

High resolution characterisation of corrosion and hydrogen pickup of Zr-Nb cladding alloys



A thesis submitted for the degree of Doctor of Philosophy

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6/1/2016

ABSTRACT

Zr cladding alloys have been used for many years as the first safety barrier layer of a nuclear reactor. However, the recent Fukushima accidents and industrial demands to increase the burnup of fuels have led to increasing interest in a detailed mechanistic understanding of aqueous corrosion and hydrogen pickup and the performance at high temperatures.

As part of an international MUZIC-2 programme (Mechanistic Understanding of Zr Corrosion and Hydrogen pickup), I have used a range of advanced microscopy techniques to study the microstructure, the nanoscale chemistry and the porosity in a series of zirconium alloys at different stages of corrosion and hydrogen pickup. Samples from both autoclave and in-reactor conditions were available to compare, I have focussed on RXA (recrystallised 580°C) Zr-1.0Nb and annealed (720°C) Zr-1.0Nb alloys. A set of samples from different exposures times were chosen to represent early, pre-transition and post-transition samples in order to compare the microstructure and microchemistry of the oxides, the metal-oxide interface and the metal.

(Scanning) Transmission Electron Microscopy ((S)TEM), Transmission Kikuchi Diffraction (TKD) and automated crystal orientation mapping with TEM (ASTAR mapping) were used to study the grain structure and phase distribution. Significant differences in grain morphology were observed between samples oxidised in the autoclave with different corrosion rates, with more uneven metal-oxide interface, more parallel cracks and less organised oxide grains in the fast corroding samples. Comparing with autoclave samples, the in-reactor samples have shorter, less well-aligned monoclinic grains and more tetragonal grains. The rapidly oxidising annealed Zr-1.0Nb alloy also have much higher tetragonal grain fraction comparing with the slow corrosion rate RXA Zr-1.0Nb alloys. Porosity in the oxide is predicted to have a major influence on the overall rate of corrosion and hydrogen pickup, and there is much more

porosity in the annealed Zr-1.0Nb alloy than found in either the RXA alloy or the similar alloy exposed to neutron irradiation. A combination of Energy Dispersion X-ray (EDX) mapping in STEM and Electron Energy Loss Spectroscopy (EELS) analysis of second phase particles can reveal the main and the minor element distributions respectively. The annealed Zr-1.0Nb alloys have β -Zr SPPs with nano crystalline structure and much larger size. Although they does not relate with the higher density of cracks in the oxide, the large SPP size can connect together all the small cracks that are generated by the huge amount of tetragonal to monoclinic phase transformation during corrosion and provides pathway for corrosion and hydrogen pickup. Two kinds of SPPs are found in the RXA Zr-1.0Nb alloys, one is β -Nb and another one is Zr-Nb-Fe Laves phase. Neutron irradiation seems to have little effect on promoting fast oxidation or dissolution of β -Nb precipitates, but encourages dissolution of Fe from Laves phase precipitates. Electron Energy Loss Spectroscopy (EELS) analysis of the oxidation state of Nb in β -Nb SPPs in the oxide revealed the fully oxidised Nb^{5+} state in the SPPs deep into the oxide, but Nb^{2+} in the crystalline SPPs near the metal-oxide interface. EELS, TKD and ASTAR mapping have also revealed the presence of suboxide layers with the hexagonal ZrO structure predicted by ab initio modelling. The combined thickness of the ZrO suboxide and oxygen-saturated layers at the metal-oxide interface correlates well to the estimated instantaneous oxidation rate, suggesting that the presence of this oxygen- rich zone combining with the part where porosity is not interconnected is the protective oxide that is rate limiting in the key in the transport processes involved in corrosion and hydrogen pickup.

ACKNOWLEDGEMENTS

From my apartment in Schwedenplatz in the city center to Vienna International Center where the IAEA is located, there are five metro stops, mostly underground in the dark. But there is one stop called Donauinsel, under the bridge across the Danube river. When the weather is nice, there will be 20 seconds of brightness in the metro trip, with a beautiful view of shining river surface, trees and flowers on the island near the river. There are often kindergarten kids who are on the trip to visit UN, the whole train will go “wow”, full of children’s surprises and smile. That is the moment when you’ll understand why it is called Blue Danube.

I’d like to think my DPhil as a similar journey as the metro ride, coming from one station with crowd of people, I was simply one of the many Chinese students who had a good score and happened to be lucky enough to be in Oxford as a student. Later on, I stayed way too much time in the dark TEM room with microscopes and diagrams, until the moment, realised the beauty of the whole trip, and without noticing, reached the final destination, on the 26th floor of the UN building, with the whole view of Vienna and Danube river underneath.

None of these would have happened without the most amazing supervisors in the world, Chris and Sergio. They are the most kind and patient people I’ve ever met. I thank my parents for teaching me how to be a good person, but I’d like to think Chris and Sergio are like my parents in academic life, teaching me from an innocent baby: how to walk (operating all the microscopes), how to talk (speaking in front of different audiences and making a clear point), how to write (papers, reports and thesis of course). They showed me the every right way to do everything, so in future, I can remember how to do things right. They are both great people, I feel very lucky to be their students.

Chris taught me the idea of freedom which I didn’t understand too much from my early years in study. He encouraged me to try new ideas, new experiments, go to impossible trips,

manage impossible tasks, he asked me to make my own choices. He said things are difficult, because if they were easy, everyone else will be doing it. I still remember on the night before the ASTM Zr conference, we were heavily jetlagged, worked on our presentation in the hotel lobby until 10 pm and he said: you made a decision whether you want to give the talk before 12 pm tomorrow. His trust made everything possible and I know I will try my best not to let him down. The talk went very well, having done it in the Zr Olympics put a good closure to my DPhil project. The final day at the ASTM meeting, Chris, Sue and I went out for dinner at the Hilton Head seaside, there were beautiful sunset and dolphins in the sea. For a moment, Chris said, “now I’ve no one to give concerts tickets to”. I guess the sunset was just too shiny or the sea water has just gone to my eyes.

I also remembered there were so many times Sergio says “Things happen” with a typical Sergio’s smile on his face. Some of the Spanish jokes I would still take a moment to realise but thinking about them is a sweet moment. The ability to screw things up (either destroying a delicate TEM sample in the FIB or messing up the microscopes) and be OK with it is another way of learning. I appreciate Sergio has a lot of patience of teaching us and tolerating our ignorance. No one would be able to learn anything unless learnt from mistakes.

A lot of the work in this thesis comes from the MUZIC-2 consortium which I feel very lucky to be in: it makes me understand how to tackle a problem in different perspective, how to understand others and how to make yourself understandable. It also makes me travel around the world. Some of the new techniques used in this thesis such as TKD and ASTAR mapping are thanks to the fruitful collaboration within MUZIC-2 with Dr. Al Garner, Dr. Philipp Frankel and Prof. Michael Preuss from Manchester University (Figure 3-7, Figure 3-8, Figure 3-9, Figure 3-10, Figure 3-11, Figure 4-7 and Figure 5-4) and Dr. Ali Gholinia, Dr. Allen Harte and Matthew Topping for operating the microscopes, also many 6 am train rides from Oxford to Manchester to hand deliver the delicate TEM samples. The TKD map in Figure 5-6

is thanks to Dr. Arantxa Vilalta-Clemente and Prof. Angus Wilkinson from Oxford. The neutron irradiated samples in Chapter 5 are made by Pia Tejlund from the hot lab in Studsvik. I personally grow a lot during the twice a year MUZIC-2 meetings, special thanks to many lively discussions and personal encouragements from WestinghouseTM (Bob Comstock, Lars Hallstadius, Mats Dahlback, Clara Anghel, Javier Romero and Jonna Partezana), EDF (Antoine Ambard and Martine Blat-Yrieix), Rolls-Royce (Ted Darby), NNL (Sue Ortner), PSI (Sousan Abolhassani and Johannes Bertsch), EPRI (Erik Mader and Jon Beale), Chalmers (Gustav Sundell, Mattias Thuvander, Itai Panas and Hans-Olof Andrén), Imperial College (Na Ni), Penn State (Adrien Couet and Author Motta).

The days with all my lab mates makes my D.Phil life so much fun. I cherish many days when Tom and I were on the expensive ARM microscope, making sure we need two pairs of eyes to see difficult contrast and trying new things but without messing around too much. I'll miss the time three of our little "Zr gang": me, Tom and Brian staying in the EM lab room, explaining each other what we have found and making silly drawings of atoms or electrons having battles. Several figures in this thesis are teamwork effort, (Figure 6-2, Figure 6-4, Figure 6-6 and Table 6-1). I love bumping into Judith in the FIB room, complaining to each other about some machine is broken again (there is always one machine broken or they are all suddenly broken in one of the weeks in August when every technician is on holiday). I also remember the always warm hug from Aidan, Yina and her cute baby Luna, the delicious dinners we had with Arantxa, the lovely notebook from Gemma, the always incisive questions from Andy and many EM experts and technicians in the lab who taught me/ saved my day in the past three years, including Neil Young, Gareth Hughes, Graham Wyatt.

And of course, our little team in 21 Banbury Road: it seems that it's always the Asian students stay the latest in the evening and those evenings end in chatting and laughing. The team starts with Joven, Haibo, Xiaou and me, now Joven is in Manchester, Haibo is in Australia,

Xiaoou is in Beijing and I'll be in US, my only wish will be that one day at some wedding, we might be able to see each other again. I was the youngest one and now I'm probably the oldest in the building. I wish the younger ones all the best: Jiale, Bo, Fang, Shixiang and Shuqiu... I also would like to thank all my friends who made the journey in Oxford never boring: Yingqi for teaching me about energy efficiency and taking me to the field of environmental change, Tracy for teaching me water policy and wine, Anna for taking me to swing dancing and having fun, Rob for writing all the talented plays and seeing them at Burton Taylor, Xiuting for all the museums, beautiful paintings and amazing concerts.

I also thank my roommates, aka "28 Temple Street sitcom" cast members. I often dream about our little garden in the back yard with the apple tree when I am in Vienna. I think I'll remember many summer afternoons staying there with flowers, birds and the tranquillity from nowhere else.

My final five months in Vienna are wonderful not only because of the gorgeous city and delicious cafés open until 10 pm, but also because the job is challenging and opens my eyes on international collaboration. My work at the IAEA started with a job in Zr, but ends up in publishing. But I'd like to think I did it well because I challenged myself to find new questions and solve new problems. In a way, the job makes me realise I can do a lot of things as long as I have passions for it. I thank Victor Inozemtsev for always meeting me in the last week he retired (he retired twice for this reason), Clement Hill for being so supportive to my work, Mikhail Veshchunov for having a lot of scientific discussions on Zr oxidation rather than my job, John Killeen for teaching me how things work or not work at the Agency, Kit Coleman for being the Zr God and spending so much effort and time finishing the Zr bible which is simply amazing. This also makes me realise that the field of Zr is limitless.

Five months after leaving, Oxford still feels like a beautiful dream I don't want to wake up. It is never about the degree or the title, not even about all the fancy dinners and Harry Potter culture. It is about a young kid growing to a young person knowing confidently what she can do and never being afraid to try new things. It is about all the beautiful things and people in life and eye-opening experiences. I wish I can always stay here for my life.

I started writing my thesis on Christmas, luckily my Christmas wish was not finishing the thesis in three months. I had a lot of courage and will to continue. I travelled a lot during the time of writing, many of them were actually done on the train or at the airport. It feels like the train ride in Vienna, I hate to get out of the station at Oxford, and I have no idea where it is going to take me, but I'd like to think that is the beautiful part of life. Thanks for everyone and myself for making the ride a wonderful journey, these are all the pearls in life. It stays for life.

Jing Hu

1st June 2016

PREFACE

Part of the work in this thesis has been or will be published in the following publications:

Journal papers:

- 1) Hu, J., Garner, A., Ni, N., Gholinia, A., Nicholls, R. J., Lozano-Perez, S., Grovenor, C. R. M. (2015). Identifying suboxide grains at the metal-oxide interface of a corroded Zr-1.0%Nb alloy using (S)TEM, transmission-EBSD and EELS. *Micron*, 69, 35–42.
- 2) Hu, J., Setiadinata, B., Aarholt, T., Bagot, P., Moody, M., Grovenor, C., Ni, N. (2015). High-resolution characterization of corrosion and hydrogen pickup of Zr cladding alloys. *TopFuel 2015*, (September).
- 3) Hu, J., Setiadinata, B., Aarholt, T., Garner, A., Partezana, J., Bagot, P., Lozano-Perez, S., Preuss, M., Moody, M. and Grovenor, C. High-resolution characterization of Zr nuclear fuel cladding alloys. In *Zirconium in the nuclear industry: Eighteenth international symposium. American Society of Testing Materials*. 2016
- 4) Garner, A., Hu, J., Harte, A., Frankel, P., Grovenor, C., Lozano-Perez, S., & Preuss, M. (2015). The effect of Sn concentration on oxide texture and microstructure formation in zirconium alloys. *Acta Materialia*, 99, 259–272.
- 5) S Eggeman, A., Duncan J , Robert K, Hu J, Lozano-Perez S, Grovenor C, & A. Midgley, P. (2015). Decomposing Electron Diffraction Signals in Multi-Component Microstructures. *Microscopy and Microanalysis*, 21(S3), 1241–1242.

Conference oral presentations:

- 1) High-resolution characterization of Zr nuclear fuel cladding alloys. In *Zirconium in the nuclear industry: Eighteenth international symposium. American Society of Testing Materials*. Hilton Head, SC, USA May 2016

- 2) High-resolution characterization of corrosion of nuclear fuel cladding alloys. In
TopFuel 2015, Zurich, Switzerland September 2015
- 3) Identifying suboxide grains at the metal-oxide interface of a corroded Zr-1.0Nb alloy.
In *18th International Microscopy Congress*, Prague, Czech Republic September 2014
- 4) TEM characterization of oxidised Zr-alloy fuel cladding for nuclear reactors. In
International Microscopy of Oxidation, University of Nottingham, UK April 2013

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1 CHAPTER 1 BACKGROUND AND LITERATURE

1.1 Zr and Zr alloys in nuclear industry

In a typical fission reactor fuel assembly, as seen in Figure 1-1, the uranium dioxide (UO_2) fuel rods and the coolant are separated by cladding alloys. Together they form a fuel assembly, and several assemblies are packed in fuel bundles to form the nuclear core in the reactor. The cladding alloys keep the cooling water from contacting the radioactive fission products. For this purpose, the cladding alloys must have good mechanical properties and corrosion resistance at elevated temperatures and pressures, intense neutron irradiation and corrosive conditions. It is also important for the cladding to have a low thermal neutron absorption cross section to allow the neutrons to give high efficiency in nuclear fission reactions¹⁻⁶.

For the past six decades, zirconium alloys have been selected for use as nuclear fuel cladding alloys in both light water reactors and heavy water reactors⁷⁻⁹. Zirconium has an atomic number of 40, an atomic weight of 91.22 and a density of 6.52 g/cm^3 . Below 860°C (which is well above the normal reactor operation temperature which is around 285°C for a boiling water reactor and 350°C for a pressurised water reactor), zirconium has a hexagonal close packed (HCP) crystal structure (α phase) with lattice parameters a and c equal to 0.323nm and 0.514nm respectively¹⁰. Above 860°C , zirconium changes to a body centred cubic (BCC) crystal structure (β phase) and melts at 1855°C ¹⁰. The most important property of zirconium is that it has a low thermal neutron absorption cross section of 0.18 barns ⁷ which makes it almost transparent to neutrons. Furthermore, its mechanical and corrosion resistance properties are reasonable for usage as a cladding material¹.

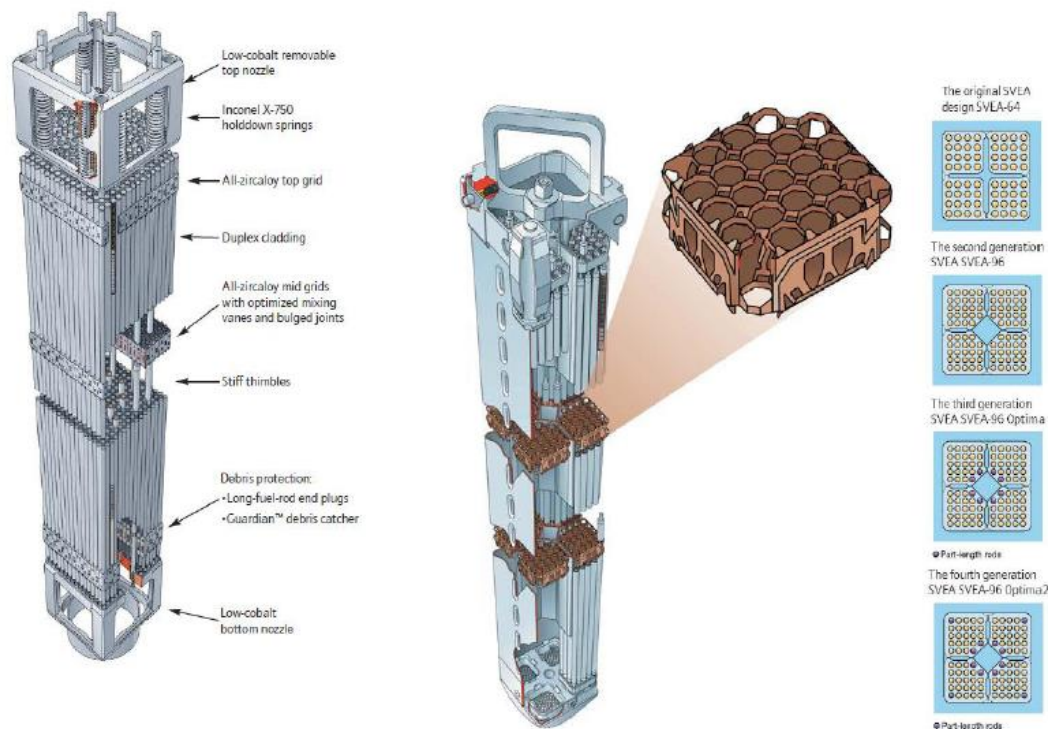


Figure 1-1: Fuel assembly. The left assembly is a Westinghouse™ PWR fuel design. The middle assembly is a Westinghouse™ SVEA- 96 OPTIMA2 BWR design¹¹.

By adding other alloying elements, the properties of zirconium can be improved further. Generally speaking, these added elements can be divided into two categories¹²: elements like aluminium, oxygen, tin and nitrogen are called α stabilisers, because they can raise the α - β transition temperature; while elements like iron, nickel, chromium and molybdenum are called β stabilisers, since they can lower the α - β transition temperature.

The first use of zirconium alloys were the Zircaloy series, introduced by the US Navy nuclear program in 1952². The element tin (Sn) is added as an α stabiliser to form a more uniform oxide. This was necessary to balance the nitrogen impurities introduced by the manufacturing process at that time which can lead to poor corrosion resistance. Tin forms a solid solution in the zirconium matrix, so it can also improve the mechanical properties by the hardening effect¹³. Zircaloy-1 contained 2.5 wt% Sn, however its corrosion resistance was not good.

Later, Zircaloy-2 was developed with a composition of Zr-1.5Sn-0.2Fe-0.1Cr-0.05Ni. It shows relatively good corrosion resistance, but the Ni leads to higher hydrogen pickup¹⁴. Zircaloy-4 was developed by replacing Ni with Fe, which solved this problem^{15,16}. Zircaloy-2 (Zr-Sn-O-Fe-Ni-Cr) is still used in boiling water reactors (BWRs) and Zircaloy-4 (Zr-Sn-O-Fe-Cr) in pressurised water reactors (PWRs) and the Canadian deuterium uranium (CANDU) reactors.

Table 1-1: Composition of the Zircaloy series of alloys ¹⁷

Alloying	addition	Zircaloy-1	Zircaloy-2	Zircaloy-3			Zircaloy-4							
				a	b	c								
Sn		2.5	1.50 (1.20–1.70)	0.25	0.5	0.5	1.50 (1.20–1.70)							
Fe			0.12 (0.07–0.20)	0.25	0.4	0.2	0.20 (0.18–0.24)							
Cr		-	0.10 (0.05–0.15)	-	-		0.10 (0.70–0.13)							
Ni			0.05 (0.03–0.08)	-	-	0.2	<0.007							
Total Fe, Cr, Ni		-	(0.18–0.38)	-	-		>0.28							
O [ppm]		-	1000–1400			-	1000–1400							
Maximum impurityconcentrations:														
Element:	A1	B	Cd	C	Co	Cu	Hf	H	Mn	N	Si	Ti	W	U
[ppm]:	75	0.5	0.5	270	20	50	200	25	50	80	200	50	100	3.5

With better and modern manufacturing processes less nitrogen is introduced into Zr alloys, thus new low-Sn alloys were developed¹⁸. The optimisation of alloying is achieved by

lowering the Sn content to 1.2-1.5wt%, and adding Fe to 0.24 wt%, and Cr to 0.13 wt%. This, combined with better designed heat treatments, gives low-Sn Zircaloy-4 with better corrosion resistance in high temperature steam corrosion tests¹⁹. Table 1-1 shows the Zircaloy series of alloys.

Table 1-2: Composition of Zr-Nb alloys developed in Russia and other later derivatives ¹⁷

Alloying addition	Ozhennite	Zr-1Nb		Zr-2.5Nb	Zr-Nb-Sn-Fe alloys	
[wt%]	0.5	E110	M5 TM	E125	E 635	ZIRLO [®]
Sn	0.20 (0.18–0.22)	-	-	-	0.8–1.2	0.7–1.0
Nb	0.10 (0.09–0.11)	1.0 (0.9–1.1)	0.8–1.2	2.50	1.0	1.0
Fe	0.10 (0.09–0.11)	0.1	0.04–0.06	0.05	0.4	0.1
Ni	0.10 (0.09–0.11)	<0.007	-	<0.007	-	-
B (*)	-	(0.20) (*)		(0.10) (*)		
O	(0.09–0.12)	(0.07–0.1)	0.12	(0.09–0.12)	(0.09–0.12)	(0.09–0.12)

Maximum impurity concentrations:

Element:	Al	B	Cd	C	Cr	Co	Cu	Hf	H	Pb	Mg	Mn	Mo	N	Si	Na	Ta	Ti	W	V
[ppm]:	75	0.5	0.5	270	200	20	50	150	24	130	20	50	50	60	120	10	200	50	200	50

(*): Added when burnable poison is included in fuel assembly

Niobium (Nb) is added as a β stabiliser. Examples include the E110 (Zr-1.0wt%Nb) alloy^{17,20,21} in the Soviet Union, M5 (Zr-1.0wt%Nb)²² in France, the Zr-2.5wt%Nb alloy²³ in

CANDU and the Zr-2.5Nb-0.5Cu²⁴, all of which show better corrosion resistance and mechanical properties comparing with Zircalloys.

