ region, whereas Nb clusters can still be observed in the ZrO₂ region, indicating that Nb clusters show delayed oxidation and

can persist a period of time after full oxidation. The difference in the response to oxidation of these types of clusters could be due to the different electrochemical properties and diffusivities, i.e., Nb clusters are nobler than other clusters, and Nb has a lower diffusivity [238]. The redistribution of these irradiation-induced solute features may be relevant to the matrix phase transformation. The crystal structure starts to change in Zr(O) region where O gets into the metal lattice, and the phase transformation to hexagonal ZrO happens, and then to ZrO₂. It is likely that the crystal defects like vacancies and dislocations are removed during these transformations, and clusters originally nucleated on these defects should redistribute during the oxidation reactions. The observation of residual Nb clusters in ZrO₂ may suggest that the formation of some of the Nb clusters are not related to the irradiation-induced defects.

Nb clusters during oxidation

In order to confirm that the Nb clusters lose Nb during oxidation, the compositions of Nb clusters in the regions of underlying metal and Zr(O) from the dataset in **Figure 7-16** are directly compared. Clusters in the underlying metal are considered similar to those in the irradiated-only metal, (Section 5.2), so same isosurface thresholds of 0.6% and 50 nm³ are used to identify them. The clusters in the Zr(O) region are identified using lower thresholds due to the potential effect of O, 0.6% and 50 nm³.

Proxigrams from clusters in these two regions are compared in **Figure 7-18**(a and b). For clusters in the metal, there is still ~40% Nb in the cluster core giving a ~0.7 Nb/Zr ratio, and clusters have a radius of ~4 nm, confirming that although this region is immediately below the Zr(O) region, there is limited O content and the existing irradiation-induced clusters remain intact. For clusters in the Zr(O) region, by contrast, the cluster core has an average composition of 25% Nb, 20% O and 50% Zr, giving a 0.5 Nb/Zr ratio, and the cluster radius decreases to 2 nm. Therefore, it is very clear that Nb clusters formed during irradiation

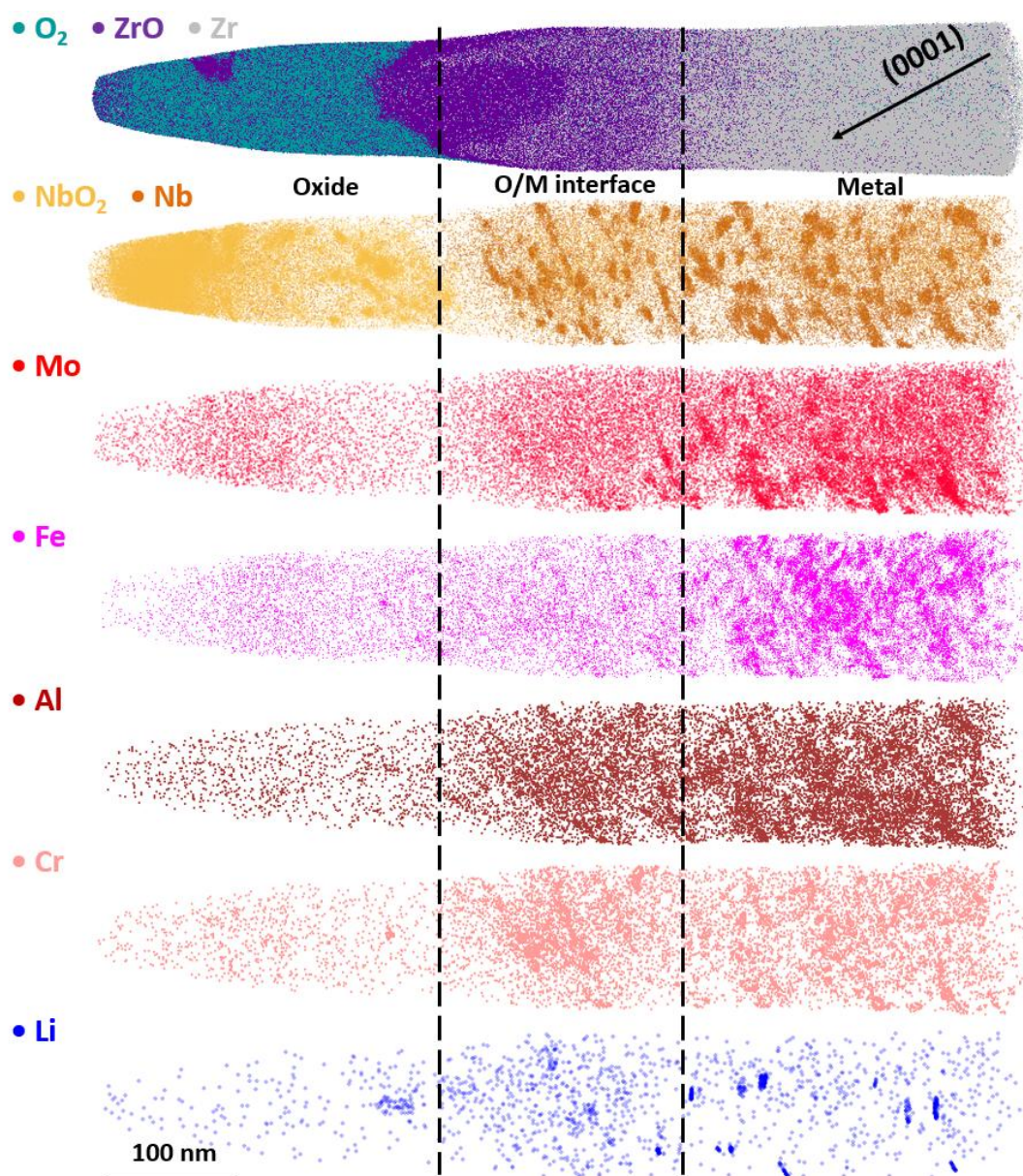


Figure 7-16. APT dataset 'PZ04_M17_4cXR' from the O/M interface of a 4-cycle Vogtle X2 alloy. Spatial distribution of O₂, ZrO, Zr, Nb, NbO₂, Mo (⁹⁴Mo³⁺), Fe (⁵⁶Fe²⁺), Al, Cr and Li (⁷Li⁺).