With increasing demand for higher burnup, new Zr-Nb-Sn alloys were developed. WestinghouseTM developed ZIRLO[®] (Zr-Nb-Sn-Fe) in the 1980s^{18,25}, which is now used in PWRs and shows superior corrosion performance. Besides this, Japan developed NDA (Zr-0.9Sn-0.2Nb-0.17Fe-0.10Cr and Korea developed HANA-4 (Zr-1.5Nb-0.4Sn-0.2Fe-0.1Cr) and HANA-6 (Zr-1.1Nb-0.06Cu) alloys. Table 1-2 show the Zr-Nb cladding alloys with their typical alloying element ratios and applications in reactors. Figure 1-2 summarised the alloy development of WestinghouseTM to improve the oxidation performance to accommodate higher burnup campaigns²⁶.

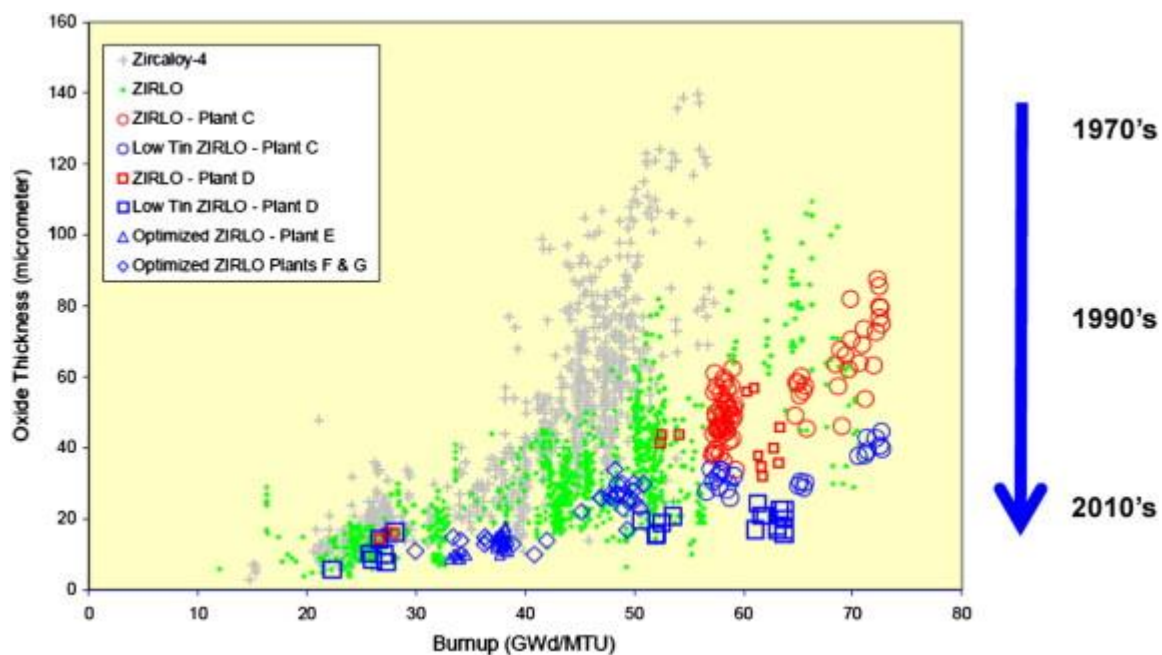


Figure 1-2: WestinghouseTM development of PWR fuel claddings²⁶

1.1.1 Zircaloy-2 and Zircaloy-4

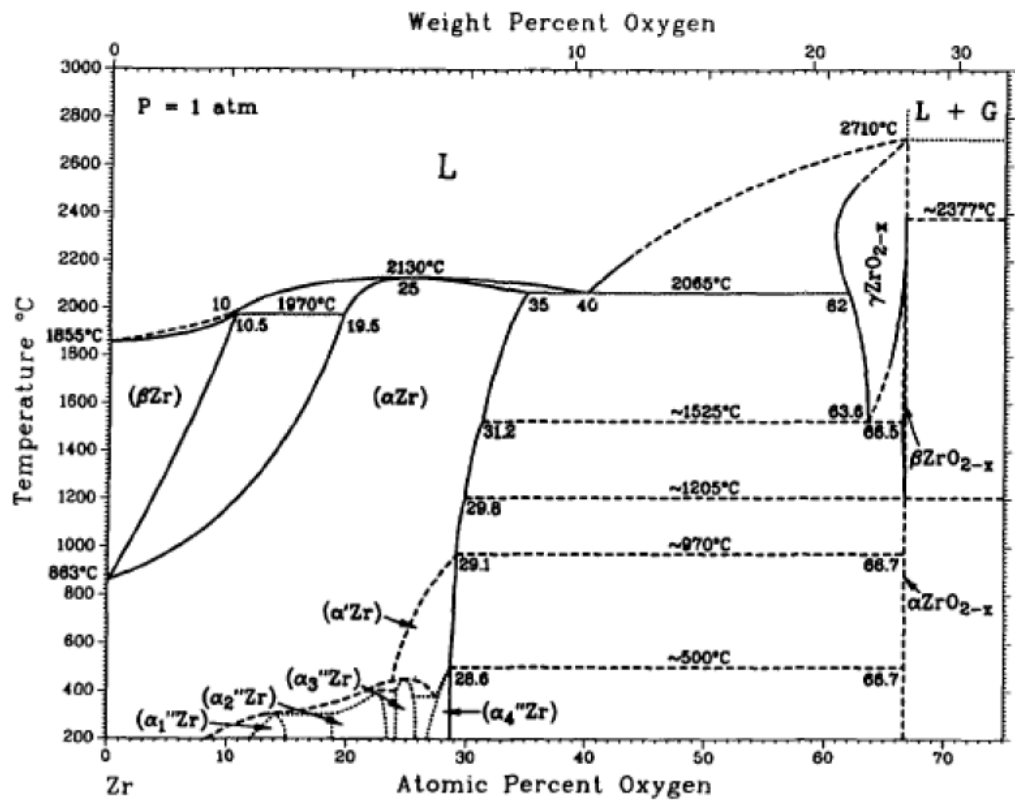
As mentioned above, Zircaloy-2 and Zircaloy-4 were two of the first developed cladding alloys, and they both have 1.2-1.7wt% tin and 0.11-0.14wt% oxygen in solid solution in an α

Zr matrix. Zircaloy-2 is primarily used in BWRs due to low corrosion rate while Zircaloy-4 with its low hydrogen pickup fraction is mainly used in PWRs.

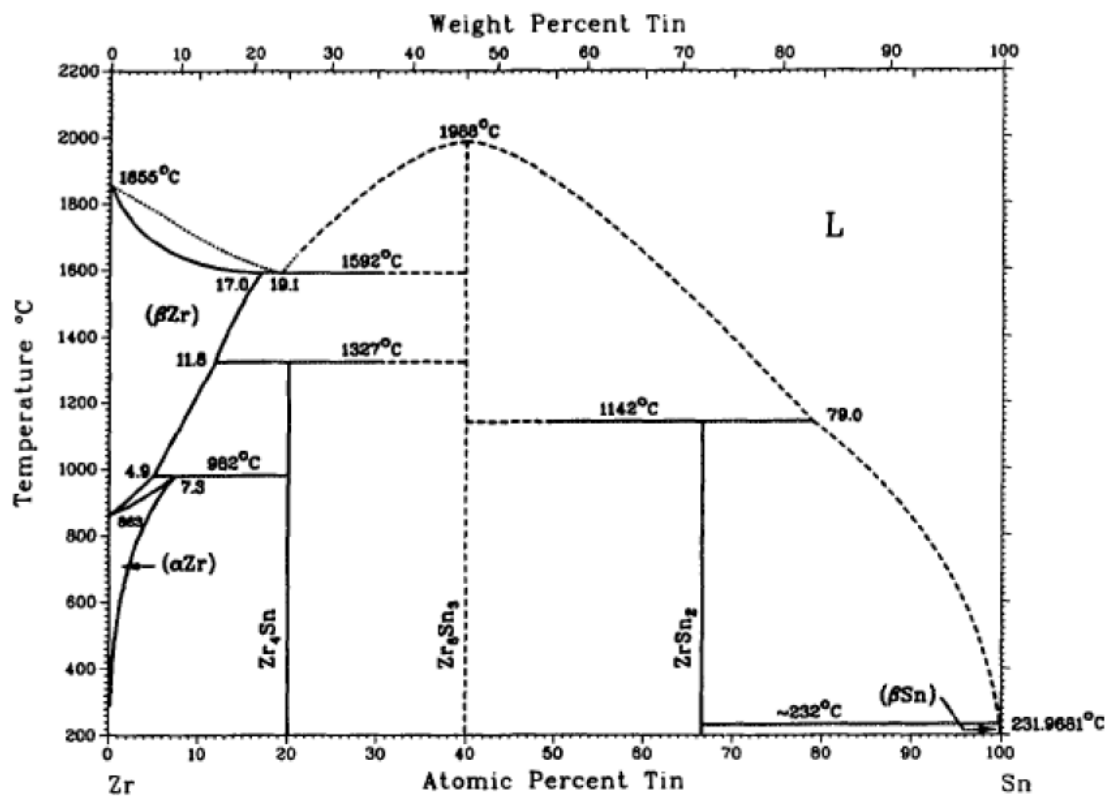
The typical manufacturing process for Zircalloys is as follows: β -quenched→ hot extrusion→ cold pilgering→ intermediate annealing→ cold rolling→ intermediate annealing→ cold rolling→ stress relief annealing.²⁷

The phase diagrams of Zr-Sn and Zr-O are shown in Figure 1-3. The α Zr matrix crystal structure is hexagonal compact (hcp) with $a = 0.323$ nm, $c = 0.515$ nm, and a c/a ratio of 1.593. While Zircaloy-2 contains iron, nickel and chromium, Zircaloy-4 has iron and chromium; these elements are fairly insoluble in zirconium which means they can form different types of second phase particles (SPPs).

Figure 1-4 shows a typical second phase particle (SPP) distribution in Zircaloy-2²⁸. The SPPs are distributed either along the grain boundaries or within grains. In Zircaloy-2, there are mainly two different types of SPPs: tetragonal $Zr_2(Fe,Ni)$ with lattice parameters of $a=0.650$ nm, $c=0.527$ nm and the C14 hexagonal Laves phase $Zr(Fe,Cr)_2$ ²⁹. Zircaloy-4 also contains $Zr(Fe,Cr)_2$ ³⁰⁻³². Griffiths et al ³³⁻³⁵ studied the microstructure change resulting from irradiation, and found that $Zr_2(Fe,Ni)$ is tetragonal at room temperature, but after irradiation at 350 K it becomes amorphous and eventually dissolves at 610-700 K. By contrast, $Zr(Fe,Cr)_2$ stays the same all the time.



a)



b)

Figure 1-3: Phase diagrams of Zr-O³⁶ and Zr-Sn¹³

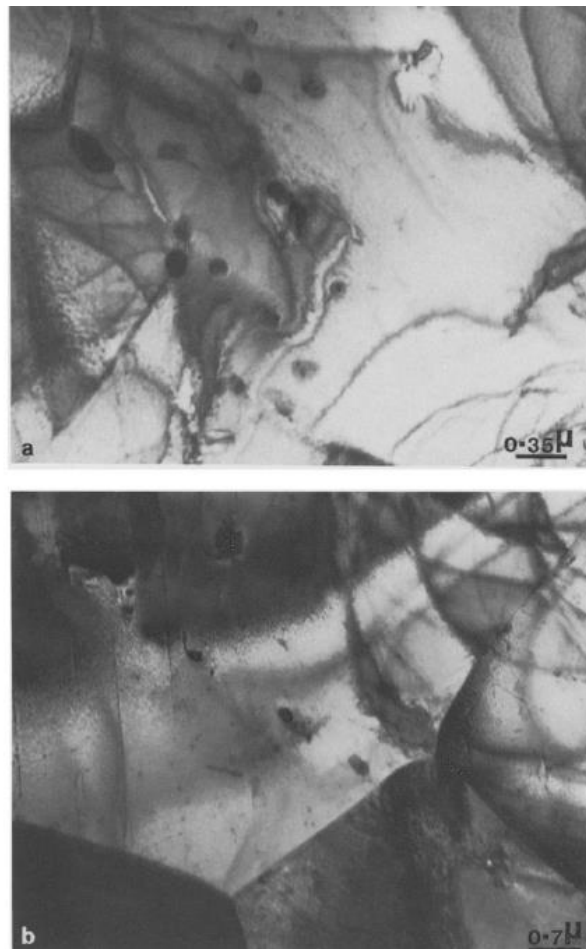


Figure 1-4: TEM micrographs showing the general distribution of second phase particles in a typical Zircaloy-2²⁸.

1.1.2 Zr-Nb alloys

Niobium is used as a β -stabilizer in zirconium alloys and Figure 1-5 shows the phase diagram of Zr-Nb³⁷. From the phase diagram, the solid solution limit of Nb in Zr matrix is 0.6 wt%, and the monotectoid temperature is about 610 °C. Normally the first step of manufacturing is called β quenching which is done by fast cooling in the β or upper α and β regions (above 610 °C), forming a martensitic structure of β -Zr grains where Nb is supersaturated in the matrix to levels up to 20% content. The β -Zr forms as a needle shaped HCP phase in between the grains of α -Zr³⁷⁻⁴¹.

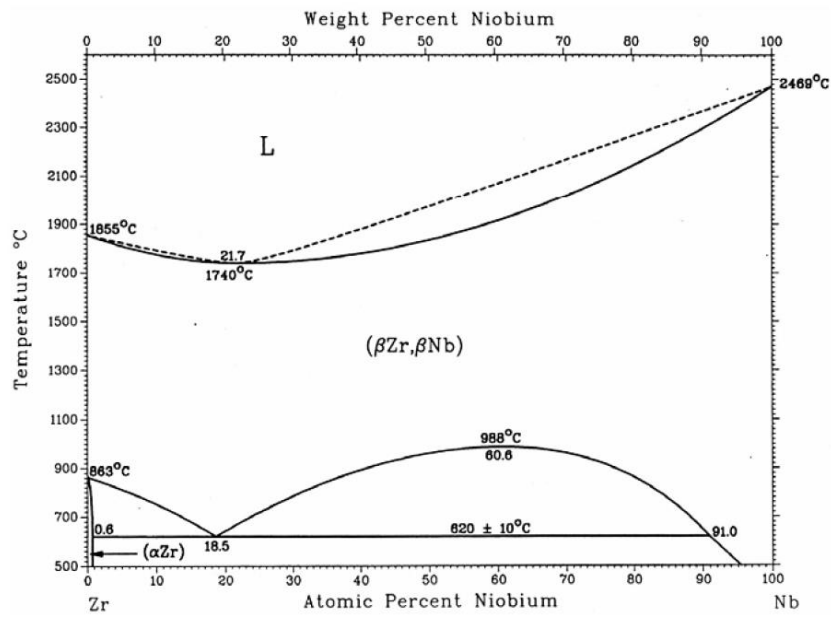


Figure 1-5: Phase diagram of Zr-Nb alloy system¹⁷

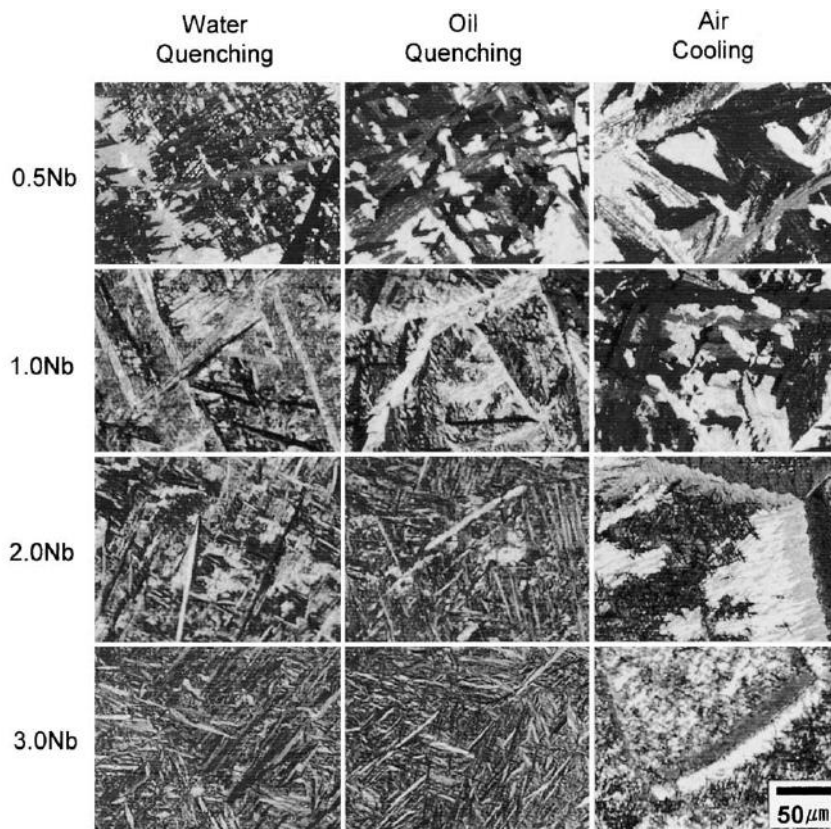


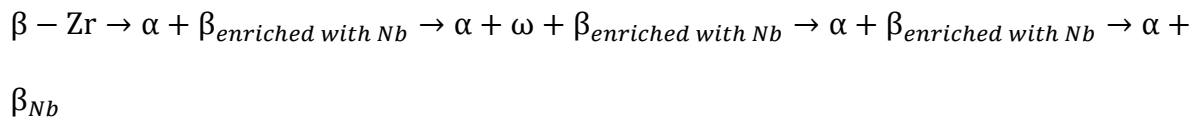
Figure 1-6: Optical micrographs of Zr-xNb alloys with different cooling rate^{37,42}.

Choices of cooling media such as water, oil or air used in β quenching and the Nb content both influence the alloy microstructure. The optical microscope pictures in Figure 1-6 show the faster the cooling rate and the higher the Nb content, the more martensitic structure and finer plates are formed^{37,42}.

After β quenching, different heat treatments play an important role in forming precipitates and β phases³⁹. Normally the β -Zr phase is metastable and will decompose after further heat treatment.

Figure 1-7 shows the microstructure of Zr-Nb alloys after 500 hours annealing at 570 °C and after 10 hours annealing at 640 °C. Above the monotectoid temperature, it forms needle shaped β -Zr (20%Nb-80%Zr) phases. Cooling from a temperature under the monotectoid transformation temperature creates equiaxed β -Nb particles with 80 wt% Nb separated by elongated α -Zr phases containing about 1 at%Nb.

Choudhuri⁴³ studied the decomposition reactions and concluded the process to be:



where ω is a transient intermetallic phase which exists only during the process.

It is worth mentioning that in Zr-Nb alloys there are always iron impurities as well, which come from the sponge zirconium that used as a manufacturing ingredient. Iron works as a β -stabiliser and lowers the solubility of Nb in α -Zr⁴⁴. So under two different heat treatment procedures there are different precipitates that contain iron: Zr_3Fe (orthorhombic, $a=0.3320\text{nm}$, $b=1.098\text{nm}$, $c=0.8800\text{nm}$) and $\text{Zr}(\text{NbFe})_2$ (hexagonal, $a=0.5401\text{ nm}$, $c=0.8665\text{ nm}$). Table 1-3 shows details of precipitates types and content found in Zr-Nb alloys.

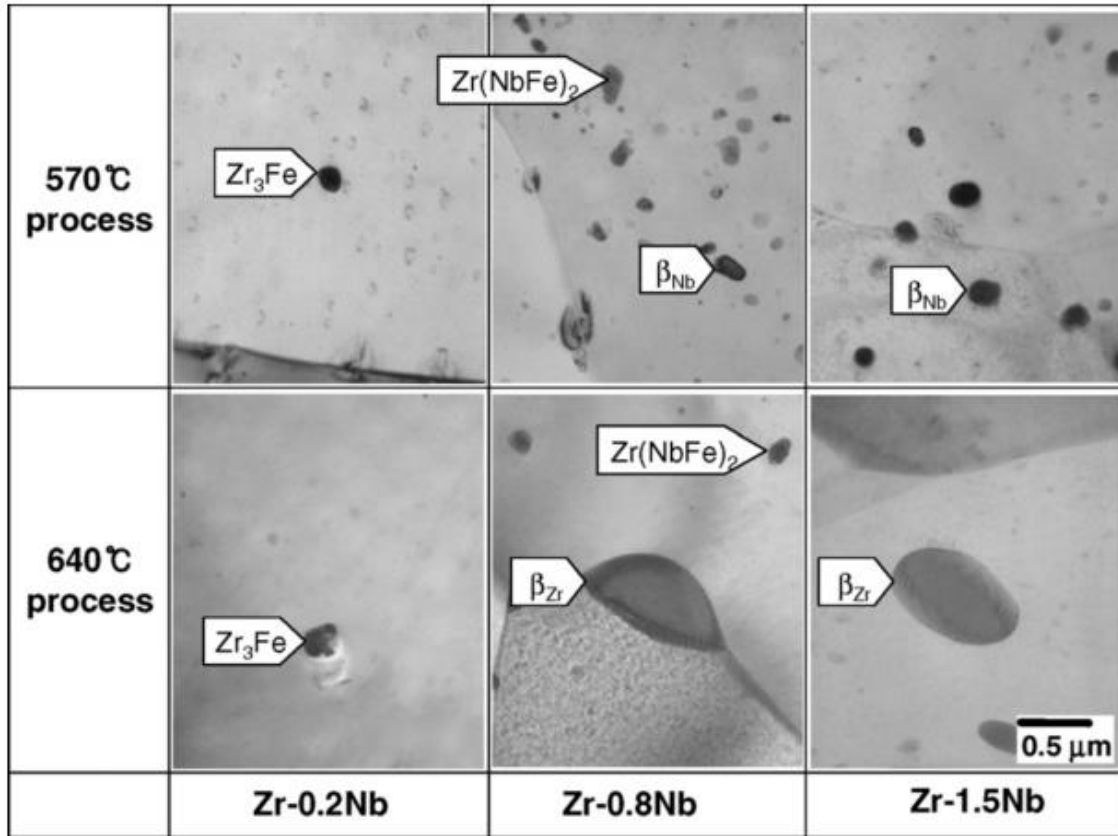


Figure 1-7: TEM micrographs of the Zr–xNb alloys annealed at 570 °C and 640 °C with variation of the Nb content³⁹.