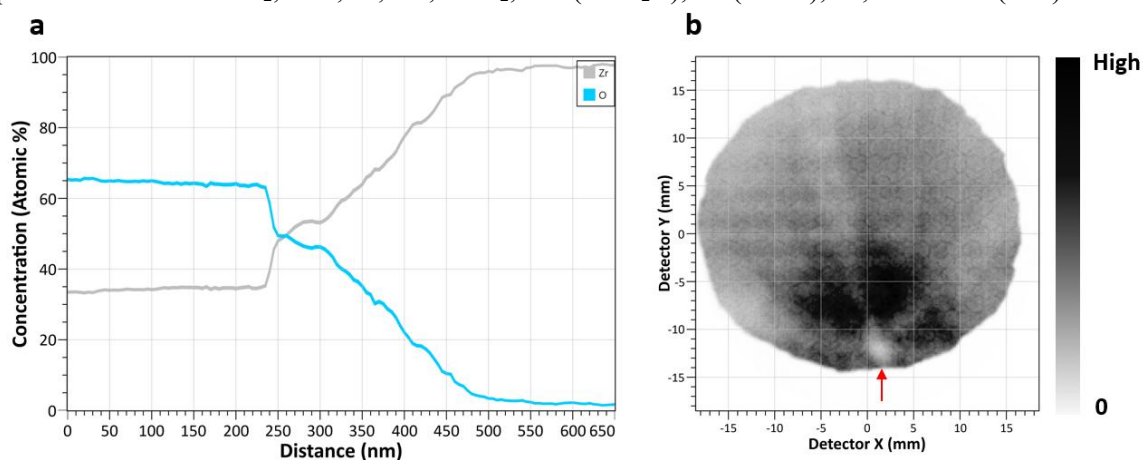


Figure 7-17. (a) 1D Zr and O chemical profile along z-axis in APT dataset in **Figure 7-16**. (b) Detector hit map taken from the metal region of **Figure 7-16**, black contrast indicates more ion hits, the white dot indicated by the red arrow is the <0001> crystal pole.

gradually dissolve to the surrounding matrix during the early stages of the oxidation process, and the Nb content in the surrounding matrix is expected to increase. Additionally, the surrounding matrix has ~35% O content, so has been oxidised to the $\alpha\text{-Zr}(\text{O}_{\text{sat}})$ state, whereas within the Nb clusters there is only ~20% O. This indicates that although Nb clusters are not as noble as $\beta\text{-Nb}$ SPPs during oxidation, they still show some extent of delayed oxidation at early stages of corrosion. The Nb/Zr ratio within $\beta\text{-Nb}$ SPPs and Nb clusters both decreases during oxidation. The results can be interpreted to show that $\beta\text{-Nb}$ SPPs evolve by intermixing with Zr (**Section 6.1**), whereas the Nb clusters release Nb. The difference might be explained by the fact that $\beta\text{-Nb}$ SPPs are the thermodynamically stable phase while the cluster have at best a dynamic equilibrium while under irradiation.

The modified microchemistry in the irradiated metal substrate redefines the electrochemical properties and thus the local corrosion resistance. The elevated Fe and Cr content induced by the release from sinks deteriorates the corrosion resistance [248]. A speculative summary of mechanisms of corrosion of dynamic Nb composition in irradiated metal are summarised in **Figure 7-19**. During irradiation, **Figure 7-19(a)**, in-solution Nb is depleted to form Nb clusters, and the matrix has a decreased Nb content (from 0.4% Nb to <0.2%) and so a degraded corrosion resistance. However, these Nb clusters can themselves offer delayed oxidation and protect the surrounding matrix locally. During oxidation, they are continuously dissolving and releasing Nb back into the surrounding oxide matrix, **Figure 7-19(b)**. The protectiveness from these Nb clusters weakens as they dissolve but since there is more Nb in the matrix, the corrosion resistance of the matrix improves. Therefore, this is a competition between the decreased protectiveness provided by the dissolving Nb clusters, and the increased corrosion resistance by having more Nb back in the matrix.

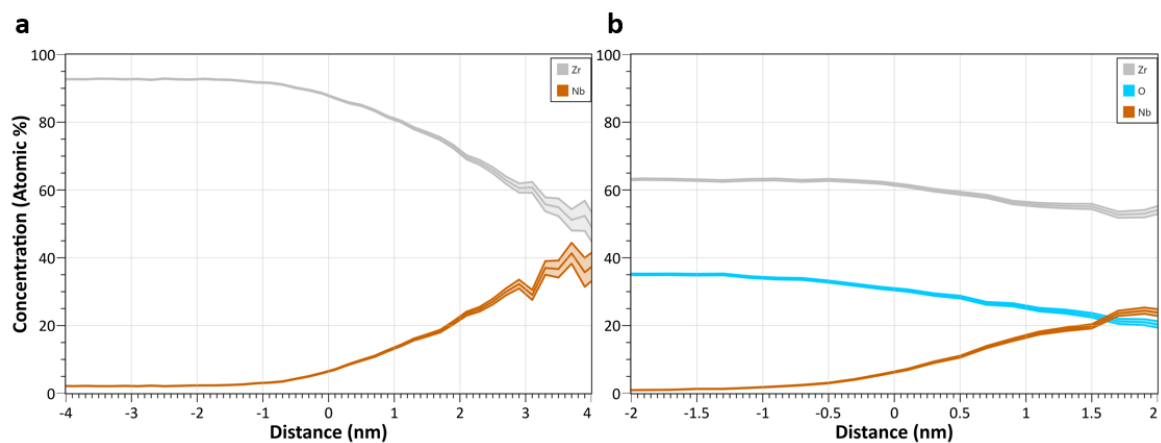


Figure 7-18. Proxigrams of Nb clusters in the regions of (a) α -Zr metal, and (b) Zr(O) from **Figure 7-16**.

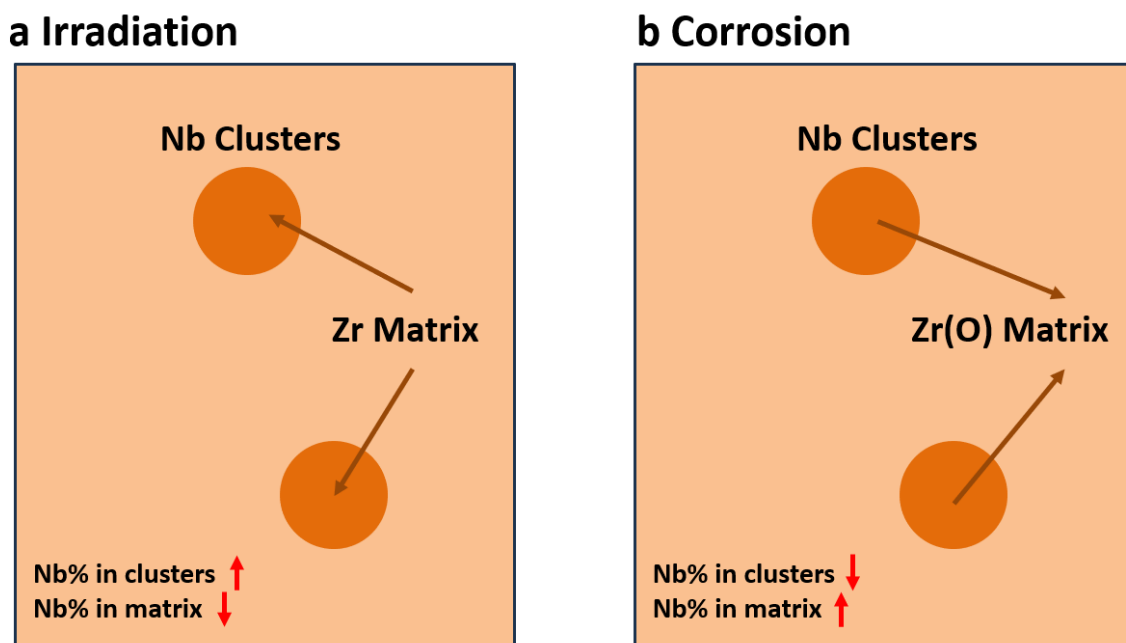


Figure 7-19. Diagram of Nb content change between the Nb clusters and matrix during (a) irradiation and (b) early-stage corrosion.