Table 1-3: precipitate types and fractions in Zr-Nb alloys³⁹

Summary of precipitate characteristics of Zr–xNb alloys

Nb-content (wt%)		0.1	0.3	0.5	0.8	1.0	3.0
570 °C (β_{Nb})	Type	• Zr_3Fe –	◦ Zr_3Fe • $Zr(NbFe)_2$ –	◦ Zr_3Fe • $Zr(NbFe)_2$ –	– • $Zr(NbFe)_2$ ◦ β_{en}	– ◦ $Zr(NbFe)_2$ • β_{en} , β_{Nb}	– ◦ $Zr(NbFe)_2$ • β_{en} , β_{Nb}
	Distribution	Grain boundary	Grain boundary	Grain boundary	In α -grain and grain-boundary	Plate boundary	In α -grain and plate-boundary
640 °C (β_{Zr})	Type	• Zr_3Fe –	◦ Zr_3Fe • $Zr(NbFe)_2$ –	◦ Zr_3Fe • $Zr(NbFe)_2$ –	– • $Zr(NbFe)_2$ ◦ β_{Zr}	– ◦ $Zr(NbFe)_2$ • β_{Zr}	– ◦ $Zr(NbFe)_2$ • β_{Zr}
	Distribution	Grain boundary	Grain boundary	In α -grain and grain-boundary	In α -grain and grain-boundary	Plate boundary	Plate boundary

•: Major; ◦: minor.

Rudling⁴⁵ also reported that with high Nb and moderate Fe content, the SPPs are normally hexagonal $Zr(NbFe)_2$ besides the fine β -Nb precipitates. With decreasing Nb content, there will be more Laves phase $Zr(NbFe)_2$. At high Fe and rather lower Nb concentrations a cubic

(ZrNb)₂Fe phase may be formed in addition to the Laves phase or even replacing the Laves phase.

1.1.3 HANA, ZIRLO[®] and M5[™]

Other common Zr alloys include ZIRLO[®] (Zr–1.0Nb–1.0Sn–0.1Fe), M5[™] (Zr–1Nb–O), HANA-3 (Zr–1.5Nb–0.4Sn–0.1Fe–0.1Cu), HANA-4 (Zr–1.5Nb–0.4Sn–0.2Fe–0.1Cr) and HANA-6 (Zr–1.1Nb–0.05Cu).

Kim⁴⁰ studied the new alloy HANA-4 after different annealing times and temperatures. They showed that when annealing at 570 °C the second phase particles in α -Zr are Zr(NbFeCr)₂ and the mean size of these SPPs increases with annealing time. When annealing at 630 °C, β -Nb is formed as well as Zr(NbFeCr)₂ particles, and the size of β -Nb increased a lot while Zr(NbFeCr)₂ had similar size as at 570 °C. Microstructural analysis of other HANA alloys⁴⁶ reveals that they all contain β -Nb which is more stable in HANA-3 than in HANA-6. Zr(Nb,Fe)₂ with a hexagonal structure was observed in HANA-3, while (Zr,Nb)₂Fe with an fcc structure was observed in HANA-6.

The microstructure of ZIRLO[®] and M5[™] both contain β -Nb precipitates and ZrFeNb Laves phases⁴⁷, and iron is an impurity coming from the metal ingot.

1.2 Oxidation of Zr alloys

In both PWR and BWRs, oxidation and hydrogen pickup are the two main problems with zirconium cladding alloys, as shown in Figure 1-8. Oxidation happens because zirconium alloys are exposed to the coolant, and different types of oxidation are observed depending on the reactor type, the coolant environment, temperature and pressure^{29,48–51}. Normally in a PWR, the cladding alloys grow uniform oxide, while in a BWR, besides a relatively thinner uniform oxide, there is also nodular oxide grown in localized white spots with a diameter of

about 0.5-2 mm with faster speed and a thickness of more than 100 μm . This kind of white nodular oxide will eventually lead to oxide spalling. Figure 1-9 shows an example where nodules are formed on zirconium alloy following a 500°C steam test at 10.3MPa, and a cross-section view of a nodule shows circumferential and vertical cracks^{4,48}. Also galvanic corrosion introduces shadowing of the oxide which normally happens when Zircaloy touches with another type of metal-alloy which is nobler. Figure 1-10 shows shadow corrosion of Zircaloy from a control rod panel.

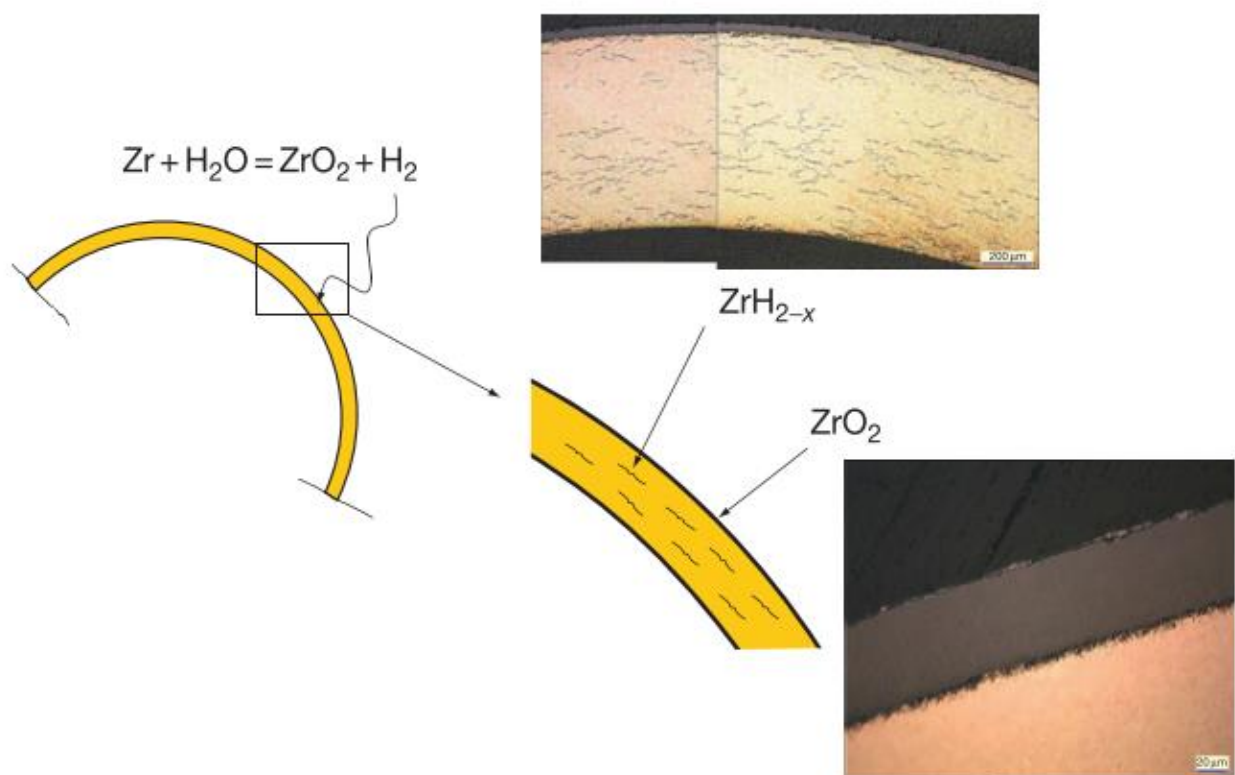


Figure 1-8: Uniform oxide layer formation and hydride precipitation in Zircaloy cladding. © European Atomic Energy

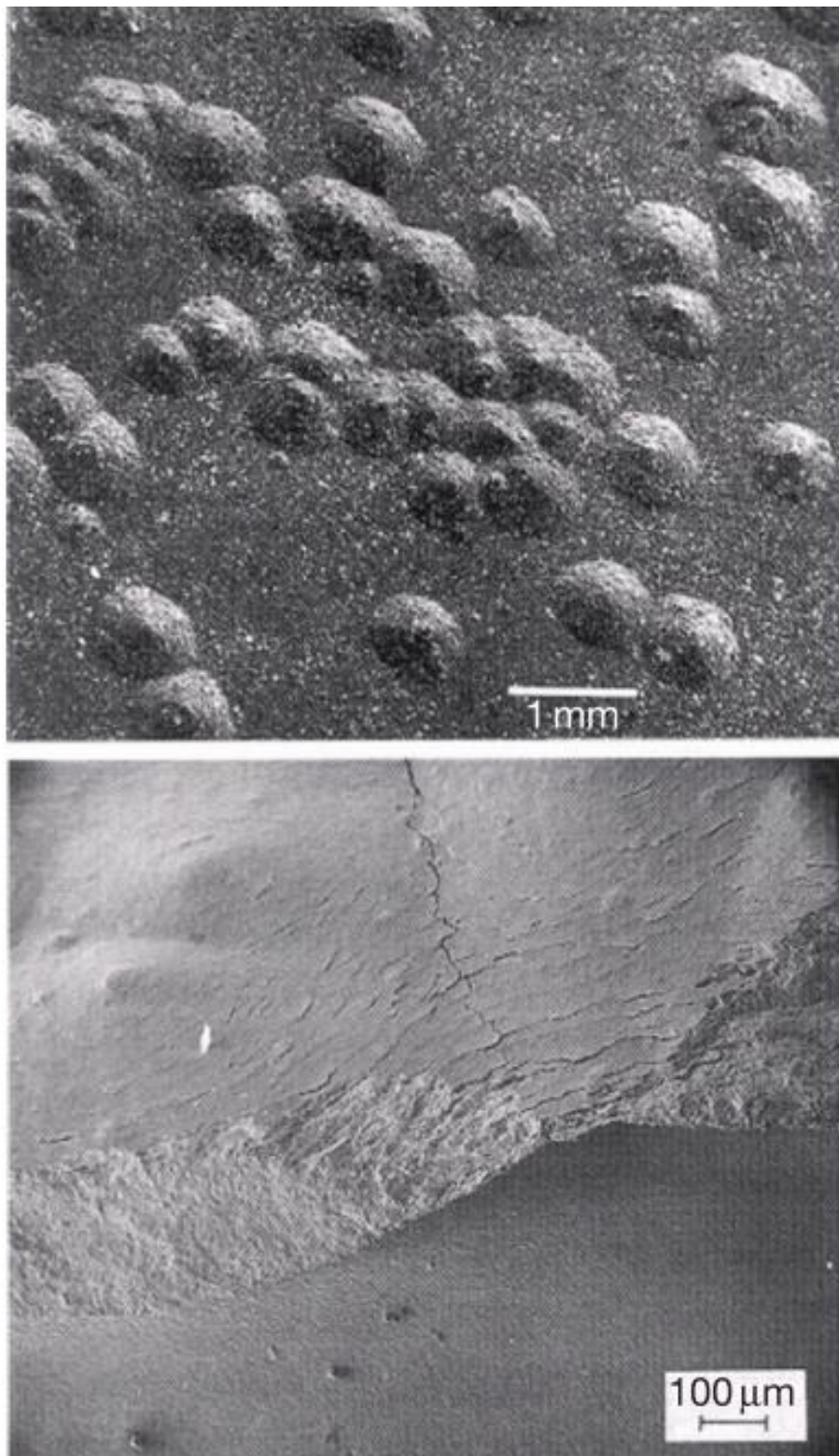


Figure 1-9 General appearance of nodules formed on a zirconium alloy following a 500°C steam test at 10.3MPa. In the bottom, a cross-section view of a nodule is shown, exhibiting circumferential and vertical cracks⁴

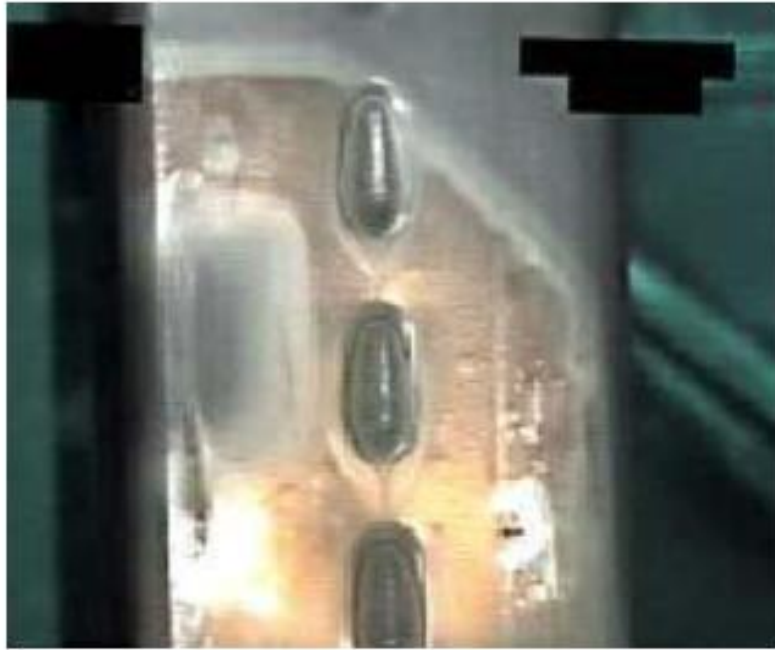
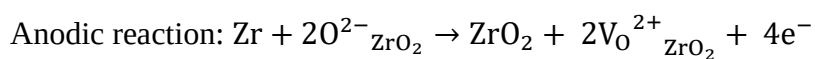


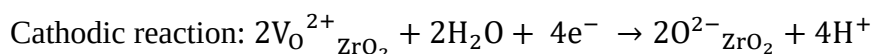
Figure 1-10: Shadow corrosion of Zircaloy from a control rod panel⁵²

Figure 1-11 illustrates schematically the key mechanisms that are involved in the waterside corrosion of zirconium alloys in service. During the oxidation reaction oxygen anions diffuse from the oxide-water interface to the metal-oxide interface, while oxygen vacancies diffuse in the opposite direction. The anodic reaction is the rate-determining part. Possible sites for oxygen anions to diffuse are grain boundaries, dislocations, etc, while intermetallics or SPPs in metal oxide may be preferential sites for electron diffusion.

At the metal-oxide interface:



At the oxide-water interface:



The general waterside corrosion kinetics of zirconium alloys is shown in /Figure 1-12. The first stage is an initial pre-transition period of slow parabolic or cubic corrosion rate which

can be described as $\Delta W = Kt^n$ (W is the weight gain of mg/dm², K depends on both alloying element and reactor temperature and t is the oxidation time in days). The cladding alloys form a thin and uniform oxide in this stage.

The second stage is when the oxide has grown to about 2 μm in thickness where there is an abrupt increase in corrosion rate named “breakaway”⁵³ to almost linear and cyclic rate which can be described as $\Delta W = Kt + C$ (W is the weight gain of mg/dm², K depends on both alloying element and reactor temperature and C is the initial weight gain)

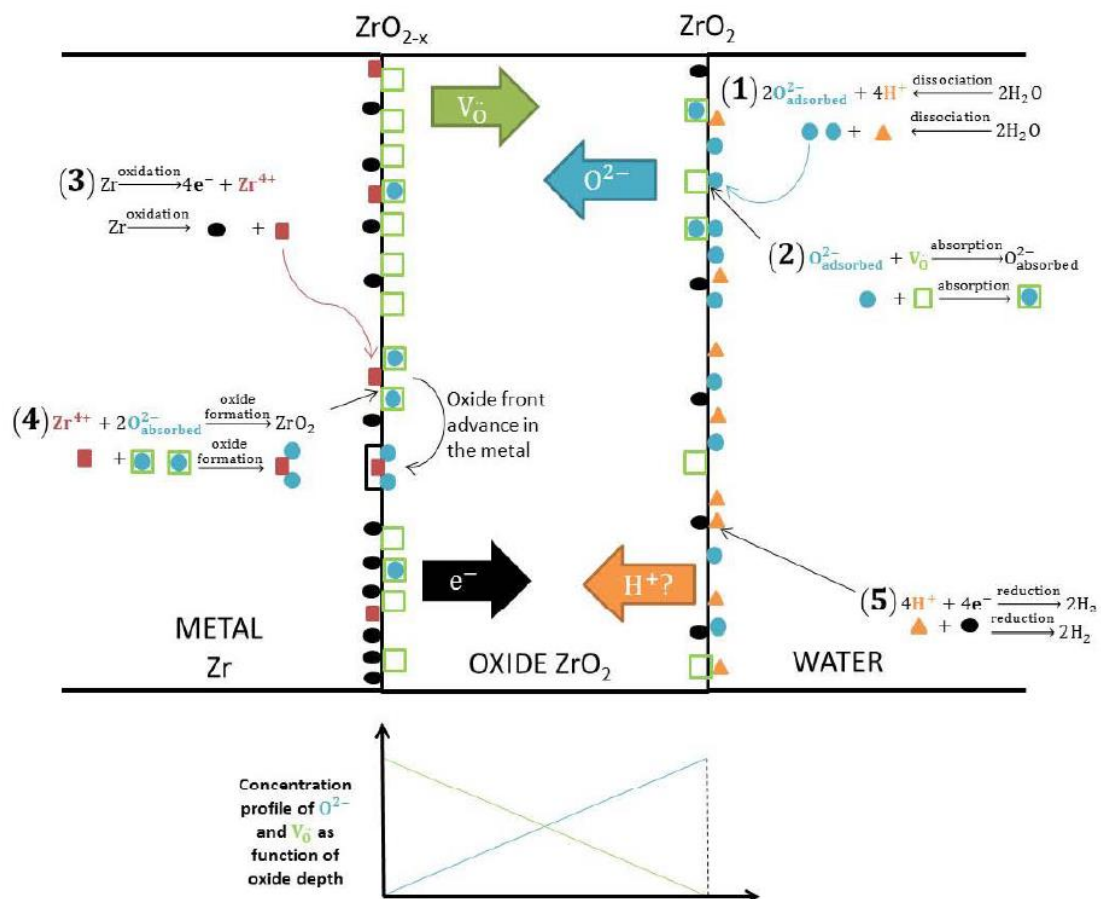
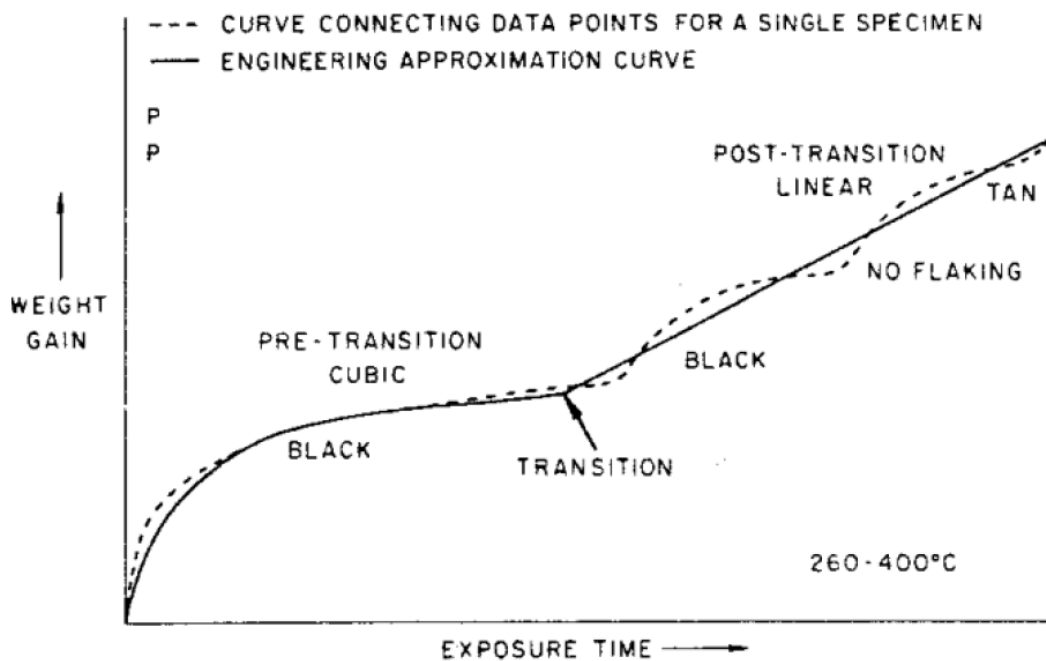


Figure 1-11: Schematic of the reactions taking place during uniform corrosion of Zr²⁷



/Figure 1-12: A general representation of the oxidation kinetics of Zr and Zr alloys.⁵

There are a few factors affecting oxide formation and growth: oxide phase and morphology, heat treatment procedure, surface modification and working environment. These all affect corrosion resistance in different but interconnected ways.

I.1.1. Oxide phase and morphology

At a function of temperature and pressure, zirconium oxide has three different phases⁵⁴. Below 1200 °C it is m-ZrO_{2-x} containing 61 ~ 66.6 at% oxygen with the monoclinic structure. Between 1200 and 2372 °C it is t-ZrO_{2-x} containing 66.5 ~ 66.6 at% oxygen with the tetragonal structure. After 2372 °C up to the melting point, it is γ-ZrO_{2-x} containing 66.5 ~ 66.6 at% oxygen with the face-centred cubic structure. Figure 1-13 shows the phase diagram and crystal structure of these three phases.

t-ZrO_{2-x} is stable at high temperature, but at lower temperature its stability depends on inner pressure of the tube, grain sizes and precipitates⁵⁵. m-ZrO_{2-x} is stable at room temperature or liquid environment at 247~ 367°C . Many researchers⁵⁶ have shown that when oxides grow on the metal, there is volume expansion which can introduce compressive stress. This can help

stabilize t-ZrO_{2-x}. Sawabe et.al⁵⁷ studied the microstructure of Zr alloys and oxides, found that before breakaway there is an interlayer at the metal-oxide interface which contains mostly t-ZrO_{2-x} and the outside layer away from the interface that is m-ZrO_{2-x}. Using synchrotron irradiation and optical microscopy, a cyclic arrangement of higher monoclinic and lower tetragonal phase was observed in the oxide, and vice versa⁵⁸ Figure 1-14.