7.3 Vogtle ZIRLO alloy

Oxide analysis

An APT dataset from the O/M interface of a 1-cycle ZIRLO sample is shown in **Figure 7-20**.

The O/M interface is located at the bottom of the dataset, so this region of oxide is several hundreds of nm above the O/M interface. Similar to the X2 oxide in **Figure 7-13**, Fe clusters

are mostly dissolved once incorporated into the oxide, while Nb clusters can still be observed in the oxide. Segregation of Fe, Nb and Sn on an oxide GB is observed (red arrows). Sn is also observed in several other GBs that can be identified in the density map (black arrows). Sn segregation on oxide GBs is less evident as in the metal, **Figure 5-20**. Some high contrast regions in the density map could be nanovoids (highlighted in circles).

Nb clusters in the oxide are identified using the isosurface method with parameters of 0.6% and 50 nm³, **Figure 7-21(a)**. There is 4% Nb, 40% Zr and 55% O in the cluster cores, whereas the surrounding matrix has more than 60% O, indicating that these Nb clusters in ZIRLO oxide also show delayed oxidation. The Nb/Zr ratio now is only ~0.1, much lower than the Nb/Zr ratio in Nb clusters in 1-cycle ZIRLO metal (~0.3), confirming that Nb has been released from Nb clusters into the matrix during corrosion.

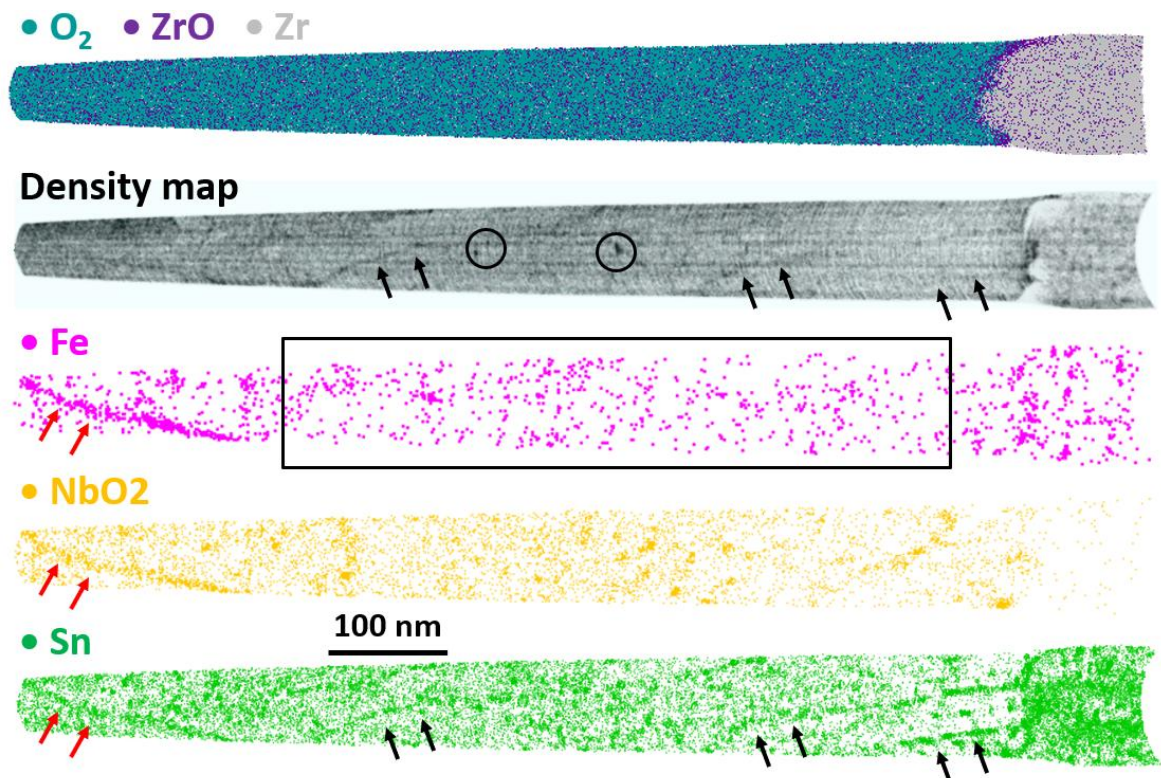


Figure 7-20. 10-nm slice of APT dataset ‘PZ16_M19_1cZR’ from the O/M interface of a 1-cycle ZIRLO oxide. Spatial distribution of O₂, ZrO, Zr, NbO₂, Fe and Sn, and the density map.

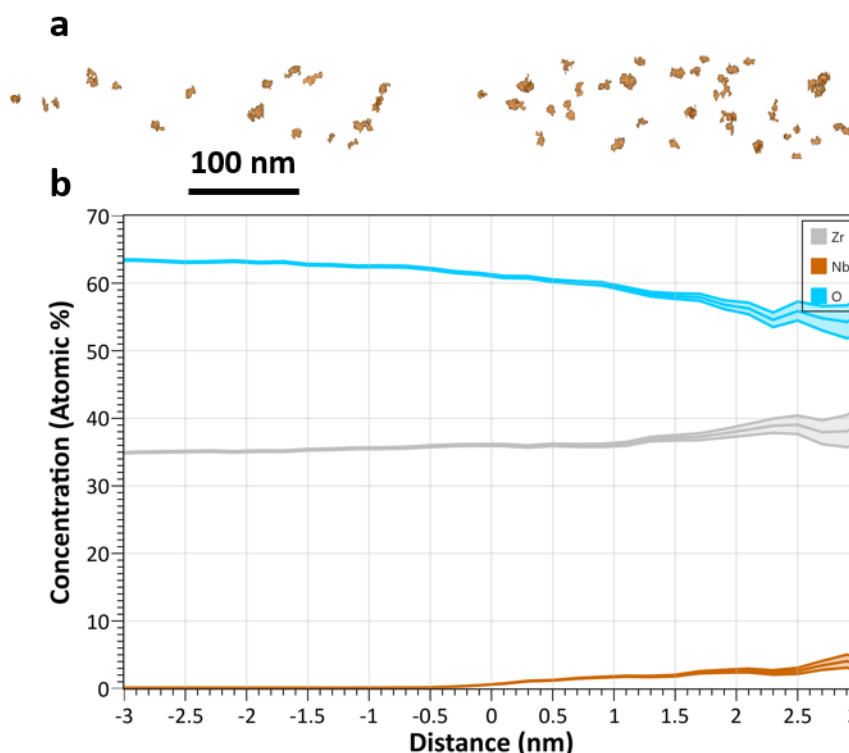


Figure 7-21. (a) Nb clusters in oxide identified in the dataset in **Figure 7-20** using isosurface thresholds of 0.6% and 50 nm³. (b) Proxigram of Nb clusters.