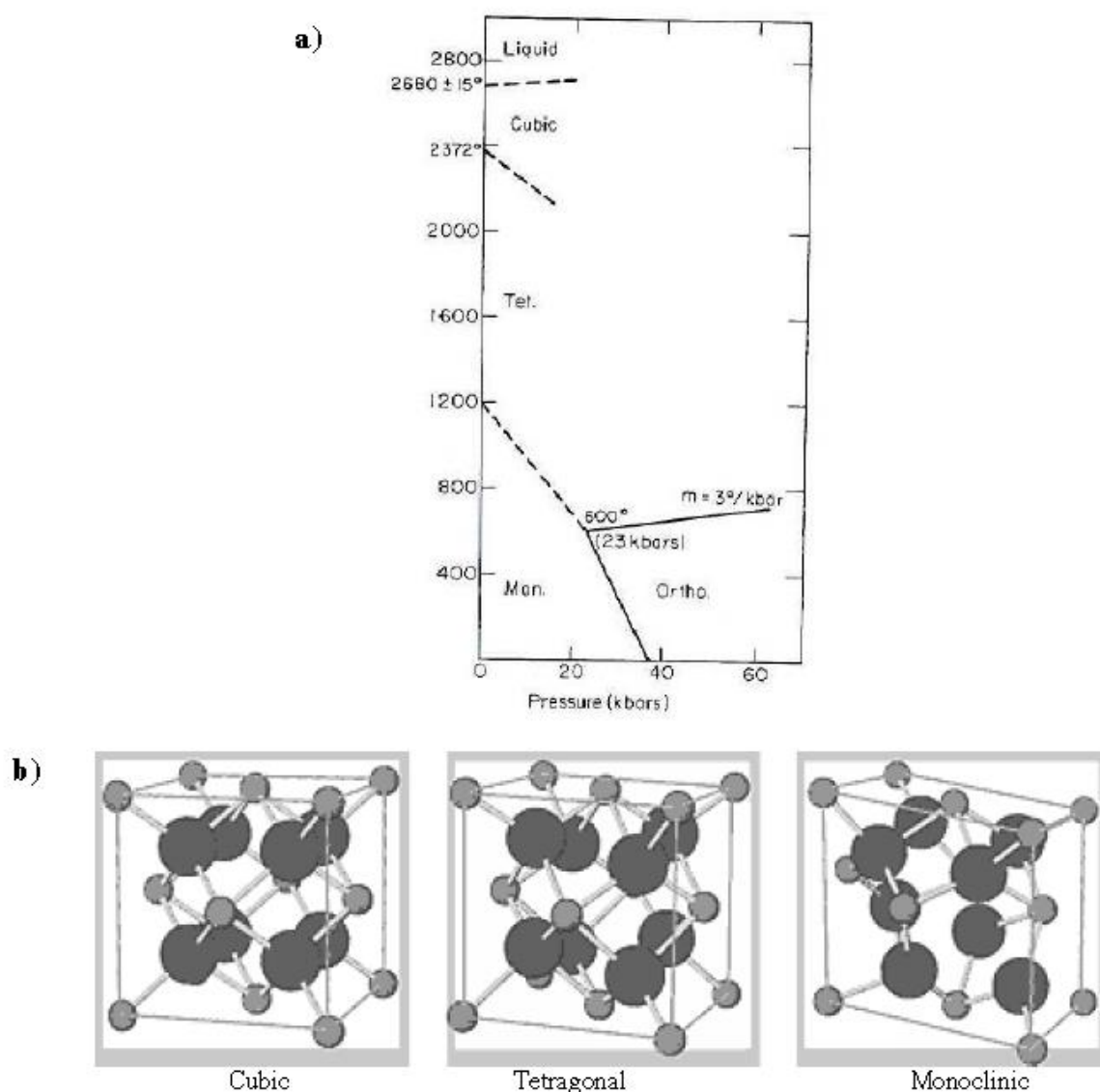


Figure 1-13: a) Temperature-pressure phase diagram of ZrO₂⁵⁹. b) Schematic drawings of monoclinic, tetragonal and cubic crystal structures which illustrate the atomic arrangement⁵⁴. Bigger and darker spheres = O atoms, and smaller and lighter ones = Zr atoms.

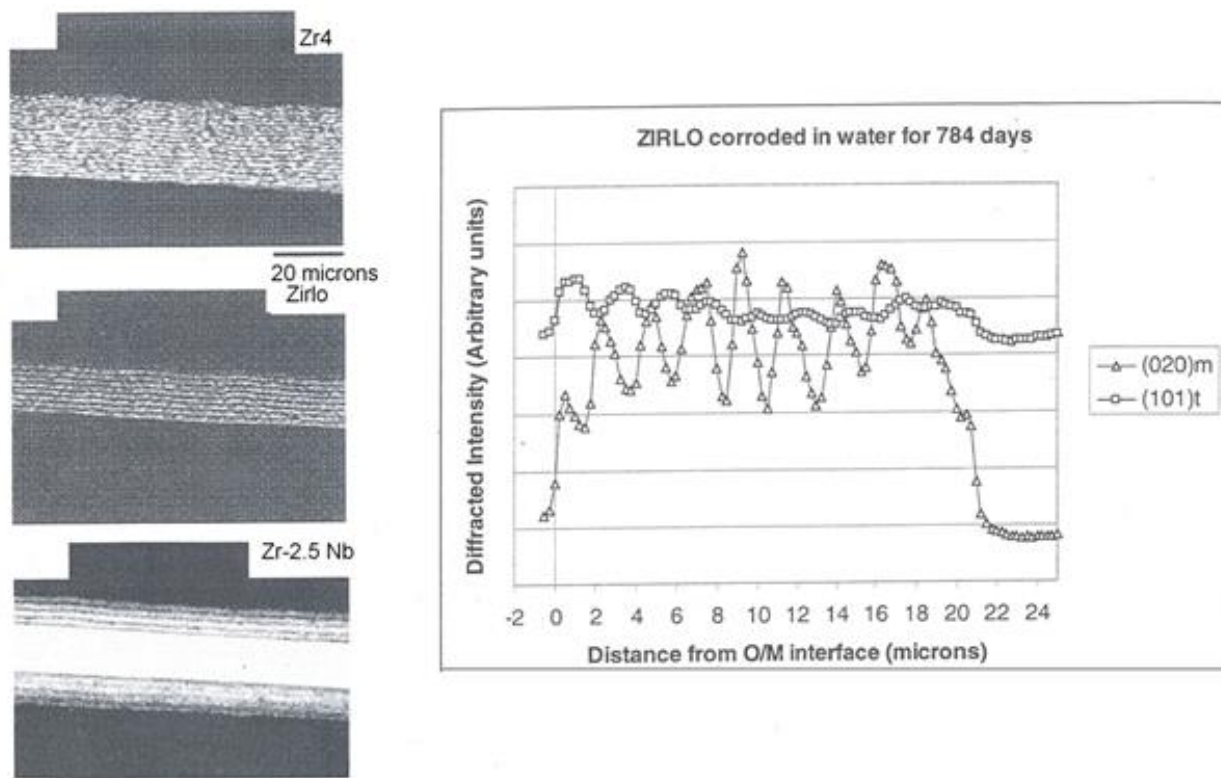


Figure 1-14: Layers visible in oxide films in transmitted light, (a), and cycles of monoclinic and tetragonal oxide, (b), formed on ZIRLO[®] at 360°C (633 K) by oxidation for 784 days⁵⁸

Ni et al.⁶⁰ used Electron Energy Loss Spectroscopy (EELS) to study ZIRLO[®] alloys and found that at the metal-oxide interface there is a suboxide layer with composition of ZrO. Figure 1-15. At this time, oxide has very good adhesion to the metal. As the oxidation continues, the oxide/metal interface continues to move into the metal, and the compressive stress in the oxide produced initially decreases, so the t-ZrO_{2-x} transfers to m-ZrO_{2-x}. When there is less t-ZrO_{2-x}, a kinetic transition takes place where oxygen ions move faster to the metal which makes the oxidation rate increase, and the thickness of the suboxide near the oxide/metal interface decreases or even disappears⁶¹. In the meantime, the volume of the oxide grows, and the stress in the inner part of the oxide layer keeps growing. Once the stress is more than the oxide's limit, oxide breaks, cracks form and its protection towards Zr alloys will disappear and oxygen will get into metal through cracks, this in return accelerates the oxidation. In this circumstance, the corrosion resistance of Zr alloys is related with the

transition from tetragonal phase to monoclinic phase in oxide, the more tetragonal phase there is, the better the corrosion resistance is^{6,62,63}.

Yilmazbayhan et al.⁶⁴ used Transmission Electron Microscopy (TEM) to show there are 100–150 nm wide rectangular blocky suboxide grains near the metal–oxide interface on a Zr–2.5%Nb alloy. Abolhassani et al.⁶⁵ also identified a substoichiometric phase with 40–60 at.% oxygen at the interface of irradiated Zr–2.5%Nb using Energy Dispersive X-ray Spectroscopy (EDS).

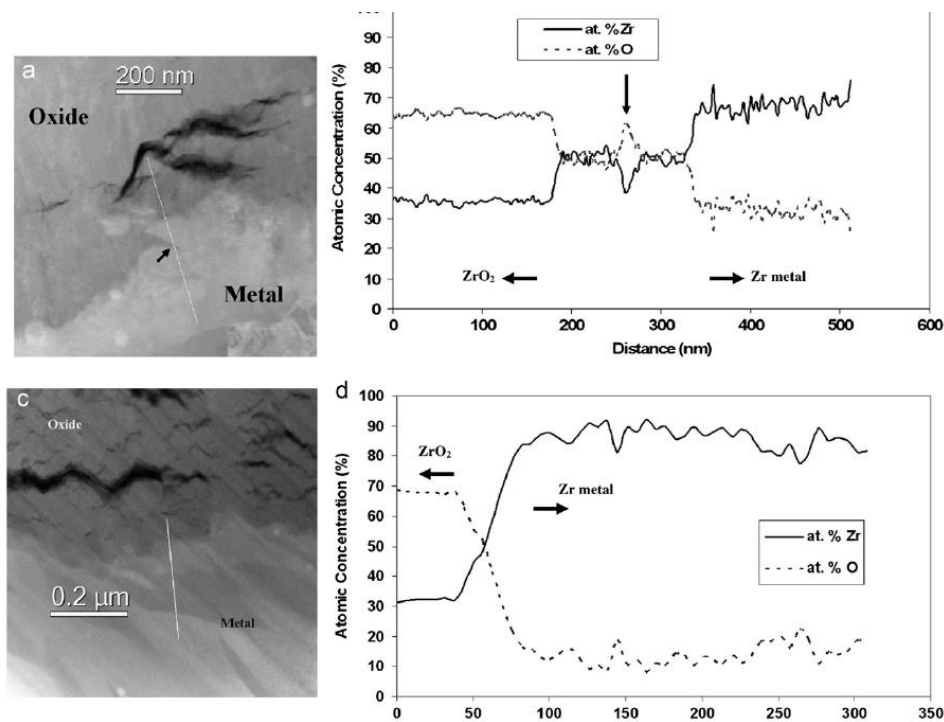


Figure 1-15: (a) HAADF image of the metal-oxide interface region and (b) oxygen concentration line profile across the metal-oxide interface in sample A (the pre-transition ZIRLO[®] oxide) showing the presence of a sub-stoichiometric oxide layer; (c) HAADF image of the metal-oxide interface region and (d) oxygen concentration line profile across the metal-oxide interface in sample B (the post-second transition oxide grown on the model Zr–Ti–Nb–Fe alloy), where no suboxide layer can be identified. Note that the darker elongated features in the HAADF images are cracks⁶⁶.

The equilibrium ZrO binary phase diagram contains no stable phases with these stoichiometries, but Density Functional Theory (DFT) modelling performed by Puchala and Van der Ven⁶⁷ and Nicholls et al.⁶⁸ predicts a stable ZrO suboxide phase with a hexagonal

structure as well as other stoichiometric phases not in the ZrO binary phase diagram, including Zr₂O, Figure 1-16.

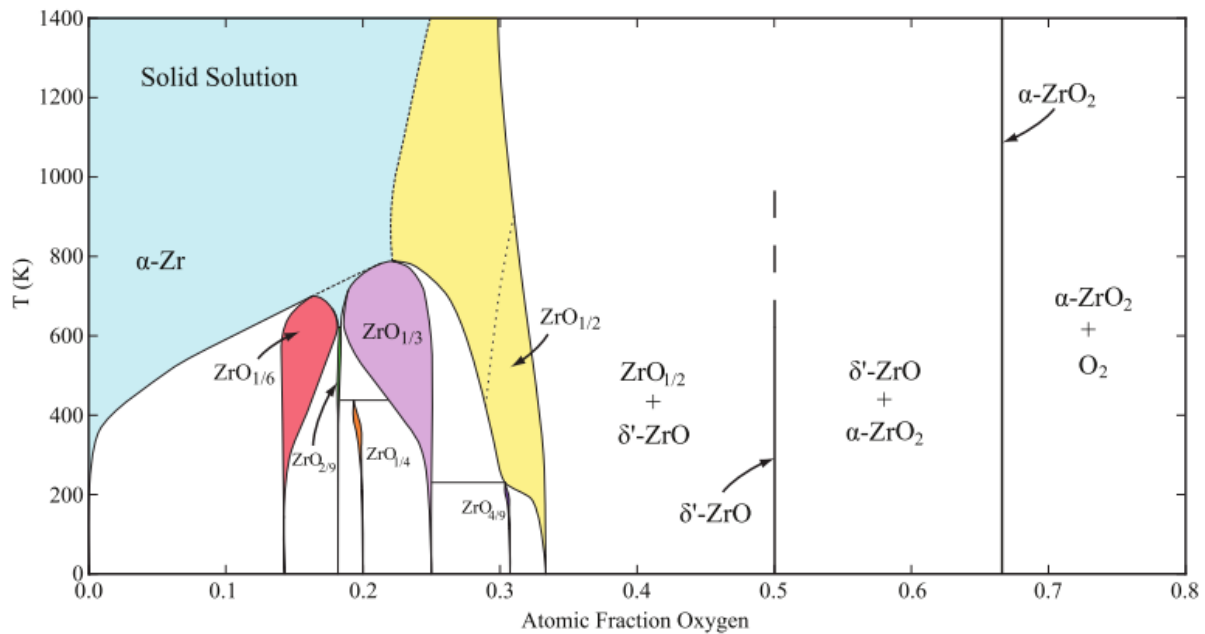


Figure 1-16: (Color online) The calculated phase diagram of hcp ZrOx⁶⁷.

1.2.1 Microstructure

As said before, during the oxidation, oxygen anions diffuse from the oxide-water interface to the metal-oxide interface, while the oxygen vacancies diffuse in the opposite direction. The possible transport sites of oxygen and hydrogen ions include through the oxide lattice, through the micropores in the oxide film, through the second phase particles (SPPs) and along grain boundaries. These ions may migrate in pores close to the metal-oxide interface and concentrate here till they damage the oxide at the pore bottom causing local oxidation and HPU.

The oxide normally makes of both columnar and equiaxed grains, although the detailed structure depends on the sample^{58,69}. Cox compared Zircaloy-2 samples and unalloyed zirconium alloys, found out that the latter can grow columnar oxide without growing any

lateral cracks for up to $10\text{ }\mu\text{m}$ ^{6,17} (Figure 1-17). The transition from columnar to equiaxed grains usually happens where SPPs are oxidised and this also accompanies crack formation⁶⁴.

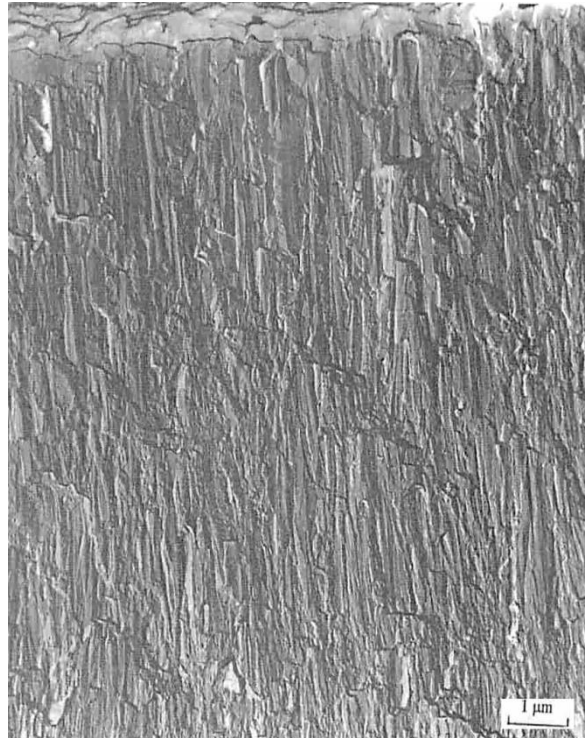


Figure 1-17: Columnar oxide crystallites on Zr oxidized in air at 650°C ^{6,17}.

More equiaxed grains are observed in the outer layer of oxide. In most oxides, the growth direction of columnar oxides is perpendicular to the oxide/metal interface, and samples with larger and better oriented columnar oxides have better corrosion resistance⁷⁰. Yilmazbayhan^{64,70} investigated the microstructure and microchemistry of three different Zr alloys: Zircaloy-4, ZIRLO[®] and Zr-2.5Nb. The TEM pictures in Figure 1-18 show that there are columnar grains on each side of equiaxed grains, and cracks in the equiaxed grain which may due to the ion milling for thin foil sample preparation. The equiaxed grains are mainly tetragonal while the columnar grains are monoclinic.

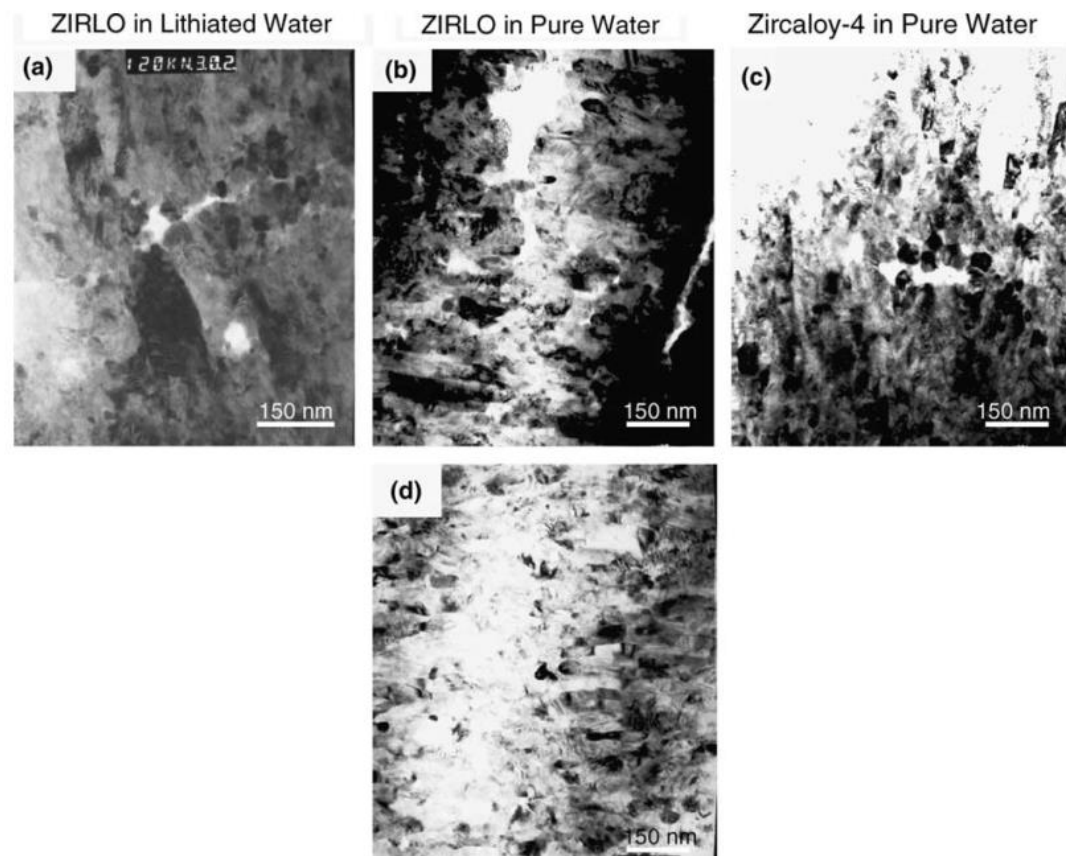


Figure 1-18: Grain size comparison around the cracks of (a) ZIRLO[®] alloy oxide in 360 °C lithiated water, (b) ZIRLO[®] and (c) Zircaloy-4 alloy oxides formed in 360 °C pure water and (d) columnar–equiaxed–columnar type grain structure in ZIRLO[®] alloy oxide formed in 360°C pure water^{64,70}.

Ni et. al^{71,66} studied nano-porosity in the oxide of Zircaloy-4 recrystallized tube using Fresnel contrast. Figure 1-19 shows there are isolated pores at pre-transition the metal-oxide interface and they will connect each other in both lateral and vertical directions. It was also found that in the post-transition oxide, these isolated pores connected together to form interconnected ones along the grain boundaries along the oxide growth direction. Figure 1-19 shows the oxide porosity distribution at increasing distance away from the metal-oxide interface in the grey oxide of the 140 days ZIRLO[®] RXA sample: an array of nano-pores along the direction perpendicular to the oxide growth direction is shown adjacent to the interface; 200 nm away from the interface, there is no nano-porosity; further away the interface, there is an

interconnected porosity with pores parallel to the metal-oxide interface. The author concluded that these interconnected pores provided pathway for accelerated oxidation.

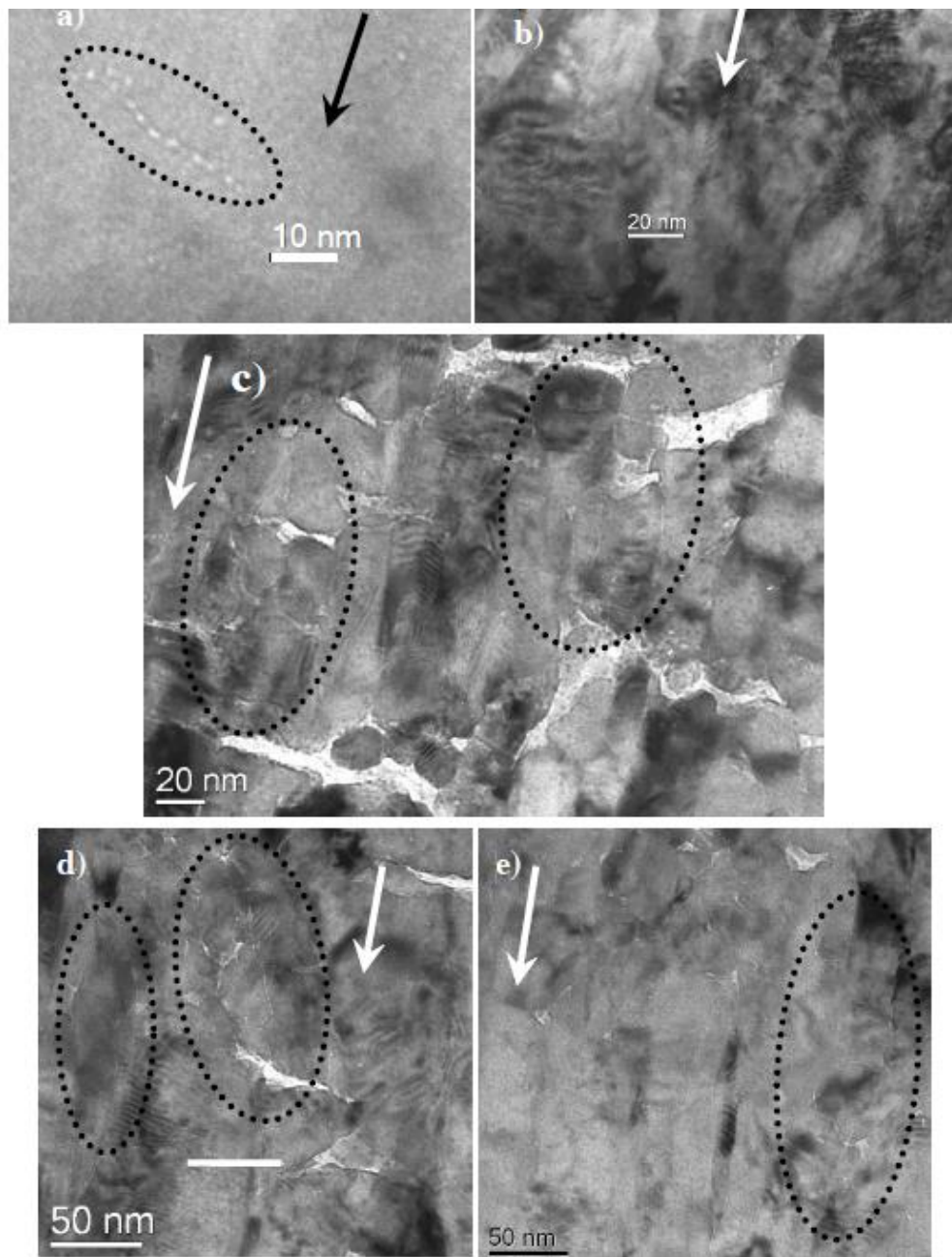


Figure 1-19: Oxide porosity at increasing distance away from the metal-oxide interface in the grey oxide of the 140 days ZIRLO[®] RXA sample. Arrows indicate the oxide growth direction^{71,66}.

Saporiti⁷² studied the oxidation process of $Zr_2(Fe,Ni)$ precipitates in the oxide film, and found out that SPPs release Fe and Ni when they are oxidised. The volumetric increase and straining

between SPP and oxide, which stabilises tetragonal phases, improves the oxidation resistance. To some extent, the mechanism of other SPPs like Zr(Fe,Cr)_2 in Zircaloy-2 is similar⁷³.

Bradley⁷⁴ also investigated the microstructure change using Transmission Electron Microscope (TEM). When Zr alloys start to oxidize, the α -Zr matrix oxidizes to the tetragonal phase of ZrO_2 . The oxidation rate of SPPs is slower than the matrix, so at the beginning of the oxidation, SPPs will become included into the growing oxide layer. As the oxidation proceeds further, the tetragonal phase changes to the equilibrium monoclinic phase, and the elements Fe, Cr and Ni dissolve out from the SPPs finally becoming dissolved in the ZrO_2 . For these two types of SPPs, under a 730K steam environment, the oxidation rate of Zr(Fe,Cr)_2 is much higher than that of $\text{Zr}_2(\text{Fe,Ni})$.

1.2.2 Heat treatment procedures

The general heat treatment procedure for Zr alloys includes α -annealing, β -quenching and $\alpha+\beta$ quenching. In order to consider the influence that quenching temperature and time has on alloy properties primarily by controlling the SPP sizes, researchers use an accumulated annealing parameter ($\sum A$) to combine the parameter of both annealing time (t) in hours and temperature (T) in kelvin. $\sum A$ can be described as follows⁷⁵:

$$\sum A = \sum_i t_i \exp \left[-\frac{Q}{RT_i} \right]$$

Where Q is the activation energy of intermetallic precipitation and R is the gas constant. Kilp⁷⁶ found that when $A < 6 \times 10^{-18}$, the corrosion resistance of Zircaloy-4 decreases, while for $A > 6 \times 10^{-18}$, the corrosion resistance of Zircaloy-4 remains good. Kilp also concluded that choosing the best A value should consider the β -quenching rate, with faster quenching encouraging more Fe, Cr and Ni to dissolve into the matrix thus needs more time for annealing to grow SPPs. They also suggest the best Zircaloy-4 composition, within the

ASTM standard, is observed by lowering the Sn content, increasing Fe and Cr and also controlling impurities like C, N and Si. Kim et. al⁴² did isothermal annealing at about 570°C on Zr-xNb (x= 0.1%-2.0%) alloys and showed that when the Nb content comes to terminal solid solubility, the corrosion resistance is the best, while other high Nb content alloys needs to have more than 50 hours annealing for β -Zr phase to decompose into β -Nb precipitation and dissolved Nb in α -Zr matrix, this relates with better corrosion resistance. Kim⁴⁰ studies the influence of annealing process on the corrosion resistance of Zr alloys. The results show corrosion rate increases as the annealing temperature increases because the iron rich precipitates will grow during annealing.

1.2.3 Working environment

H₃BO₃ is added in the coolant in PWRs⁷⁷ to absorb the neutrons, and LiOH is added to adjust the pH to between 10.0-10.7. However, LiOH in water has a detrimental effect on corrosion resistance²¹, possibly by developing porosity rapidly over the oxide surface⁷⁸, (Figure 1-20).

Zirconium alloys are normally used in the nuclear industry in the pickled condition where surface impurities have been removed. Luscher⁷⁹ used electroplating to modify Zircaloy-4 with NiZr intermetallic on alloy surface. Corrosion result shows that the general oxidation resistance is improved.

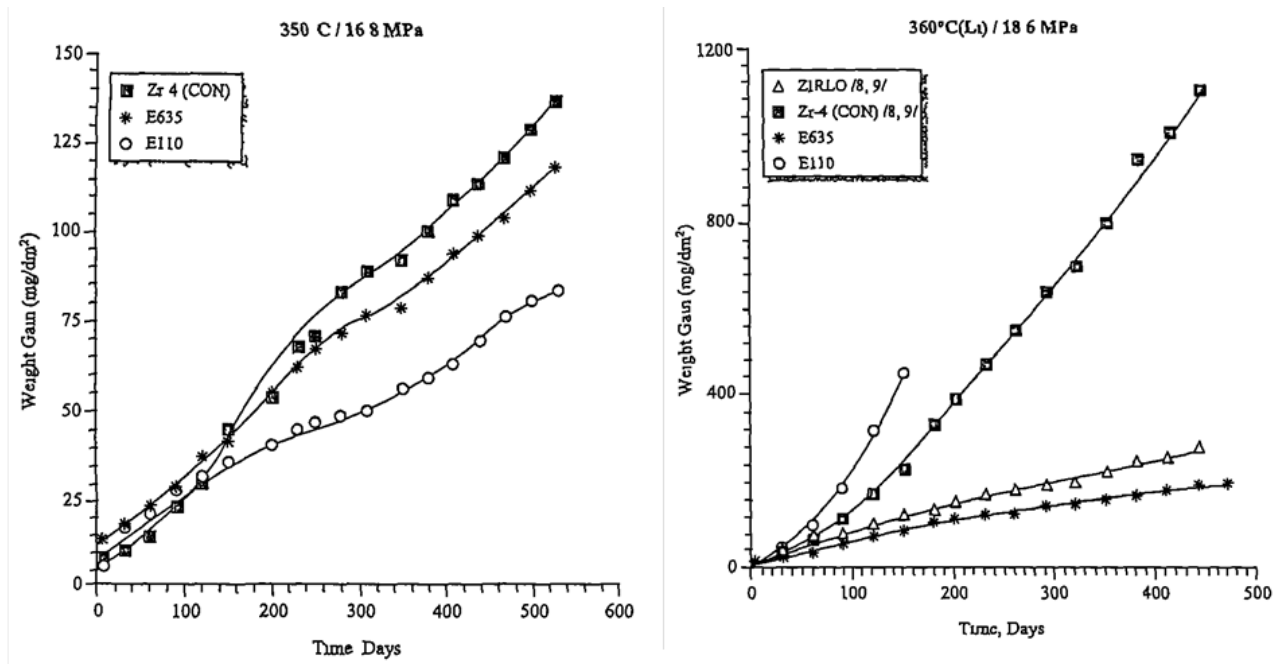
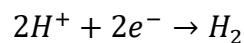


Figure 1-20: Autoclave corrosion of alloys in de-ionized water at 350°C(623 K), 16.8 MPa., (left) and autoclave corrosion of alloys in water containing 70 ppm lithium at 360°C (633 K), 18.6 MPa., (right) ²¹.

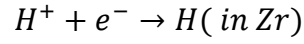
1.3 HYDROGEN PICKUP OF ZR ALLOYS

1.3.1. Definition of hydrogen pickup

Hydrogen pickup happens during the oxidation process. During oxidation, hydrogen ions are produced by the reaction between coolant and zirconium. There are two ways for the hydrogen ions to be absorbed by the system: the first one is when two H ions recombine together to form a hydrogen molecule which is then transferred to the environment. This requires electrons to be provided by the anodic reaction and for this to occur the oxide layer must have a low electronic resistance.



The second reaction occurs when H ions are absorbed by zirconium alloys to form a solid solution at the operative temperature. This requires the protons to diffuse or move by another mechanism from the water-oxide interface to the metal-oxide interface.



The solubility of hydrogen in zirconium, Zircaloy-2 and Zircaloy-4 was defined by Kearns in 1967⁸⁰ as the Terminal Solid Solubility (TSS), as shown in Figure 1-21.

$$C_H = 9.9 \times 10^4 e^{-8250/RT} \text{ ppm}$$

R is the universal gas constant and T is the reactor operation temperature in Kelvin. When T is about 350°C, a normal PWR operative temperature, the TSS of hydrogen is around 100-150 wtppm. Hydrogen will remain in solid solution until it reaches this limit, then hydride platelets begin to precipitate which can cause mechanical degradation.

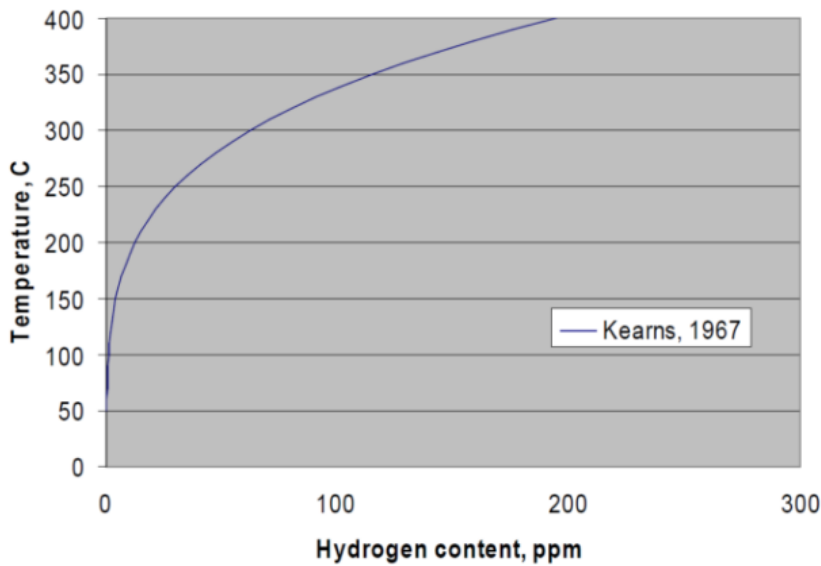


Figure 1-21: Hydrogen solution in Zircaloy as a function of temperature⁸⁰.

The hydrogen pickup fraction (HPUF) is defined as the ratio of the hydrogen absorbed and generated by the overall oxidation process.

$$f_H = \frac{H_{\text{absorbed}}}{H_{\text{generated}}}$$

It is well-known that hydrogen embrittlement can make the Zr alloys more prone to fracture in service⁵². Thermal gradients between the inner and outer part of a cladding tube also

contribute to degradation. The lower temperature part, which is further away from the fuel rods will reach the TSS limit of hydrogen first thus forming hydride rims. Figure 1-22 shows in PWR, when Zircaloy-4 is irradiated for 6 cycles, the hydride distribution and oxide layer¹⁹. Also hydride blisters as in Figure 1-23 are caused by the corrosion of inner side of cladding alloys and hydrogen can go through the cladding walls and then form radial hydrides⁵².

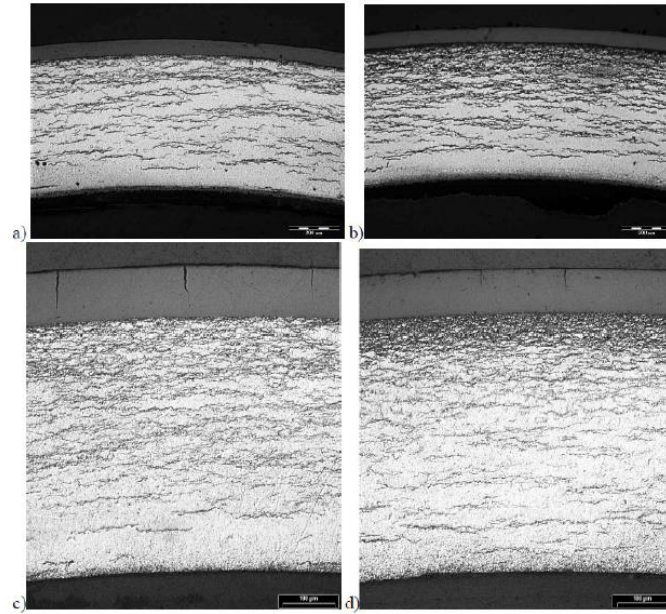


Figure 1-22: Optical micrographs of the hydride distribution and oxide layer on Zircaloy-4 irradiated for 6 cycles in PWR at (a) and (b) span 4, 1851-2001 mm from fuel rod bottom, (c) and (d) span 6, 3000-3200 mm elevation from fuel rod bottom¹⁹.

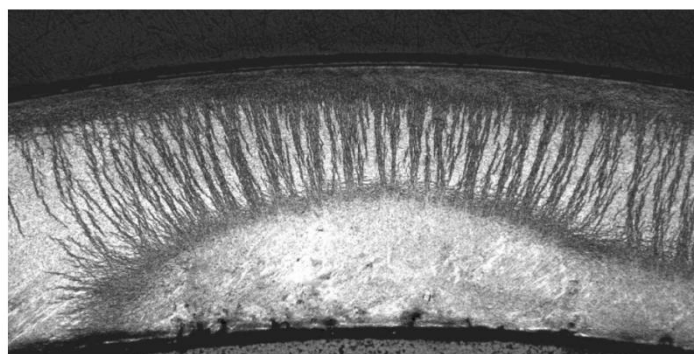


Figure 1-23: photo of a hydride blister⁵².

Delayed hydride cracking (DHC) is a common problem in CANDU reactors and is due to the stress gradients at crack tips at the inner side of the cladding alloy. The model in Figure 1-24

shows the elevated stress at the crack tip results in a lower chemical potential of hydrogen, so hydrogen moves to the crack tip. The more it moves, the larger potential difference is, in this way the process repeats until the local stress reaches the actual applied stress for fracture, causing material failure.

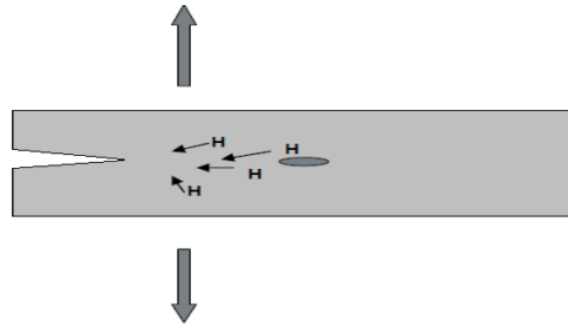


Figure 1-24: Schematic illustration of the diffusion of hydrogen towards a crack tip. The arrows indicate the direction of the external stress. The crack propagation direction is normal to the direction of applied stress⁸¹.

It is worth mentioning that there are several sources of hydrogen. Besides the oxidation process of the cladding alloy, radiolysis of the coolant can provide hydrogen ions by the reaction $2H_2O \rightarrow 2OH^- + 2H^+$. There is also some dissolved hydrogen already in the coolant; the hydrogen left in the cladding during fabrication is relatively smaller amount.⁸²

Three different zirconium hydride phases are shown in the phase diagram of Zr-H in Figure 1-25. Hydrogen is also a β -stabilizer which means it can lower the α/β transition temperature of zirconium. Below 550 °C, there are three types of hydrides⁸³: 1) γ -hydride with composition of around ZrH and a face centred tetragonal (FCT) structure with $a=4.596 \text{ \AA}$; $c=4.969 \text{ \AA}$, Mishra^{84,85} suggested this phase is stable, while Lanzani⁸⁶ reported this phase is metastable and can only be found after rapid cooling; 2) δ -hydride with composition of around $ZrH_{1.6}$ and a face centred cubic (FCC) structure with $a=4.778 \text{ \AA}$; 3) ϵ -hydride with composition from $ZrH_{1.65}$ to $ZrH_{1.965}$ and a face centred tetragonal (FCT) structure with $a=3.520 \text{ \AA}$, $c=4.440 \text{ \AA}$. Both δ -hydride and ϵ -hydride are stable phases.⁸⁷

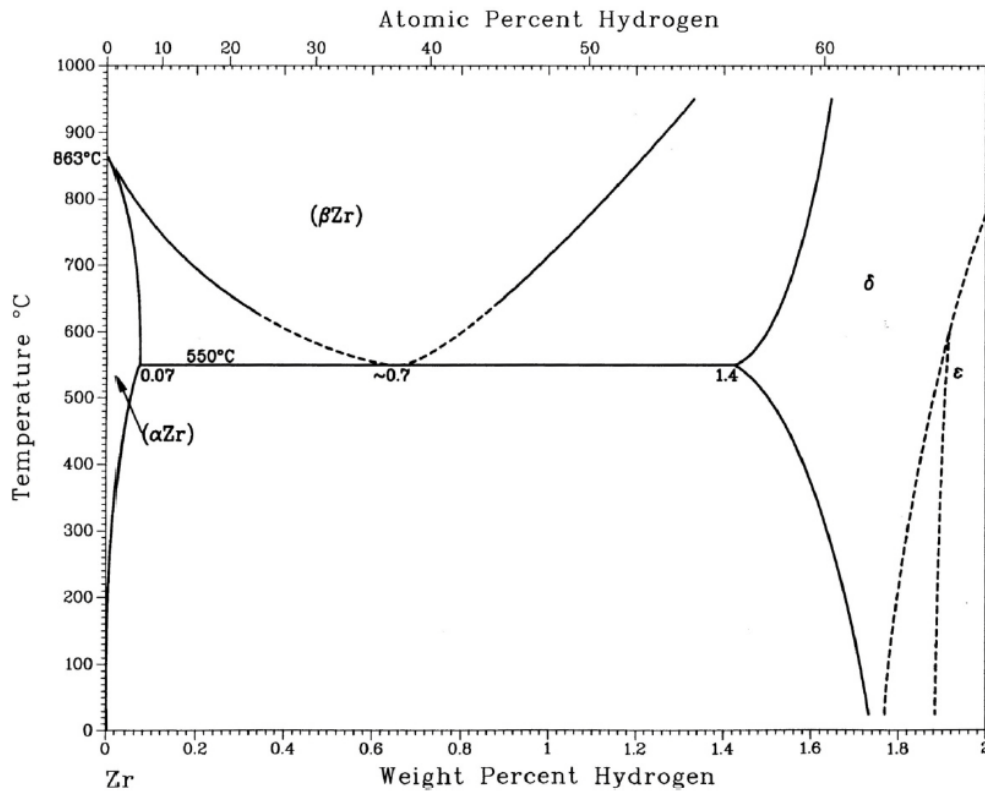


Figure 1-25: Phase diagram of Zr-H⁸⁸.

1.3.2 Factors influencing the hydrogen pickup

There are both external and internal factors influencing HPUF: internal factors such as chemical composition which will influence microstructure like SPPs, pores and cracks, external factors like working environment, including temperature and water chemistry.

1.3.2.1 Chemical composition

Alloying elements play an important role in the HPU in Zr alloys. Berry⁸⁹ studied hydrogen absorption for various binary alloys, and their HPUFs are shown in Figure 1-26. It suggested that while nickel increases HPUF, tin has little effect on HPUF. Other elements like iron, chromium and antimony reduce HPUF. The reason for this is that in zirconium alloys containing iron, chromium, or nickel the compounds of these elements are cathodic with respect to the zirconium matrix. The resulting potential difference is sufficiently high to anodically polarize the zirconium and thus improve corrosion resistance. Apparently iron and

chromium compounds readily depolarize hydrogen and thereby decrease the possibility of its passage through the oxide film. Nickel compounds probably do not depolarize hydrogen and may aid in its passage through the oxide film.