Another oxide dataset from a 2-cycle ZIRLO oxide is shown in **Figure 7-22**, however, this dataset stops before reaching the O/M interface, so it is unclear how far this oxide region is away from the O/M interface. The Fe clusters are all dissolved, but Nb clusters and Fe segregation at GBs are observed. At this stage, supposedly with longer corrosion time than that of region of material in **Figure 7-20**, there is no longer any sign of Sn segregation at oxide GBs.

Nb clusters identified with isosurface parameters of 0.6% and 50 nm³ are shown in **Figure 7-23(a)**, and the proxigram of these clusters are shown in **Figure 7-23(b)**. There is 3% Nb, 25% Zr and 60% O at the cluster core, giving a ~ 0.12 Nb/Zr ratio and a ~ 4 nm cluster radius. Because the same parameters are used to identify all of these clusters, these values should be comparable to those in 1-cycle ZIRLO oxide in **Figure 7-21(a)**. Although this region has presumably been oxidised for longer (further away from the O/M interface), the Nb/Zr ratio and cluster radius are both larger. This is because when the corrosion front reaches the

clusters, 2-cycle Nb clusters are larger and are more enriched with Nb compared to the 1-cycle Nb clusters shown in **Figure 5-23**, so the dissolution of these Nb clusters in the oxide takes longer.

The results shown above show that once a volume of material is incorporated into the oxide, the irradiation-induced clustering process stops and a corrosion-induced dissolution process starts until the clusters are fully dissolved into the oxide bulk. What we observe in these datasets is the result of these two competing processes. Therefore, when analysing in-pile corroded oxidation data of a certain region of material, we need to remember that the local chemistry is influenced by both the irradiation time before corrosion starts and the period of time that this region has spent into the oxide.

A composition profile across a Nb-rich SPP in a 1-cycle X2 is shown in **Figure 7-24**. This SPP must have been irradiated first and then oxidised. ~0.2% Cr and 0.3% Fe are seen within the SPP, so it should have started as a Laves phase SPP. This SPP has ~45% O, showing delayed oxidation compared to the ZrO_2 surroundings. It would be helpful to summarise the change of composition of SPPs after long-term irradiation and corrosion, but this would require large amounts of data on SPPs from different-cycle samples and lying at different depths in the oxides, so APT is not suitable for such analysis.

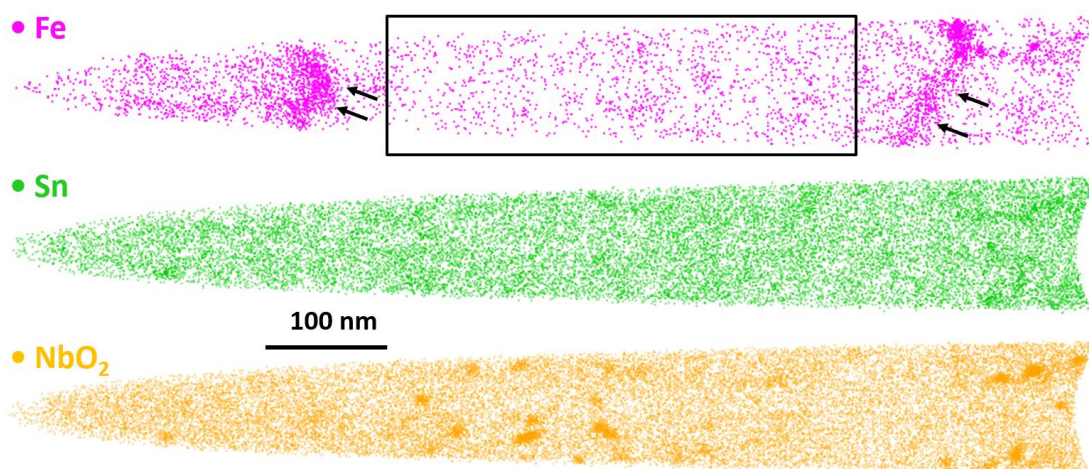


Figure 7-22. 10-nm slice APT dataset ‘PZ10_M04_2cZR’ from the oxide of a 2-cycle ZIRLO alloy. Spatial distribution of Fe, Sn and NbO_2 . Oxide GBs are indicated by arrows.

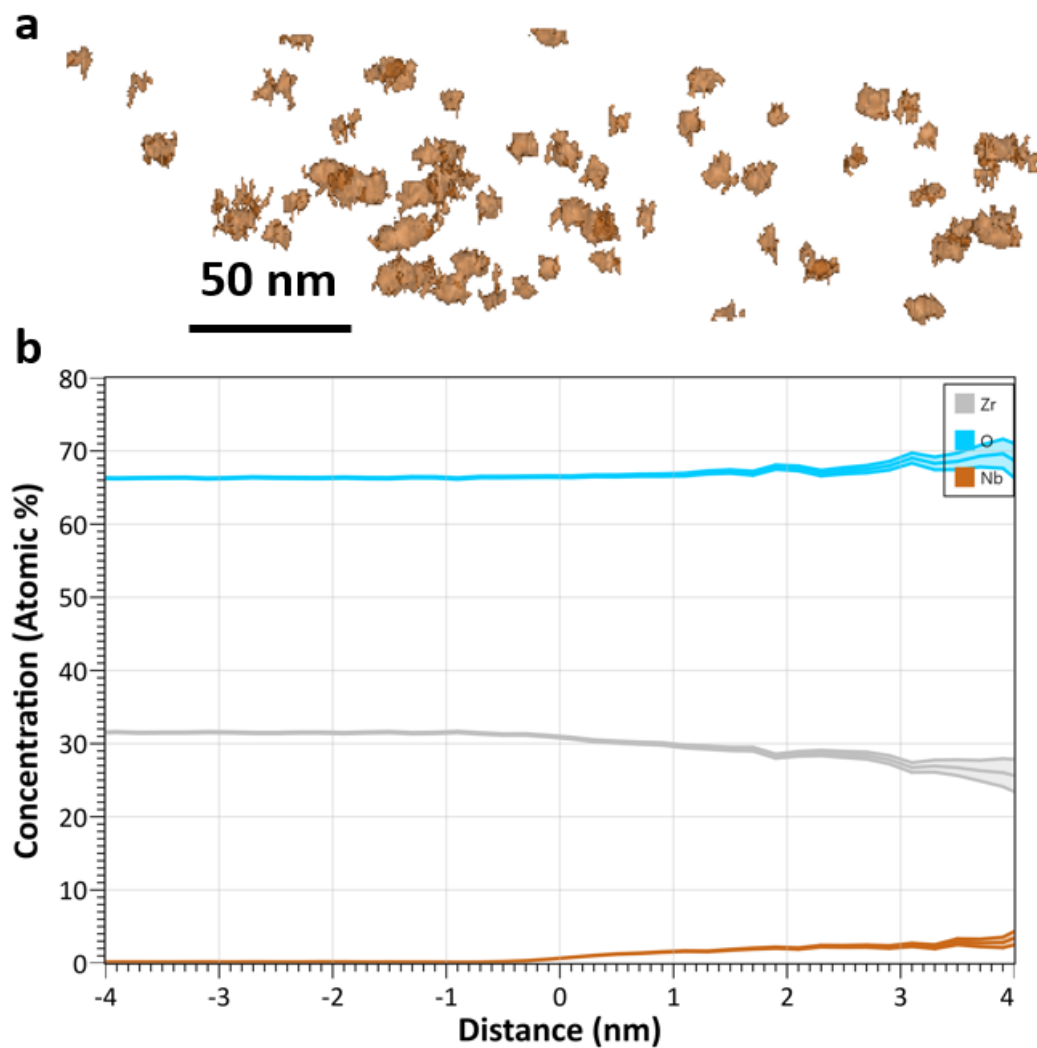


Figure 7-23. (a) Nb clusters in oxide identified in the dataset in **Figure 7-22** using isosurface thresholds of 0.6% and 50 nm³. (b) Proxigram of Nb clusters.