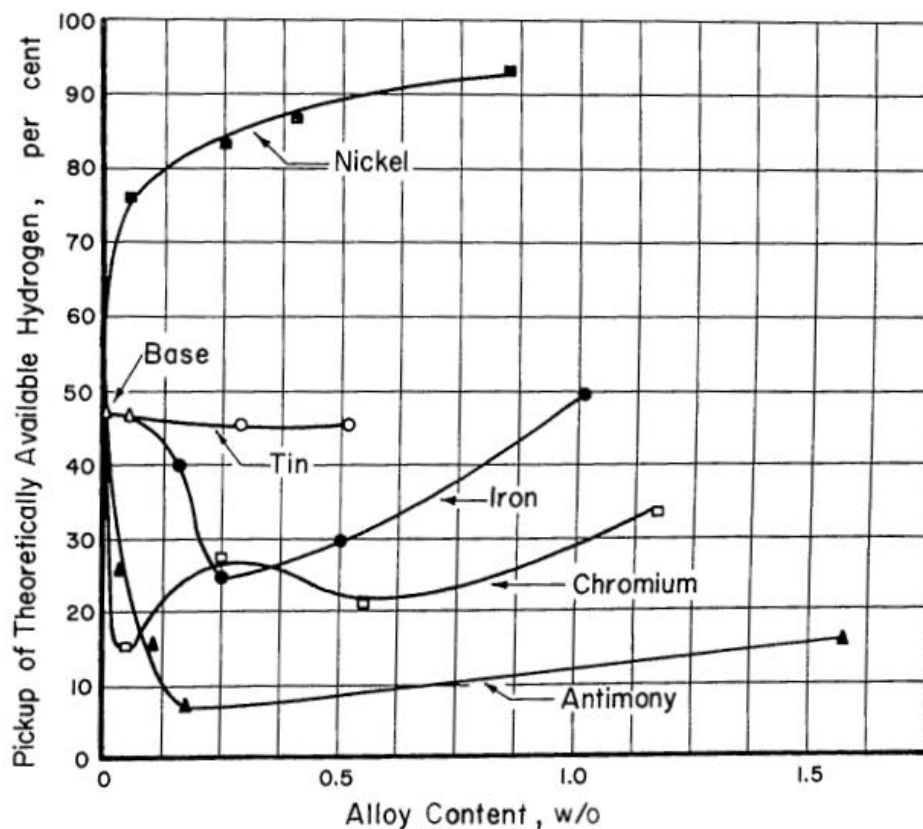


Figure 1-26: Hydrogen pickup in sponge based zirconium alloys exposed up to 575 days to static water at 360°C⁸⁹.

Kass and Kirk¹⁶ studied the difference between Ni-free Zircaloy-2 and standard Zircaloy-2.

The results in Figure 1-27 showed the detrimental effect that Ni has on HPU of Zr alloys.

Hillner⁹⁰ also studied the HPUF difference between Zircaloy-2 and Zircaloy-4. The high HPUF in Zircaloy-2 is mainly due to the nickel content, which helps water dissociation and decreases the recombination of hydrogen and oxygen, as seen in Figure 1-28.

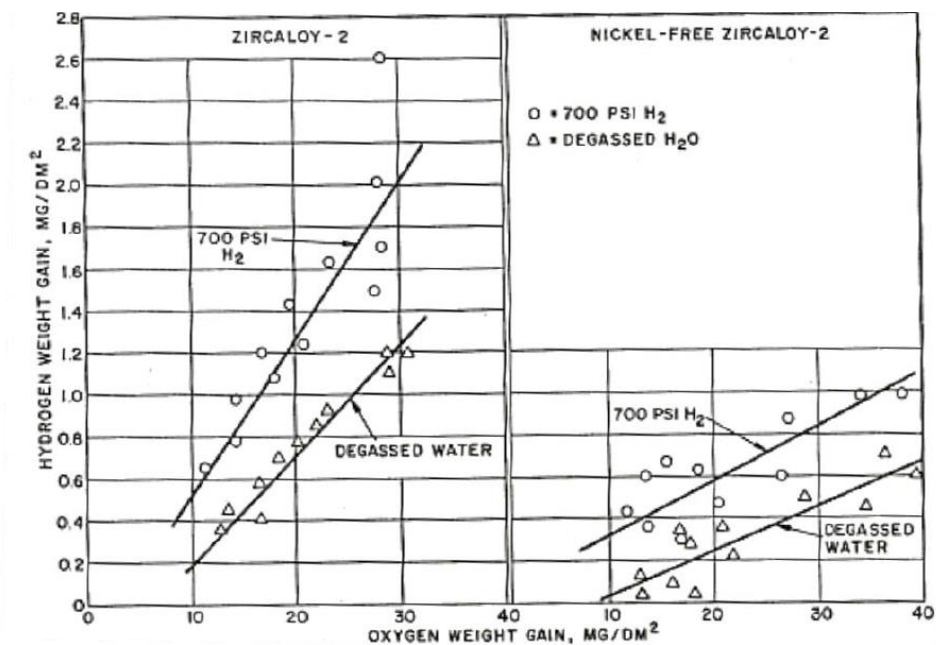


Figure 1-27: Hydrogen absorption of Zircaloy-2 and Ni-free Zircaloy-2 in hydrogenated and degassed 343°C water¹⁶.

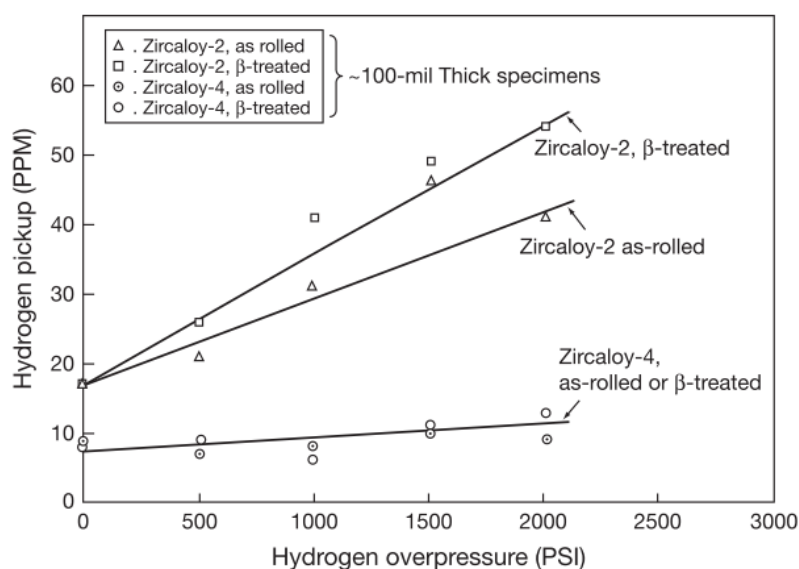


Figure 1-28: Hydrogen pickup in Zircaloy-2 and Zircaloy-4 as a function of hydrogen overpressure after 14 days in 343 °C water⁹⁰.

Choudhuri⁴³ studies the influence of adding different amount of iron into Zr-2.5Nb alloy on oxidation and hydrogen pick up performance. With increasing iron content, the oxidation resistance improved meaning less hydrogen is produced and seeing by electron microscope, there are more cracks and pores observed in oxide. However, the HPUF increases which indicates pores and cracks does not contribute to the HPU. In the meantime, there are Zr-Nb-Fe and Zr-Fe intermetallic precipitates which create large interface area between α -Zr phases where HPU can happen.

Kakiuchi⁹¹ studied the difference between HiFi (High corrosion resistance and high Fe (iron) zirconium alloy) and Zircaloy-2 by using contact potential difference (Δ CPD) on the oxide film. HiFi has HPUF of 28% while Zircaloy of 50%. Figure 1-29 shows that with increasing iron content, Δ CPD increases, and there are more anion vacancies. Δ CPD also represents the oxide /water interface electrical potential⁹², so when Δ CPD is high, there will be more electrons coming from the metal-oxide interface to move to the oxide surface/ water interface, thus less hydrogen ions need to go the opposite direction which means lower HPUF.

Northwood⁹³ gave detailed microscopic study of hydrides in Zr-2.5wt%Nb alloys. At low hydrogen content and slow cooling rates, there are more acicular or flake shape γ -ZrH. When the hydrogen content and cooling rates are higher, more equilibrium δ -ZrH_{~1.6} is formed, Table 1-4.

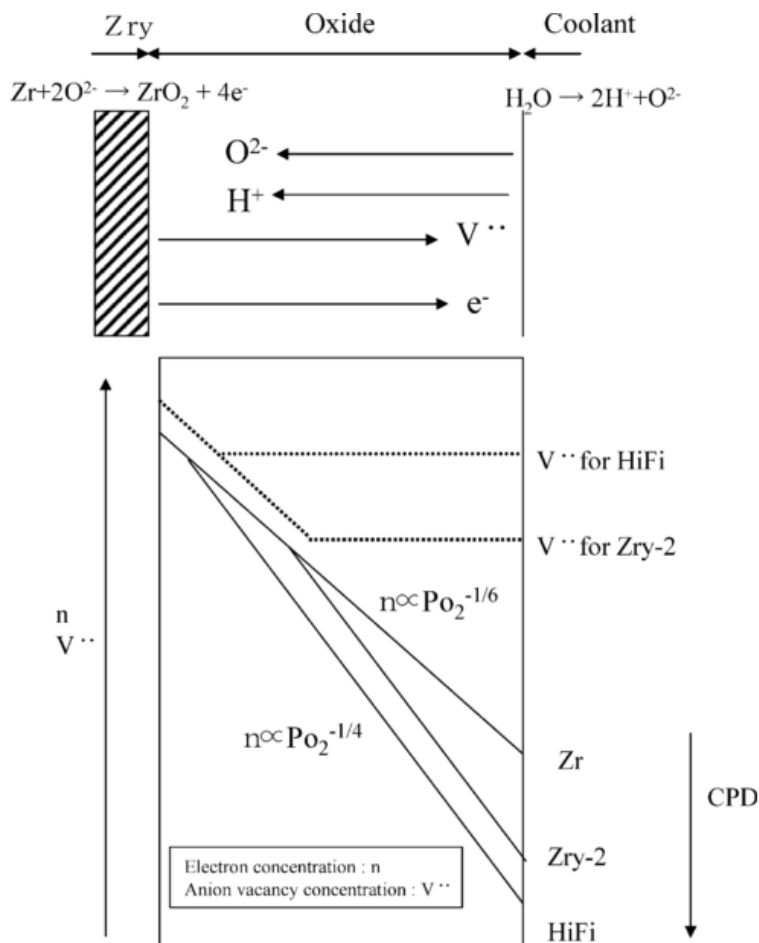


Figure 1-29: The relationship between oxide surface potential and anion vacancy⁹¹.

Table 1-4: Effect of cooling rates and hydrogen content on the hydride phases present in Zr-2.5wt%Nb pressure tubes⁹³.

Hydrogen Content (ppm by weight)	Quenching Media				
	Brine	Water	Oil	Air	Furnace
7	γ	γ	γ	γ	γ
46	γ (γ)	γ (γ)	γ (γ)	$\gamma + \delta$ (γ)	$\delta + \gamma$ ($\delta + \gamma$)
150	$\delta + \gamma$ ($\delta + \gamma$)	$\delta + \gamma$ ($\delta + \gamma$)	$\delta + \gamma$ ($\delta + \gamma$)	$\delta + \gamma$ ($\delta + \gamma$)	$\delta + \gamma$ ($\delta + \gamma$)
300	$\delta + \gamma$ ($\delta + \gamma$)	$\delta + \gamma$ ($\delta + \gamma$)	$\delta + \gamma$ ($\delta + \gamma$)	δ (δ)	δ (δ)

1.3.2.2 Microstructure (SPPs, pores, cracks and grain boundaries)

During the oxidation and HPU reactions, oxygen anions diffuse from the oxide-water interface to the metal-oxide interface, while the oxygen vacancies diffuse in the opposite direction. It is suggested that diffusion of hydrogen ions is driven by the need to maintain charge balance when electron transport through oxide is difficult. Previous work^{51,94} suggest that possible transport sites of hydrogen ions include through the oxide lattice, through the micropores in the oxide film, through the second phase particles (SPPs) and along grain boundaries. H ions may migrate in pores close to the metal-oxide interface and concentrate here till they damage the oxide at the pore bottom causing local HPU. Some believe that large SPPs in the barrier layer can serve as windows or local expressways for H ions to diffuse through^{95,96}.

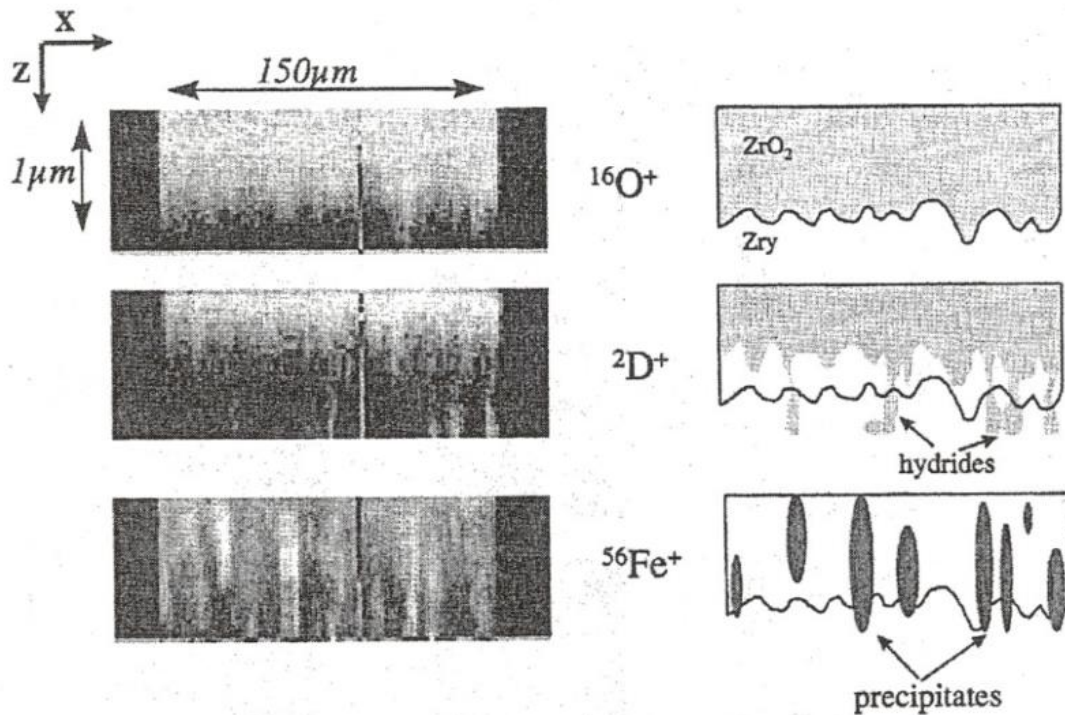


Figure 1-30: SIMS cross section of a 3D reconstitution, distribution and associated schematic representation of oxygen, deuterium and iron in the oxide of a Zircaloy-4 sample, oxidised 48 hr at 673K in heavy water⁹⁷.

Bossis⁹⁷ used secondary ion mass spectroscopy (SIMS) to study Zircaloy-4. Figure 1-30 shows that the place where the hydrides exist coincides with the place where SPPs are, which is strongly supporting the role of SPPs in hydrogen uptake in Zircaloy-4.

Hatano⁹⁸ studied the influence of SPP size on HPUF of Zircaloy-4 before transition. They show that β quenched materials with finer $\text{Zr}(\text{Fe,Cr})_2$ SPPs have lower HPUF values than materials by β slow-cooled with coarser SPPs. Also as seen in Figure 1-31. HPUF of the materials with finer SPPs is independent of temperature while that with coarser SPPs increases with decreasing temperature. Similar results on Zircaloy-2 with SPPs of $\text{Zr}_2(\text{Fe,Ni})$ and $\text{Zr}(\text{Fe,Cr})_2$ are observed⁹⁹.

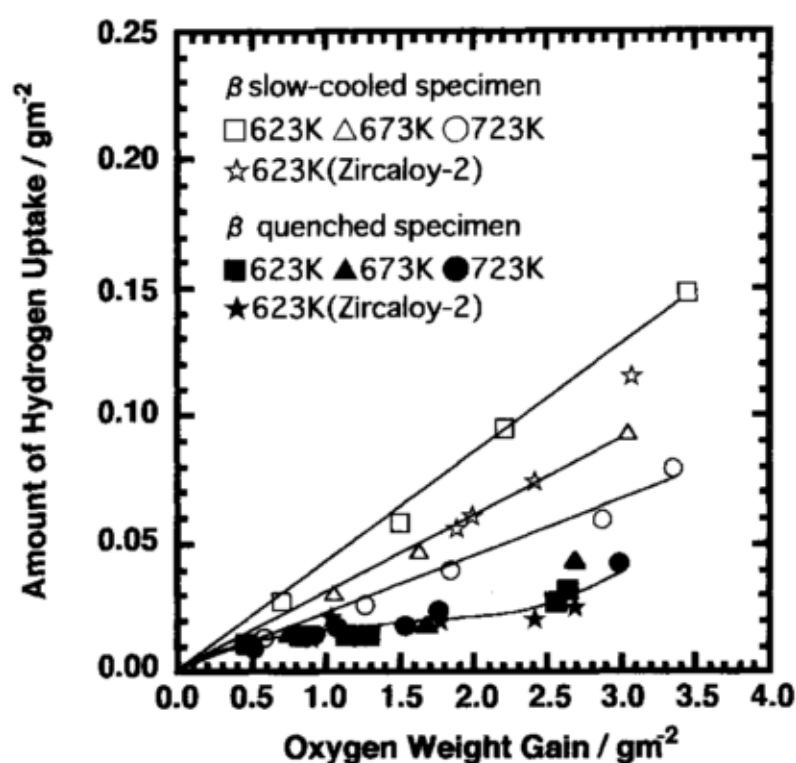


Figure 1-31: Hydrogen uptake of β quenched and β slow-cooled specimens⁹⁸.

Hanato¹⁰⁰ also compared Zircaloy-2 and Zircaloy-4 showing that β slow-cooled Zircaloy-4 has the highest HPUF while HPUF of β quenched Zircaloy-2 and Zircaloy-4 are comparable,

Figure 1-32. They concluded using the model in Figure 1-33 that unoxidised SPPs stay in a metallic state and have high chemical affinity for hydrogen, so the hydrogen will enter the SPPs until they are fully saturated. Only then can hydrogen dissolve into the metallic matrix, so SPPs work as the short-circuiting route in the hydrogen transport (Figure 1-33). The β quenched alloys have finer SPPs which means they can be fully oxidised before any hydrogen can enter.

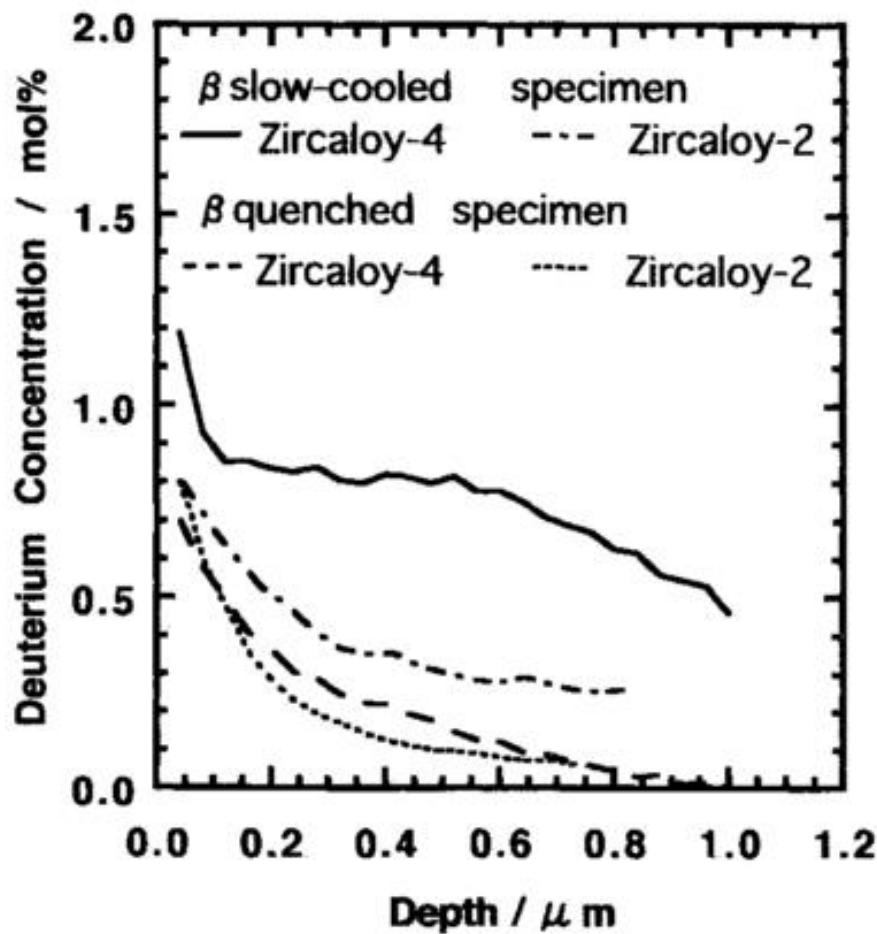


Figure 1-32: Concentration profile of deuterium in the oxide film formed on β quenched and β slow-cooled specimens at 673 K¹⁰⁰.

The tritium autoradiography method has been used in several studies^{100,101,102} to study the spatial distribution of hydrogen in Zr alloys. This uses tritium water in cathodic charging of room temperature. It shows tritium exists largely along the grain boundary and inner side of

the metal rather than the oxide, it concludes that hydrides prefer grain boundaries to precipitate and the SPPs in the oxide layer offer a supplementary expressway for hydrogen.