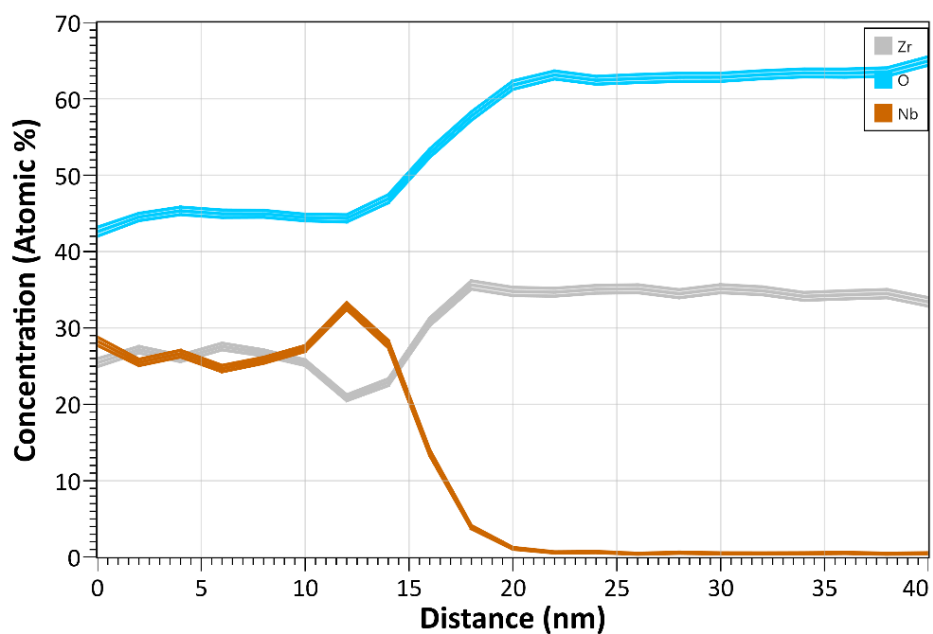


Figure 7-24. Chemical profile of Zr, Nb and O from a SPP in APT dataset 'PZ09_M02_1cZR' in 1-cycle ZIRLO oxide.

Chemistry of the O/M Interface

A complex O/M interface of a 1-cycle ZIRLO alloy is shown in **Figure 7-25**. The Zr-O concentration ratio decreases from ZrO_2 to ZrO , but instead of decreasing further to Zr(O) , it increases back to ZrO_2 again, and this change repeats several times. This suggests that the oxidation front is extremely non-planar, possibly due to the preferential O diffusion along some features. Similar ZrO_2 blocks in the underlying metal have also been observed in TEM images [27, 137, 141, 249], and is likely because that some GBs are oxidised preferentially to ZrO_2 , leaving the in-grain bulk partially oxidized to ZrO , and these ZrO regions then look like ZrO blocks embedded in ZrO_2 . Similar APT results of complex Zr-O compositions at the O/M interface have been reported in [144]. The fast diffusion of O along and the early oxidation of the GBs are indeed observed in **Figure 6-7** and **Figure 6-8**. In this thesis, this complex O/M interface are only seen in ZIRLO samples (not in X2), so may be related with the complicated columnar grain structures resulting from the SRA state, as identified with Sn and Al segregation in **Figure 5-20**.

Interestingly, higher C concentrations are also observed in the ZrO_2 regions (up to 10%), but not in the ZrO or Zr(O) regions. From the literature and other observations in this thesis, C is not in the baseline metal, is not a transmutation product of a known elements, and should not be corrosion products, so this can only be explained by more C-containing gas from the analysis chamber adsorbing onto the tip apex when the material at the apex is ZrO_2 . Thus, detection of C as well as other gaseous elements, N, H, CO, etc, should be excluded when calculating the composition.

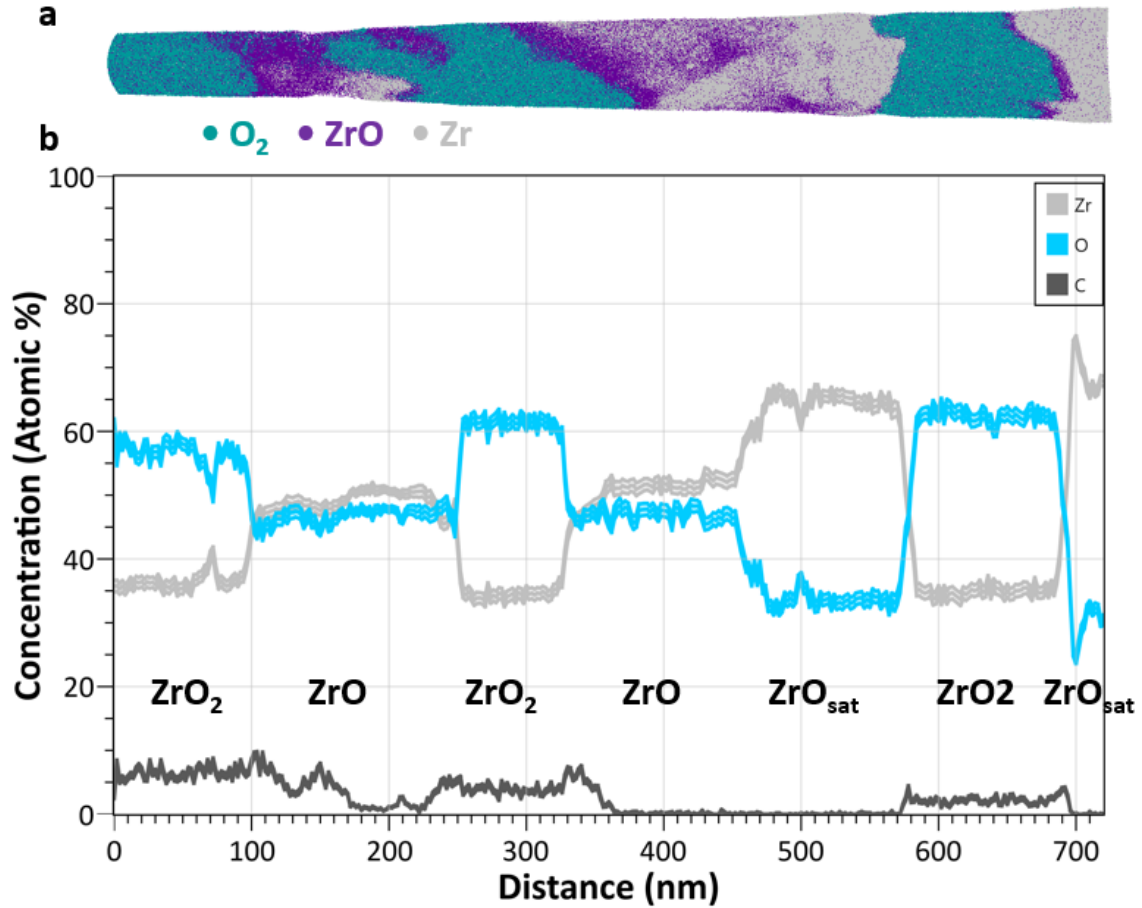


Figure 7-25. APT dataset ‘PZ16_M16_1cZR’ from the O/M interface of 1-cycle Vogtle X2 alloy. (a) overlaid spatial distribution map of O₂, ZrO and Zr. (b) 1D concentration profile of Zr, O and C from the top to the bottom of the dataset.

A 20-nm slice from **Figure 7-25(a)** is taken to study the solute distribution within these complex interface regions. The solute distribution still follows the rule at different metal to oxide phases as observed around the normal O/M interface. Sn has higher content and more Sn clusters can be observed in the ZrO and Zr(O) regions than in ZrO₂, indicating that Sn is rejected during the transformation of ZrO to ZrO₂, similar as that observed in autoclave corrosion in **Section 6.1**. Nb clusters can still be observed, but are detected as Nb in the ZrO and Zr(O) region and NbO₂ in the ZrO₂ region. Fe clusters have already been dissolved in Zr(O) region, but Fe seems to segregate at some interfaces, like the Sn, possibly also suggesting depletion from ZrO₂.

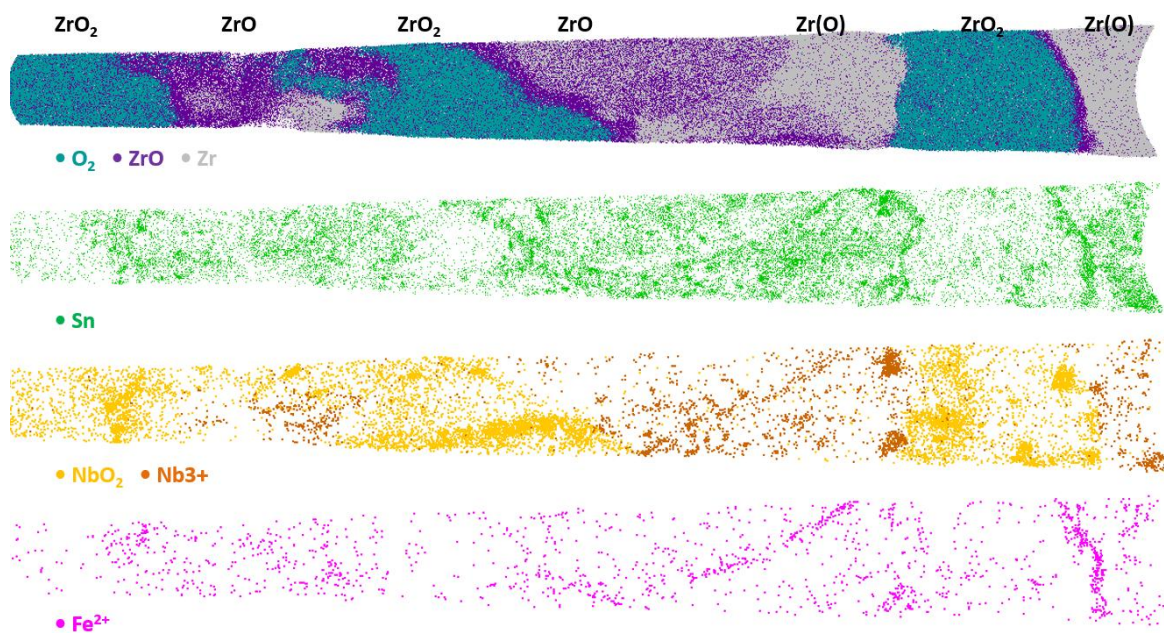


Figure 7-26. 20-nm slice from the APT dataset in **Figure 7-25**. Spatial distribution of O_2 , ZrO , Zr , Sn , Nb , and Fe .

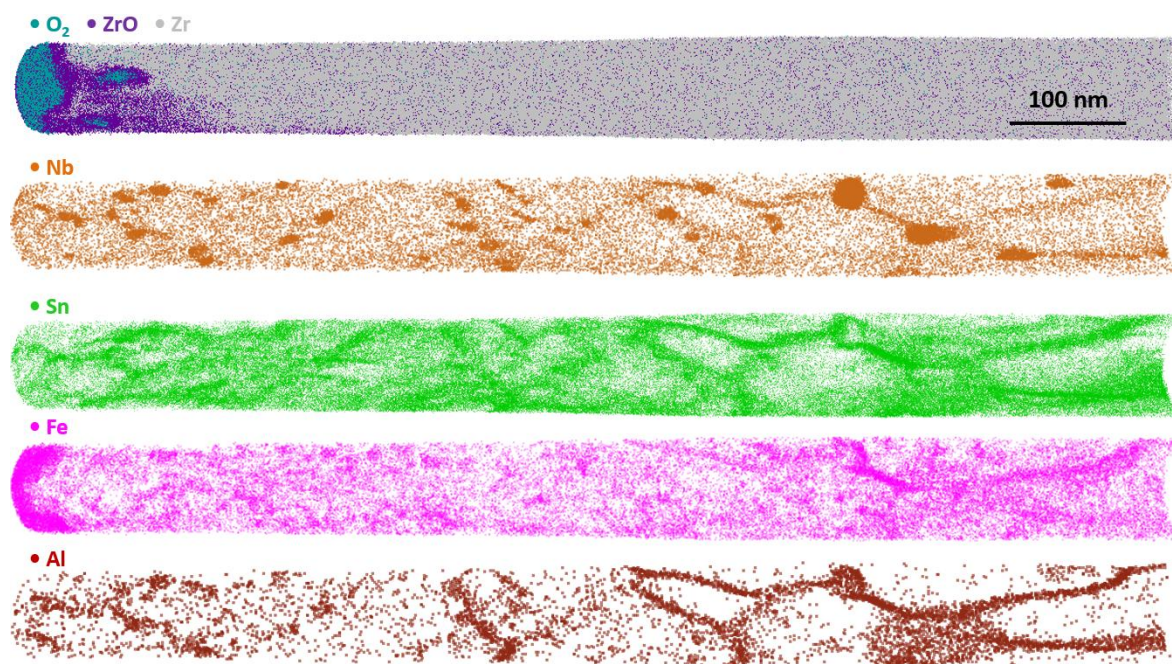


Figure 7-27. APT dataset 'PZ10_M16_4cXR' from the underlying metal of a 4-cycle ZIRLO alloy. Spatial distribution of O_2 , ZrO , Zr , Nb ($^{93}\text{Nb}_2^{3+}$), Sn , Fe ($^{56}\text{Fe}^{2+}$) and Al .