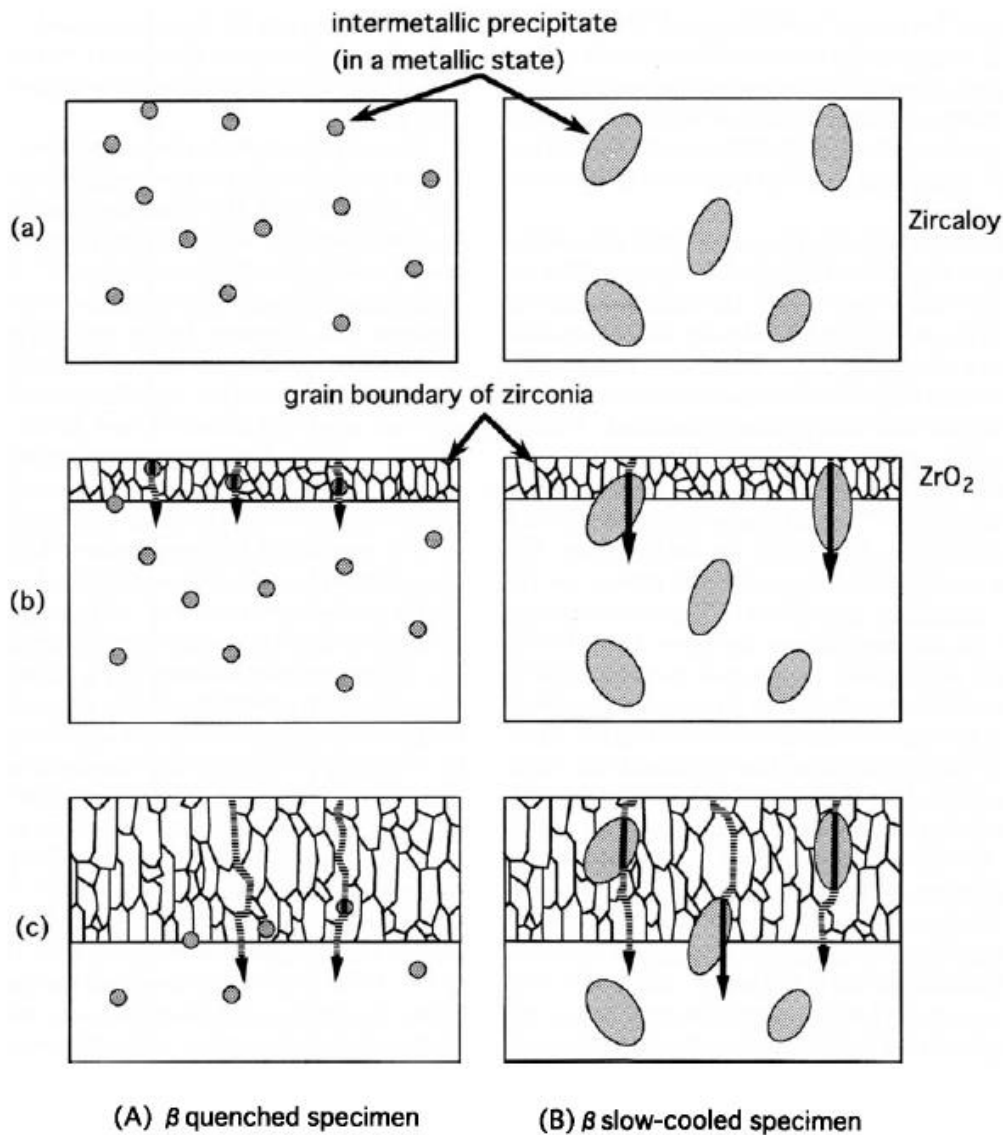


Figure 1-33: Schematic description of mechanism of hydrogen transport through the oxide film of β quenched and β slow-cooled specimens¹⁰⁰.

Cox^{103–105} tried to locate the cathodic sites in anodic oxide films of Zircaloy-2 samples by using CuSO₄ solution to deposit small Cu balls. The SEM pictures in Figure 1-34 show most of these deposit on the sites of cracks or pores, none at the sites of Zr(Fe/Cr)₂ SPPs. The authors concluded that crack and pores firstly react with steam or water and oxidation reaction produces metal oxides and hydrogen. Then the accumulated hydrogen will go through an

incubation period until it breaks down at the bottom of the pores and hydrogen will be absorbed by the metal.

Khatamian^{106,107} studied hydrogen diffusion on oxides of pure Zr and Zr-Nb alloys before and after annealing using ion-beam implantation. The hydrogen diffusion is analysed by nuclear reaction profiling using the $^{15}\text{N}(\text{H}, \text{ay})^{12}\text{C}$ reaction. It shows the hydrogen peak drops without expanding the peak area meaning there is hydrogen loss. This is due to the fact that the oxides are heterogeneous and have some interconnected pores and cracks which can contribute to hydrogen diffusion. However, there is concern about this method of ion-beam implantation since it introduces radiation damage to the vicinity of the place where the hydrogen is implanted, this can be shown by the asymmetry of the pattern in Figure 1-35.

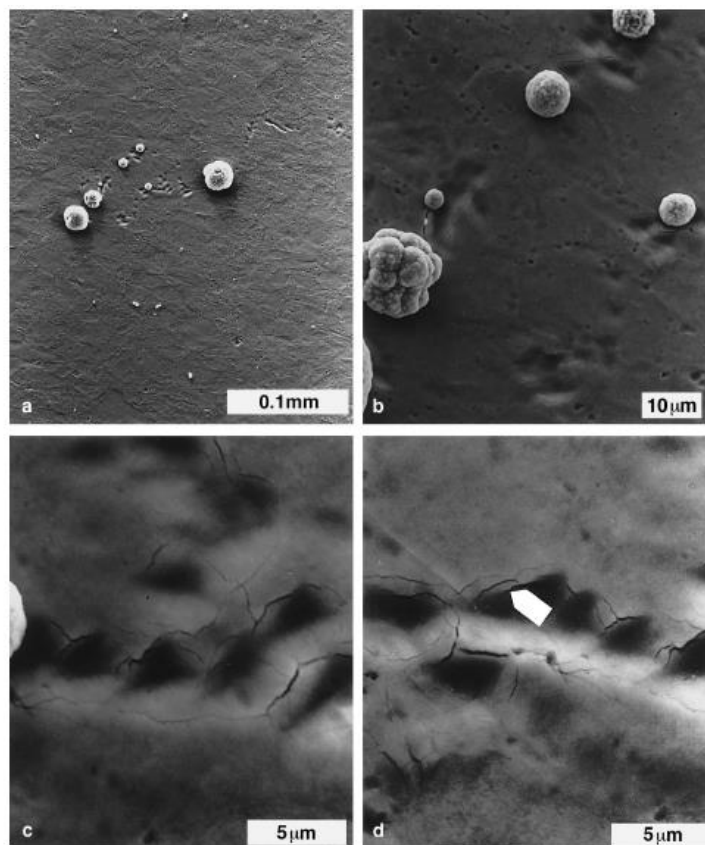


Figure 1-34: Scanning electron micrographs of Cu deposited cathodically on an oxidised Zry-2 surface (1.2 µm thick oxide), (a) distribution of large and small Cu balls on the surface (b) group of large balls from (a), (c) Crack pattern in oxide adjacent to RH ball in (c), (d) nucleation site of this ball (arrowed)¹⁰³⁻¹⁰⁵.

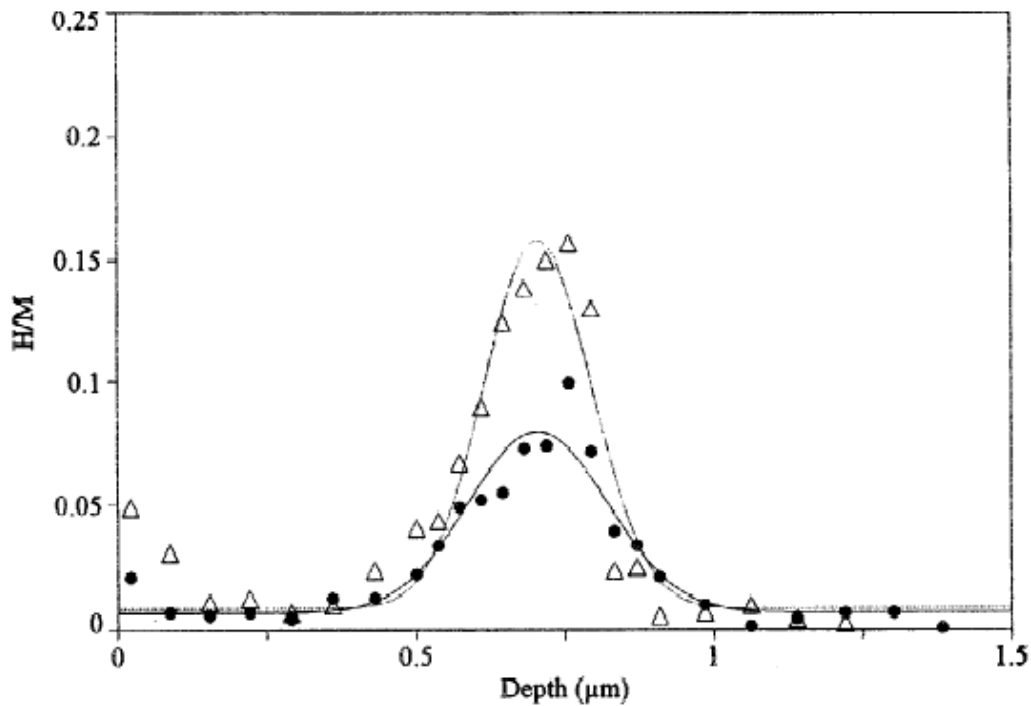


Figure 1-35: Depth profiles for implanted hydrogen showing initial implantation (triangles) and after diffusion annealing for 4 min in 720 K air (circles). The oxide film was grown in 633 K water on Zr-20Nb aged for 3 h. The curves are the best Gaussian fits to the experimental points.¹⁰⁷

1.3.2.3 Working environment

Hillner⁹⁰ studied the effect of water oxygen content and Ni content of Zry-2 on uptake of corrosion hydrogen in 360°C water without irradiation. Figure 1-36 indicates that with increasing water oxygen content, the HPUF decreases.

Cox¹⁰⁸ studied the effect of water chemistry on in-reactor hydrogen pickup rates and showed that HPUF increases with H:O ratios till about 45% and stays the same afterwards, Figure 1-37.

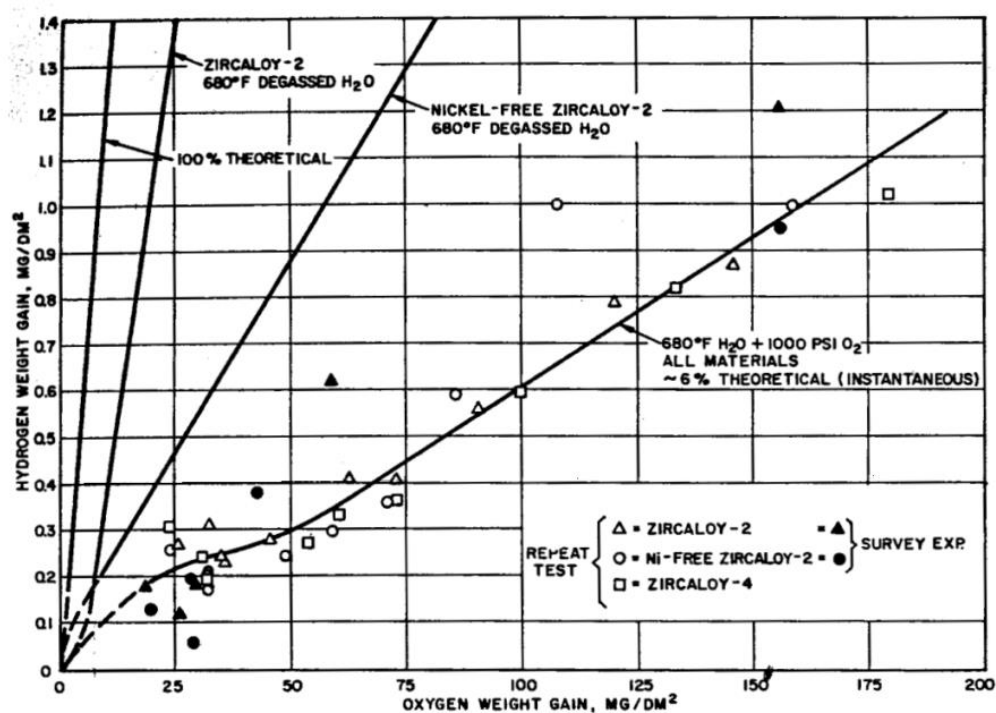


Figure 1-36: Effect of water oxygen content and Ni content of Zry-2 on uptake of corrosion hydrogen in 360°C water without irradiation. 15 mg/dm² corresponds to about 1 μm^{90}

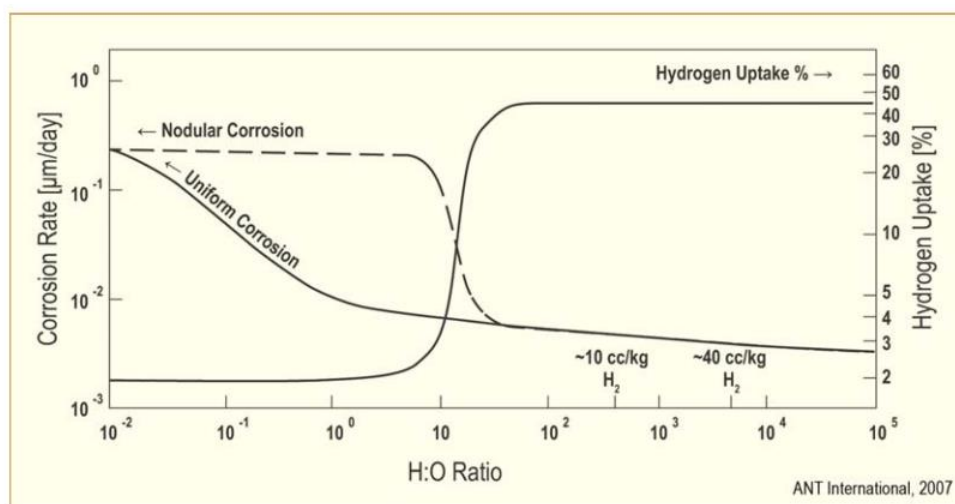


Figure 1-37: Effect of water chemistry on in-reactor oxidation and hydrogen uptake rates¹⁰⁸

2 CHAPTER 2 MATERIALS AND METHODS

2.1 MATERIALS USED IN THIS STUDY

Two types of materials were examined in this study: RXA Zr-1.0Nb and annealed Zr-1.0Nb. Here I give an overview of the samples chosen from each material, detailed information of the samples are discussed in the beginning of each chapter 3~5.

Most of the analysis on RXA Zr-1.0Nb alloys come from a WestinghouseTM developmental alloy with composition of Zr-0.9Nb-0.01Sn-0.08Fe (wt%) in the recrystallized condition with final heat treatment around 560°C. The sample is in tube shape. They were oxidized in an autoclave at EDF Energy under simulated Pressurized Water Reactor (PWR) water conditions at 360°C for up to 540 days, and some samples then received an additional exposure to deuterated water for a further 45 days. Autoclave data (Figure 2-1) shows no sign of accelerated oxidation rate even after 360 days^{63,109}. However, the hydrogen pickup data is lacking. From this set of samples, I've chosen 120-day (pre-transition), 225-day (180 day H₂O +45 day D₂O, pre transition), 360-day (transition), 540-day (post-second-transition) and 585-day (540 day H₂O +45 day D₂O).

Two coupons were received of RXA Zr-1.0Nb sheet irradiated for one cycle (540 days) in the Vogtle reactor. The estimated fast neutron fluence accumulated was 4.35×10^{21} n/cm², E>1 MeV, which can be considered to be around a third of the fluence that a typical fuel cladding sees by end of life. This treatment does not fully correspond to in-reactor conditions for the cladding tubes since the coupon was not subjected to any stress, the weight gain data is shown in Figure 2-1.

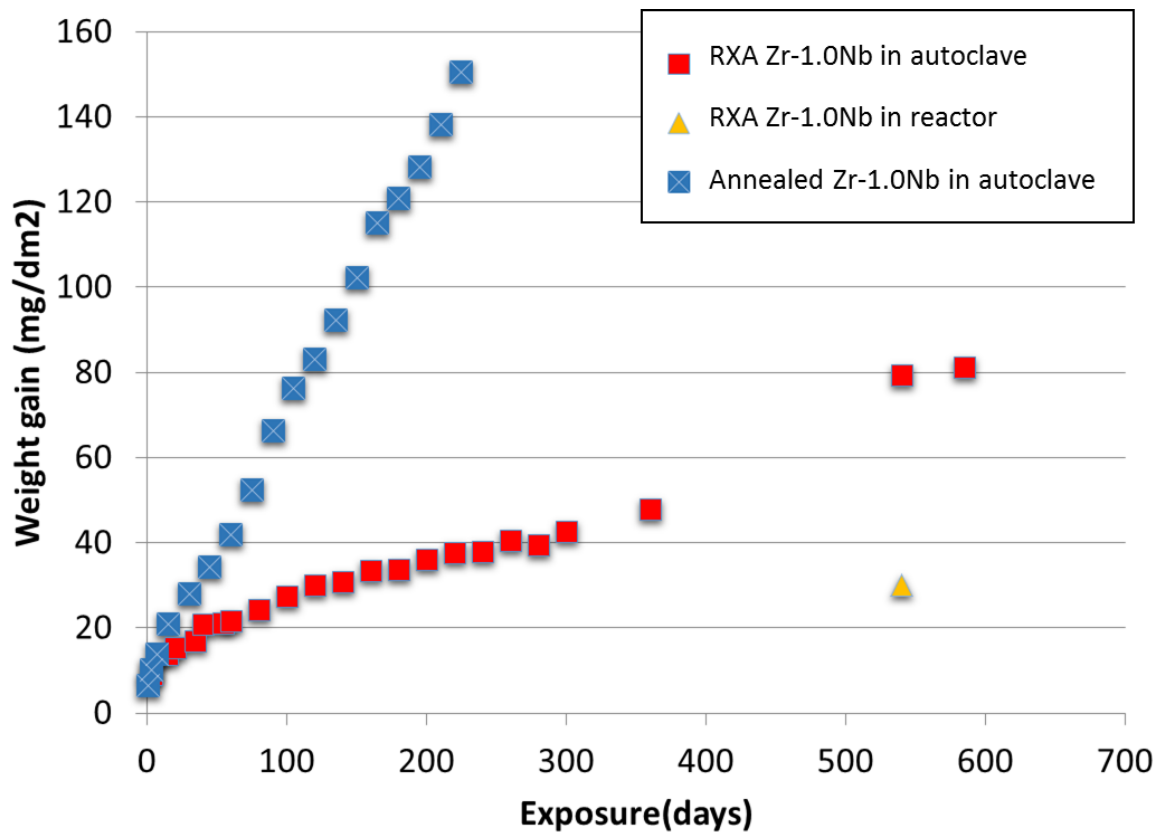


Figure 2-1: Weight gain data of RXA Zr-1.0Nb (tube) in autoclave, annealed Zr-1.0Nb (sheet) in autoclave and RXA Zr-1.0Nb (sheet) in reactor.

The first question regarding the differences between neutron irradiated and autoclave samples is that apart from the neutron irradiation, there may be other differences such as the temperature of the oxidation environment and geometry of the samples. The neutron irradiated sample spent 540 days in a commercial PWR at an estimated temperature between 305 and 315 °C, while the autoclave samples were oxidised using simulated PWR water at 360 °C for 585 days.

The lower corrosion temperature for the in-reactor sample oxidized explains the apparently anomalous in the reactor played a primary role in producing a thinner oxide. Using a published activation energy (Q) of 27103 cal/K/mol ($Q/R=13640$)⁸² for the pre-transition oxidation kinetics, we estimate the oxide thickness growth rate at 360°C (633 K) should be 6.3 times greater than at 310°C (583 K).

$$\frac{t_{\text{ox}}(633\text{K})}{t_{\text{ox}}(583\text{K})} = \frac{\text{Be}^{-13640/633}t^n}{\text{Be}^{-13640/583}t^n} = 6.3$$

Using the measured oxide thickness of 5.2 μm after 540 days of autoclave oxidation, we can then estimate the oxide thickness after the same time at 310 °C to be 0.8 μm while we measure a thickness of 2 μm . This seems to suggest that for the particular samples that we have studied there is accelerated corrosion in the pre-transition region in Zr-Nb alloys.

However, many neutron irradiation studies on ZIRLO[®] and Zircalloys have shown that irradiation increases the rate of corrosion^{110–114}, but that Zr-Nb alloys do not undergo accelerated corrosion, such as the Russian alloys E110¹¹⁵ and French Areva alloy M5^{TM 116} which have been used as the fuel rod for cladding of WWERs and RBMKs and French PWR for many years, respectively. They both show very good corrosion resistance and low hydrogen pickup fraction, with very few cases reported for abnormal corrosion in reactor^{116,117}. So in this study, the comparison between irradiated and autoclave samples must take into account not only the reactor temperature or sample geometry, but can also reflect the effect of irradiation on corrosion.

The reactor temperature from the samples we had was between 305 -315 °C, and using appropriate values of $n=1/0.45=2.22$ ¹¹², the pre exponential and activation energy values from the literature⁴, so that $(\Delta w)^n=kt$, and $k= B \times \exp(-13640/T)$, we estimate that the oxidation rate at 360 °C will be 2.52 times as fast as at 310 °C. So using the measured oxide thickness after 540 days of autoclave oxidation of 5.2 μm , we can estimate the oxide thickness we would expect after the same time of 310 °C is around 2.06 μm , very close to the observed thickness of the irradiated sample.

Later in the program, we received RXA Zr-1.0Nb alloys in sheet form, with oxidation and hydrogen pickup measurements up to 225 days in light water autoclave at Westinghouse™ at 360°C (Figure 2-4). From this sample, I've chosen a 3-day sample to look at oxide microstructure at early stage.

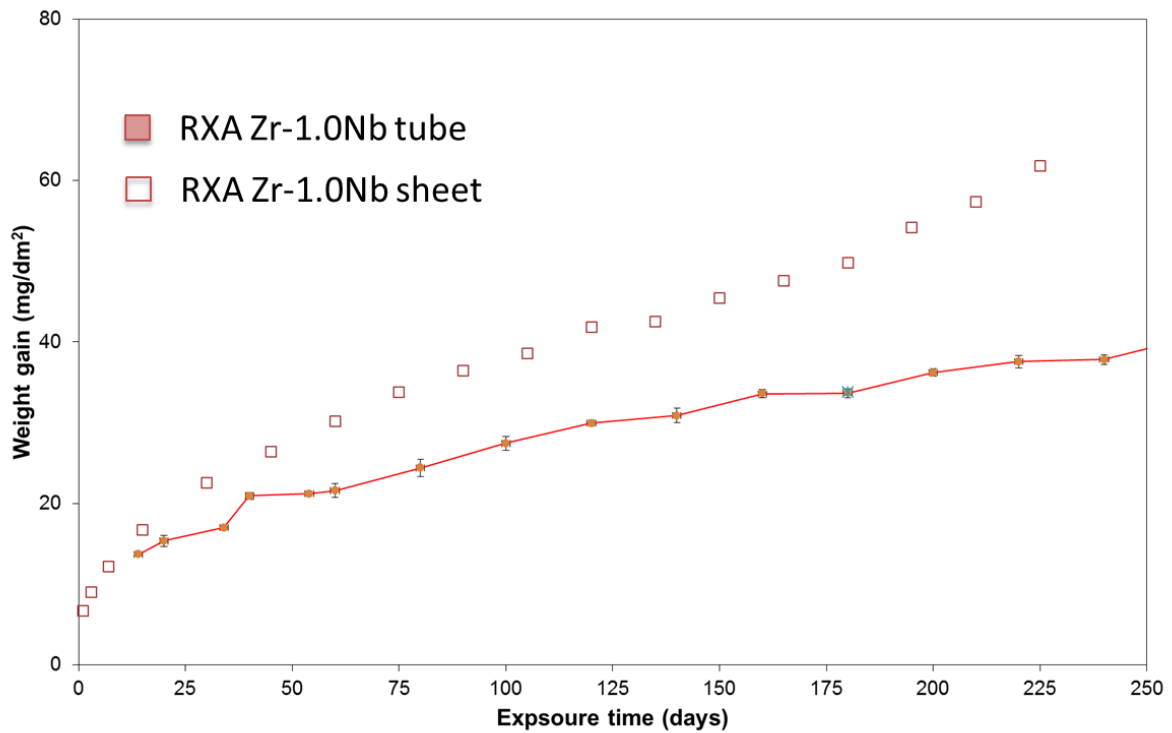


Figure 2-2: Comparison of oxidation data between RXA Zr-1.0Nb sheet and tube samples, weight gain vs exposure time. Autoclave environment: tube RXA Zr-1.0Nb : in PWR simulated water autoclave in EDF from MUZIC-1 and sheet RXA Zr-1.0Nb: in pure water autoclave in Westinghouse™.