7.4 Discussion and conclusions

The in-pile corrosion of RXA X2 alloy and SRA ZIRLO alloy in the Vogtle reactor has been studied mainly using APT. The APT specimens were made around the O/M interface to study the corrosion mechanisms on irradiated metal substrates. These in-pile corroded samples have thicker O/M interfaces than those formed during autoclave corrosion, contradicting some of the previous studies. Before the O diffuses into the underlying metal forming Zr(O), these metal regions have a similar microstructure with the irradiated metal tens of μm away from the O/M interface.

The solutes respond differently once incorporated into the oxide. Fe clusters become immediately randomly distributed in the Zr(O) region, and Cr, Al, Li, Mo (transmuted from Nb at high dose) clusters become diffuse in the Zr(O), and randomly distributed once into the ZrO₂. Sn segregation at metal GBs induced during irradiation is also gradually dissolved to the matrix since in the Zr(O) region and finally become randomly distributed after some period of time in the oxide. By contrast, Nb clusters are much more stable during corrosion and show delayed oxidation behaviour. Even though they start to dissolve in Zr(O) by releasing Nb to the surrounding oxide matrix and shrinking, from the limited volumes analysed in APT datasets in this chapter, they can persist at least 1 μm into the ZrO₂. Therefore, during in-pile corrosion, the Nb trapped in clusters during irradiation is released back to the matrix, and the local electrochemical protectiveness provided by Nb clusters weakens while the more macroscopic corrosion resistance provided by in-solution Nb improves.

ZIRLO alloy is more likely to form a O/M interface with a complex geometry because the oxide is advancing into the much more complicated irradiated microstructures shown in **Figure 5-21**. These Sn networks and non-uniform distribution of solutes may promote

preferential diffusion of O into the underlying metal, explaining the much higher in-pile corrosion rate observed in ZIRLO alloy (13.65 μm at 4 cycles) than X2 alloy (4.63 μm at 4 cycles), **Figure 3-2**. Nb-rich SPPs that have been irradiated first have decreased Nb/Zr ratio when the oxidation front reaches, but after some time incorporated in the oxide they still show delayed oxidation than the surrounding ZrO_2 matrix that is no difference to non-irradiated SPPs in the oxide. So the protectiveness from the delayed oxidation of SPPs still exist in the in-pile conditions, but with a weakened effect due to the lower initial Nb/Zr ratio.

8. Conclusions and future work

This thesis has studied a range of Zr cladding alloys in different irradiated and corroded conditions, and compared them with their baseline states to understand in-reactor degradation mechanisms. This chapter summarises the results from each chapter, followed by suggestions for future work.

8.1 Conclusions

Methods & APT

Due to their insulating nature and the high density of defects, laser-mode APT has to be used to analyse Zr oxide samples, which inevitably introduces more gaseous signals and large thermal tails in the dataset, complicating the analysis. In addition, for Nb cluster analysis or H analysis, cryoFIB must be used to prepare Zr APT tips to minimise the H ingress during FIB milling process. For instance, the isosurface and MSM methods on Nb clusters analysis described in **Section 3.4.4**, with suitable parameters selected, can give similar results on the clusters composition and statistics, as has been reported in RPV steels [212]. This is because both methods can effectively limit the influence of overlap between $^{92}\text{Zr}^1\text{H}^{2+}$ and $^{93}\text{Nb}^{2+}$ at 46.5 Da, providing that the annular milling was conducted using cryoFIB so the H ingress during FIB has been minimised. This is the first time the two most common APT cluster analysis methods have been compared on Zr alloy systems, and I have also shown that the proxigram function can visualise effectively the composition changes at the cluster interface and the cluster core composition, which can reveal thermodynamically-equilibrium states.

The EDS/FIB correlative method described in **Section 3.3.1** can be used to make APT tips containing Zr_2Cu SPPs, and this method can be readily used to make APT specimens from site-specific regions of material. The trajectory aberrations described in **Section 3.4.5** are

widely used in **Chapters 5, 6 and 7** to identify GBs and corrosion- or irradiation-induced nanovoids in both metal and oxide APT datasets by identifying higher atom density regions.

Baseline materials

Four Zr cladding alloys are studied, including the first APT analysis of Cu- and V-containing alloys. Cu segregates to GBs and other interfaces similar to Fe, and also forms Zr_2Cu SPPs (27% Cu). V forms $Zr(V,Nb,Fe)_2$ Laves phase SPPs (40% V) and is also enriched in β -Nb SPPs (5% V). It can be concluded from the careful comparison of the microstructure and chemistry of the four alloys that Sn fully dissolves in the α -Zr, but other solute and impurities reach the solubility in α -Zr and are mostly enriched in sinks including SPPs, interfaces and dislocations. The bulk solubility of Nb is $\sim 0.4\%$, whereas that of Cu, Fe and Al is only tens of ppm, in agreement with the equilibrium phase diagrams.

Irradiation effects

As has been shown in previous work [40, 49], solutes and impurities redistribute significantly during irradiation, with increasing extent at higher doses, forming segregation in the form of clusters and bands. This redistribution depends highly on the solute type and starting microstructure, being ordered in the RXA equiaxed grains but highly heterogeneous in the SRA ZIRLO on the columnar GBs. This difference probably explains the much worse structural stability (higher irradiation-induced growth) of SRA ZIRLO under irradiation.

Quantitative composition analysis of solutes like that is carried out in different regions of the irradiated materials in **Chapter 5** can be hardly found in the literature. The calculated bulk compositions excluding SPPs and GBs can be used to understand whether solutes are released from these sinks during irradiation. The bulk compositions of Sn and Nb do not increase, indicating no evident release of Nb and Sn from sinks, whereas Fe, Cu and other trace impurities are significantly released to the bulk causing substantial increase in

composition. Fe and Cu are enriched in a banding structure on the basal plane, possibly on $\langle a \rangle$ loop rafts or $\langle c \rangle$ loops, and these bands are out-of-phase with the Sn bands, as previously reported in [49]. The decrease of Nb concentration inside the SPPs is achieved by the intermixing of Zr atoms. The in-solution Nb forms clusters which gradually align on the basal plane and saturate at 40%, similar to the Nb concentration in the heavily-irradiated β -Nb SPPs (35%), and grow larger with higher irradiation doses. This $\sim 40\%$ Nb seen in both Nb clusters and SPPs indicates that this is a thermodynamically-stable composition. The higher dose rate in BOR-60 reactor than the Vogtle reactor accelerates the process of reaching this thermodynamic endpoint, but has insignificant effects on the composition. For the first time it has been observed that some of the Zr and Nb atoms transmute into ^{94}Nb and Mo isotopes [280-282], having the same distribution as ^{93}Nb , which can improve the mechanical properties but reduce the corrosion resistance [21].

Autoclave corrosion

APT analysis on normal water-corroded Zr oxide in **Section 6.1** shows that the Sn/Zr ratio decreases and Nb/Zr ratio remains the same as a volume of material transitions from metal to oxide, indicating that Sn is depleted to the metal side during oxidation (similar to [14, 145]) while Nb does not move much. Both β -Nb and Laves phase SPPs show delayed oxidation behaviour as widely reported [21, 155], and can locally protect the underlying metal. In addition, the oxidation and diffusion of O species preferentially occurs on GBs or newly-formed sub-GBs in the underlying metal immediately below the O/M interface.

APT analysis in **Section 6.3** on the D-spiked Zr oxides show similar results as previous studies [57] that the 18 Da OD^+ signal is segregated to oxide GBs identified using Fe segregation or higher atom density due to the trajectory aberrations. The new NanoSIMS results on D-spiked oxide complement to previous studies [65, 128], and with the higher spatial resolution of APT, I concluded that the D hotspots in APT and NanoSIMS data,

despite the different dimensions due to the distinct spatial resolution, represent the same microstructural feature. This indicates that nanovoids aligned on the oxide GBs act as strong traps for H species, which, before become interconnected at later-stage corrosion, can actually delay the in-diffusion process. Similar APT analysis was applied on ^{18}O spiked oxide in **Section 6.2**. 34 Da and 19 Da signals are suitable to map the distribution of ^{18}O in oxide, and showing direct evidence for the first time that ^{18}O segregates to the columnar GBs, which confirms the long-standing hypothesis that O preferentially diffuses along the oxide GBs [27, 70, 248]. Spatial correlation of the same oxide GBs is observed in correlative TEM and APT analysis, but imaging of TEM on APT specimen with nanocrystalline grain structure can be difficult due to the increasing thickness down the tip shank. Because both O and H diffuse along the oxide GBs, it is reasonable to consider whether they diffuse together in the form of hydroxyl species. Observation of D and OD signals in NanoSIMS results having the same distribution and previous FTIR results of the detection of OH and OD bonding [161, 267] both support this theory.

In-pile corrosion

Excessive Li is produced in the primary water due to the transmutation of B, so the cladding materials are actually subjected to corrosion of modified water chemistry. I have shown for the first time in **Section 7.1** that the Li atoms can diffuse through 2-10 μm oxide layer into the underlying metal, with the diffusivity coefficient estimated to be $8.89 \times 10^{-20} \text{ m}^2/\text{s}$, and segregate at irradiation-induced nanovoids because Li is not soluble in the $\alpha\text{-Zr}$. These Li segregations become diffuse once in the Zr(O) and become randomly distributed after a certain period following full oxidation. The previously-reported Li segregation on the oxide GBs [114, 127] is not seen in these samples because the Li content in the water chemistry is much lower in this study.

In-reactor corrosion happens on the irradiated metal substrate, during which irradiated-induced solute segregations redistribute at the O/M interface becoming gradually randomly distributed. A similar observation has been reported on in-reactor corroded Zr-Sn alloys [44], whereas little data can be found on Zr-Nb alloys. Most of the segregations (Fe, Al, Sn, Li, Mo) disappear immediately after incorporation into the Zr(O) region, while Nb clusters can still persist after the surrounding matrix has been fully oxidised, showing delayed oxidation behaviour. During this process, Nb clusters gradually lose Nb atoms into the surrounding oxide matrix, inducing an increased Nb/Zr ratio and can by the C4 model [62] improve the electrochemical properties of the oxide and thus the corrosion resistance.

Based on the results in this thesis, the accelerated corrosion kinetics in in-reactor corrosion compared to the autoclave corrosion can be attributed to

- The more aggressive water chemistry. The higher content of Li in the primary water is more likely to cause Li-accelerated corrosion. The higher amount of hydroxyl groups from the radiolysis of H₂O may accelerate the in-diffusion process of corrosion species.
- The significantly modified chemistry in metal and oxide. The release of Fe and Cr and also trace impurities from SPPs will increase their concentrations in the bulk, which can deteriorate the corrosion resistance [248]. Nb is depleted from the solid solution from 0.4% to 0.2% (**Section 5.1.4**) to form Nb clusters during irradiation, so the corrosion resistance of the Nb-doped matrix is decreased. In addition, the distribution of Li and Mo may also alter the electrochemical properties of the underlying metal.
- The crystal defects. An excess of point defects will promote bulk diffusion of corrosion species, and the existing dislocation loops and their local strains can also add more interconnected preferential diffusion pathways for the corroding species.

8.2 Suggestions for future work

Irradiation

Similar APT analysis should be carried out on the BOR-60 W10 alloy (ZIRLO alloy variant with V) at 4, 16, 33 dpa to compare with the results on W13 and X2 alloys, and to study the redistribution of V during irradiation and validate the thermodynamically-equilibrium compositions observed in other irradiated alloys.

Proton/ion irradiation with different dose rates but to the same total dose should be carried out to confirm the assumption that dose rate has insignificant effect on the endpoint of the cluster compositions, but affects the kinetics of the process. This will help predict how exposure in different reactor types may influence the damage processes in these alloys.

Simulations should be carried out to explain the different redistribution behaviours of solutes and the thermodynamically-equilibrium composition in matrix and clusters, i.e. whether the Zr-40% Nb seen in Nb clusters and Nb-rich SPPs is a local minimum in energy.

<c> loops [283] and ring-shaped clusters [48] are expected in highly-irradiated materials but are not observed in the APT data in this thesis. It is not sure if this is due to different alloys or the APT running parameters, so it is necessary to run these irradiated samples in voltage mode for better data quality. The Irradiated ZIRLO should be analysed using STEM-EDX to confirm that the Sn networks are on columnar metal GBs.

Corrosion

Autoclave spiked corrosion tests should be carried out with 100% D water. It is impossible to distinguish H ingress during corrosion from spurious H in APT analysis, so with 100% D water we know any H signal is from the contamination. 100% D water will also introduce more D atoms into the APT specimen so the analysis of D-containing species will be easier.

^{18}O and D spiked corrosion tests on post-irradiation samples should also be carried out to understand the in-diffusion mechanisms of corrosion species into a metal substrate full of irradiation-induced crystal defects.

Similar APT analysis on Li-spiked samples should be carried out so that the Li in-diffusion pathways and the distribution at the O/M interface can be clarified. On such non-irradiated samples, the Li distribution in the nanovoids-free underlying metal will also be interesting.

In-pile corrosion

Corrosion of post-irradiation samples. Strictly, in-pile corrosion is a parallel in-situ irradiation and corrosion process, which cannot be used to unambiguously study the corrosion of irradiation-damaged material, because of the many other in-situ factors that may accelerate the corrosion (e.g., the interrupted nucleation and growth process of the new oxide grains). Comparison of the analysis on samples after in-pile corrosion and post-irradiation corrosion can make the in-situ factors the only variable, to try and answer if the major factor for acceleration in in-pile corrosion is the irradiated metal substrate or the other in-situ factors.

APT and TEM correlative analysis on highly irradiated samples should be undertaken to better understand the relationship between solute segregation and crystal defects, e.g., whether clusters are related with $\langle a \rangle$ loops and whether solute bands are related with $\langle a \rangle$ loop rafts or $\langle c \rangle$ loops.

More experimental and simulation work is needed to understand the dynamic chemistry at the O/M interface during the in-pile corrosion, and the potential effect on the local corrosion performance.

9. References

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