The differences of weight gain data of RXA Zr-1.0Nb in tube and sheet shape is summarised in Figure 2-2. The autoclave testing were done at different labs with different water chemistry, one in PWR simulated water (tube) and one in pure water (sheet). Literature has indicated that PWR water will change the corrosion rate^{9,21,62,77}, the comparison here shows the sheet Zr-1.0Nb in pure water one corrodes faster than the tube one in PWR primary water. The possible reason is perhaps there is slight difference in materials chemistry, heat treatment and the way autoclave testing is done, also the sample geometry can play a role as well.

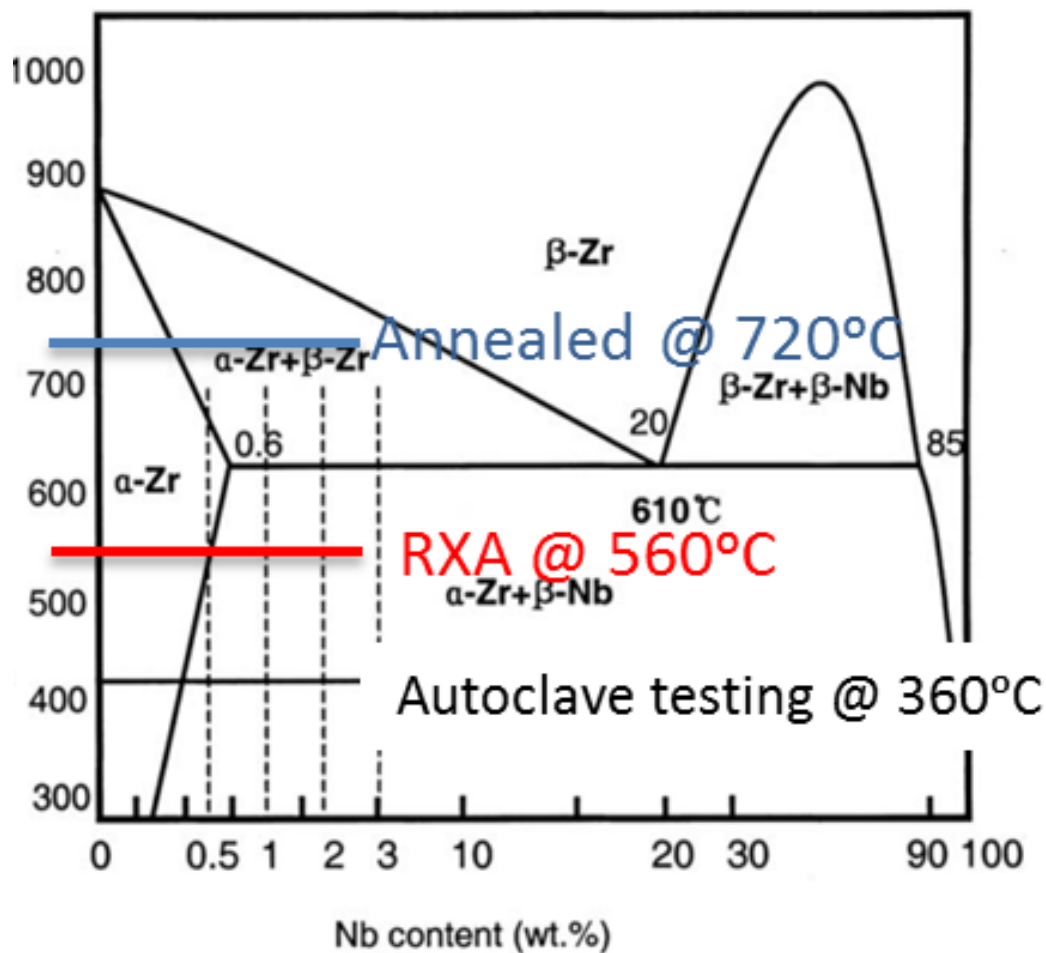


Figure 2-3: Zr-Nb phase diagram with temperature of final heat treatment of annealed and RXA samples. Autoclave testing is done at 360 °C¹¹⁸.

This sheet RXA Zr-1.0Nb alloy has been annealed further at 720°C for 24 hours to create annealed RXA Zr-1.0Nb sheet in order to obtain a larger precipitate size, but these precipitates were β -Zr rather than the small β -Nb precipitates found in the RXA alloy Figure 2-3¹¹⁸. The weight gain and hydrogen pickup measurements for up to 225 days in light water autoclave at WestinghouseTM at 360°C is shown in Figure 2-1 and Figure 2-4. Even though it has the same composition, the annealed Zr-1.0Nb alloy showed a much earlier acceleration in corrosion rate between 45 and 60 days and much faster overall oxidation kinetics^{70,47,119}. Four samples were chosen from this set of samples: 3-day (early), 46-day (15 day H₂O +31 day D₂O, pre transition), 91-day (60 day H₂O +31 day D₂O, post-transition) and 225-day (post-fourth-transition).

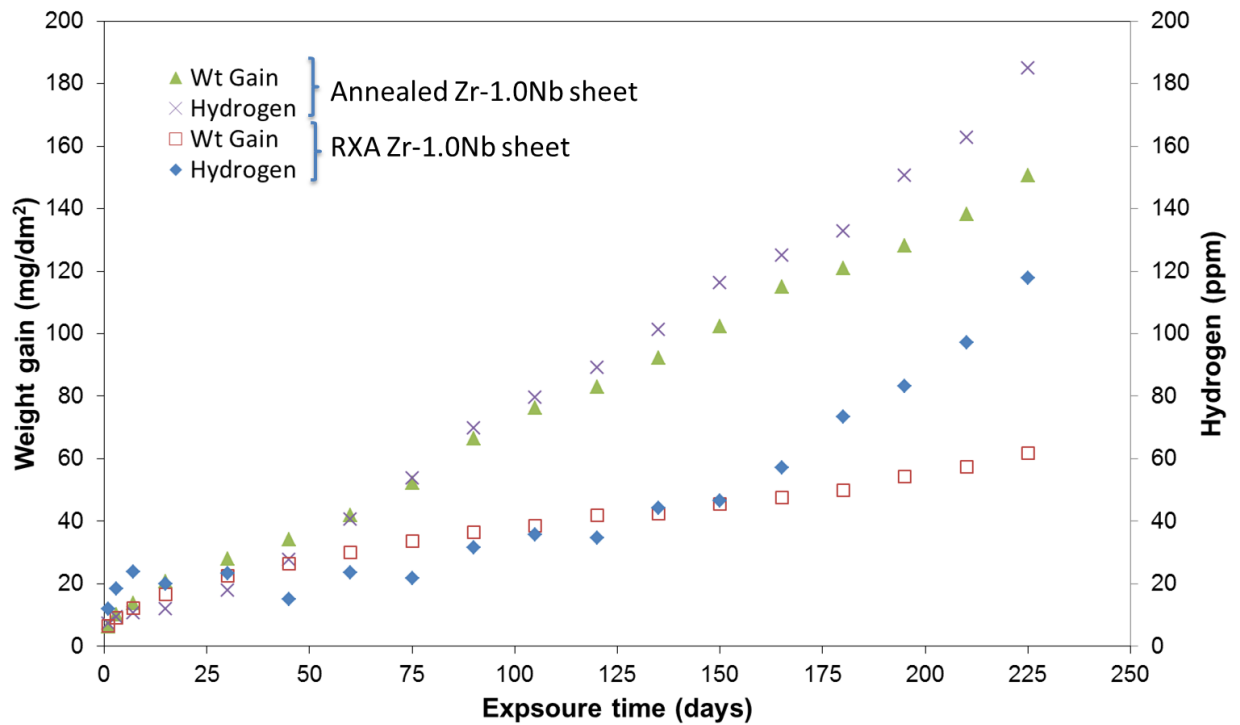


Figure 2-4: Comparison of oxidation and hydrogen data from RXA Zr-1.0Nb (sheet) in autoclave and annealed Zr-1.0Nb (sheet) in autoclave.

2.2 TECHNIQUES AND METHODOLOGY

2.2.1 Sample preparation

Conventional sample preparation techniques like electropolishing or ion beam thinning have certain drawbacks which make detailed investigation of the oxide and metal-oxide interface very difficult.^{30,64,93,120} TEM pictures as Figure 1-18(a) as seen above showed there was only limited area of interest and TEM contrast was also affected since the sample does not have homogeneous thickness. Later, the technique of focused ion beam (FIB) has been used to make TEM samples^{66,121}. The autoclave samples are made by in situ lift-out, see Figure 2-5, on a FEI 200 instrument using milling currents of 7000-100pA at 30kV, and further thinned down to a thickness below 100nm in a Zeiss Nvision 50 dual beam FIB using a beam current of 150pA at 30kV. It is worth mentioning that Jones¹²² has reported previously that the FIB making process can introduce extra hydrides in the sample due to the hydrocarbon in the FIB environment. So it is important to do a final step to finish the sample: using the low-voltage

conditions to create a homogeneous and electron-transparent sample ~50nm for TEM, STEM, TKD, ASTAR and EELS analysis.

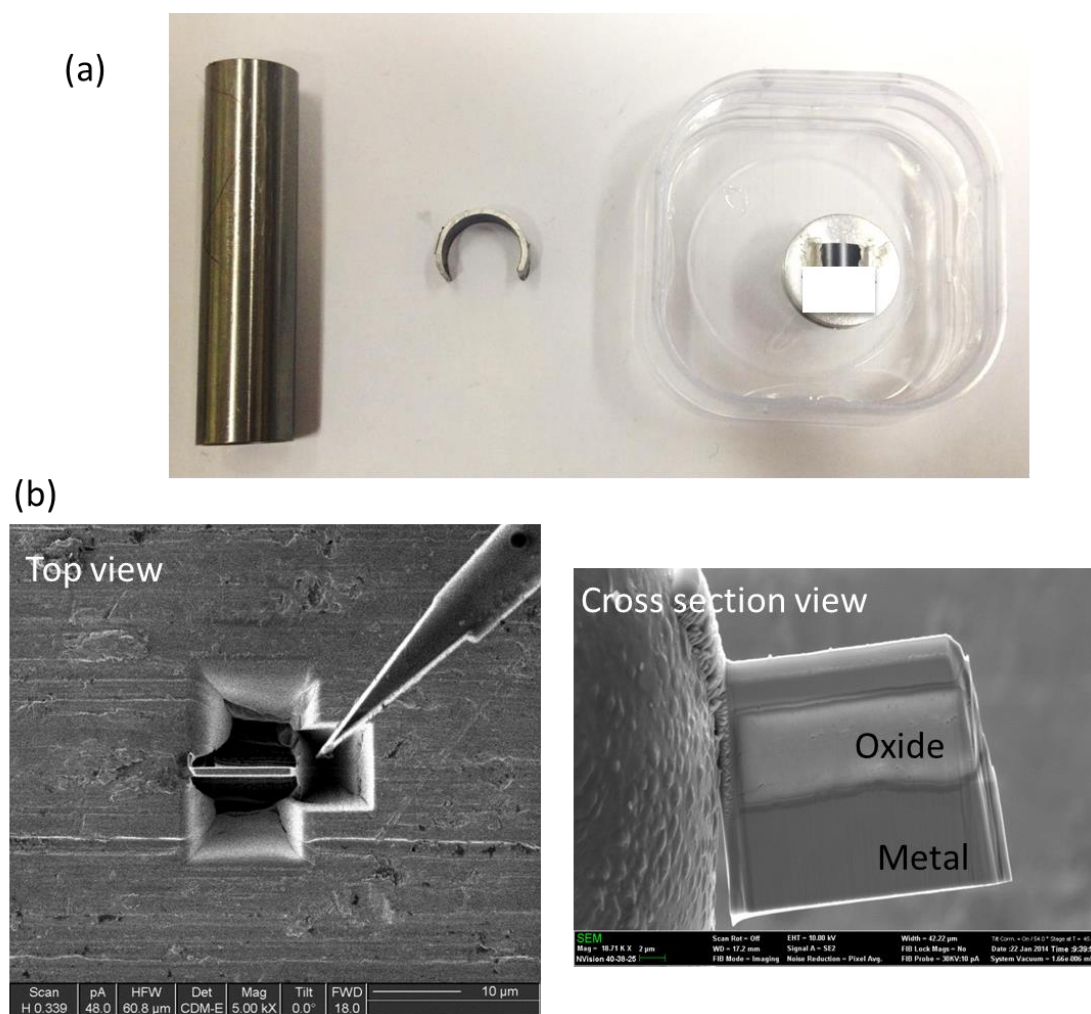


Figure 2-5: FIB in situ sample preparation steps.

For neutron irradiated samples, first stage FIB in-situ lift out was done in the active laboratories in Studvik, Sweden. There was no prior oxide polishing before lift out, i.e. the whole oxide thickness was retained during lift out. Two TEM lamella were prepared in the size of around $10 \mu\text{m} \times 10 \mu\text{m} \times 2 \mu\text{m}$, the activity value is very low due to the small sample volume, so that they can be easily transported in plastic sample box to Oxford for final FIB thinning and detailed analysis.

2.2.2 TEM BF vs STEM HAADF

Two different imaging methods (TEM BF and STEM HAADF) have been used in this study from samples at different stages of oxidation to help better understand Zr oxide. TEM and STEM analysis were performed on a JEOL 2100 microscope and a JEOL ARM microscope operated at 200 kV. The diffraction contrast in bright-field (BF) images (see left of Figure 2-6) which are obtained based on crystal structure and grain orientation can give detailed information on grain size and morphology in metal and oxide, distribution of SPPs and cracks, Figure 2-7 (a-2) gives a perfect example of columnar oxide in the autoclave RXA Zr-1.0Nb alloys with embedded amorphous and crystalline SPPs. However, diffraction contrast imaging can be difficult sometime, the neutron irradiated samples have smaller grain sizes and more complicated microstructure, which makes identifying SPPs and grain structure more challenging, Figure 2-7(b).

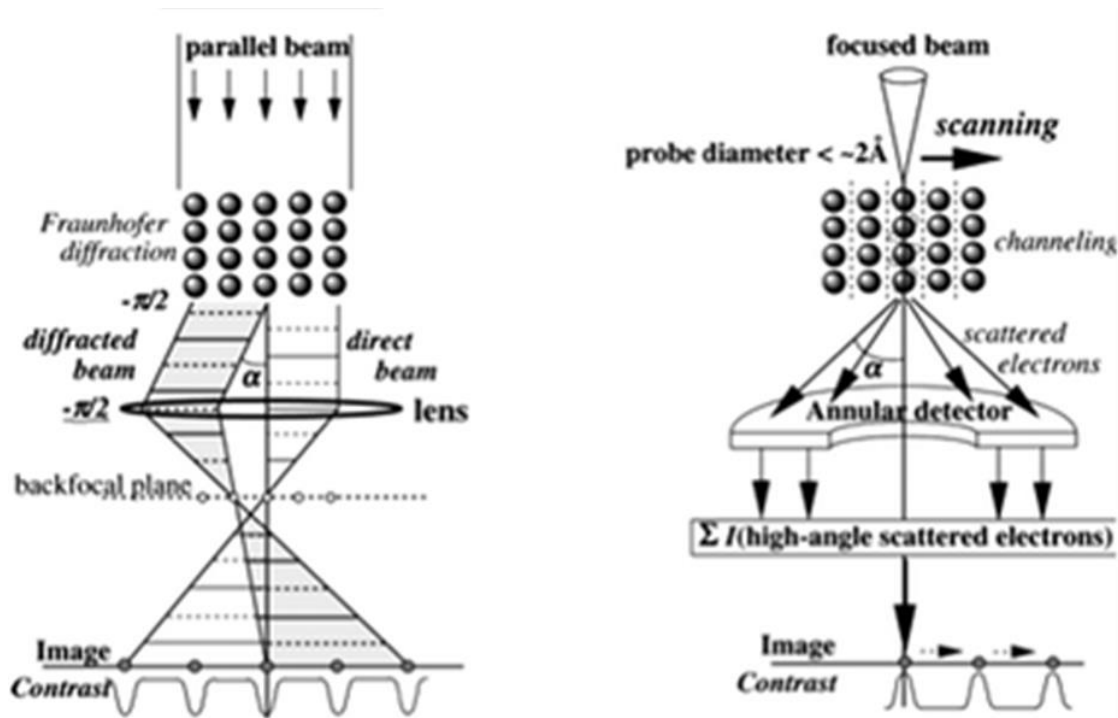


Figure 2-6: Comparison between TEM (left) and STEM (right)¹²³

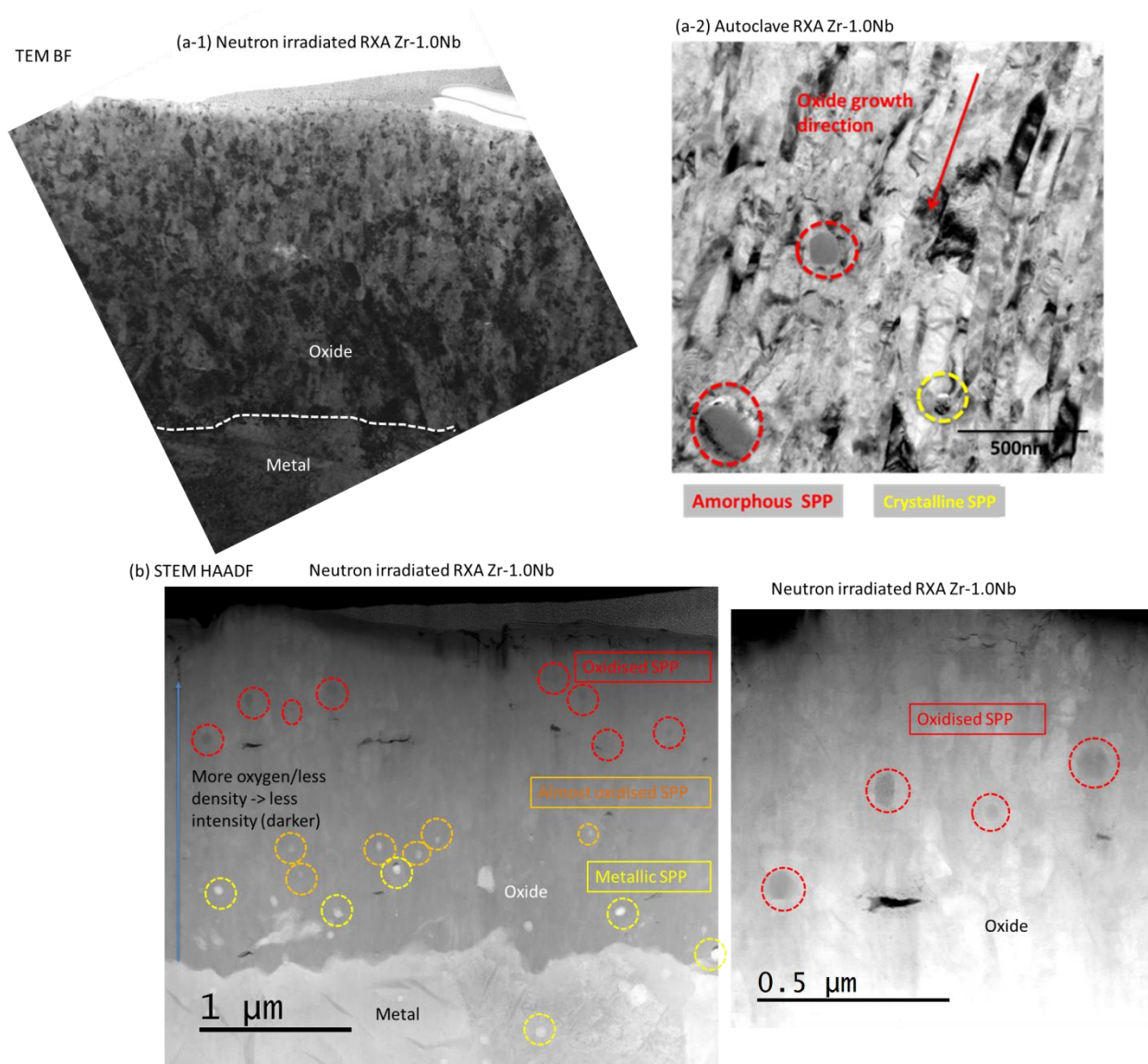


Figure 2-7: TEM BF imaging of (a-1) neutron irradiated RXA Zr-1.0Nb (a-2) autoclave RXA Zr-1.0Nb. (b) STEM HAADF image of neutron irradiated RXA Zr-1.0Nb

Another interesting outcome of using TEM BF imaging is to use Fresnel contrast to show pores of less than 10 nm in diameter. These pores are invisible in in-focus TEM pictures, however, when changing from over-focus to under-focus, the colour of pores changes from white to black, and the colour of fringes around the pores changes from black to white⁷¹ (Figure 2-8).

STEM HAADF images are more useful due to the strong atomic number contrast¹²⁴ (see right of Figure 2-6), so that the weight difference from different oxygen concentrations can easily

be visualised. For instance, in Figure 2-7(b) it is easy to see SPPs in different state based on how much oxygen there is in the SPP and how dark the contrast is. Another example is a suboxide region of different contrast at the metal-oxide interface can readily be seen in samples (Figure 3-47).

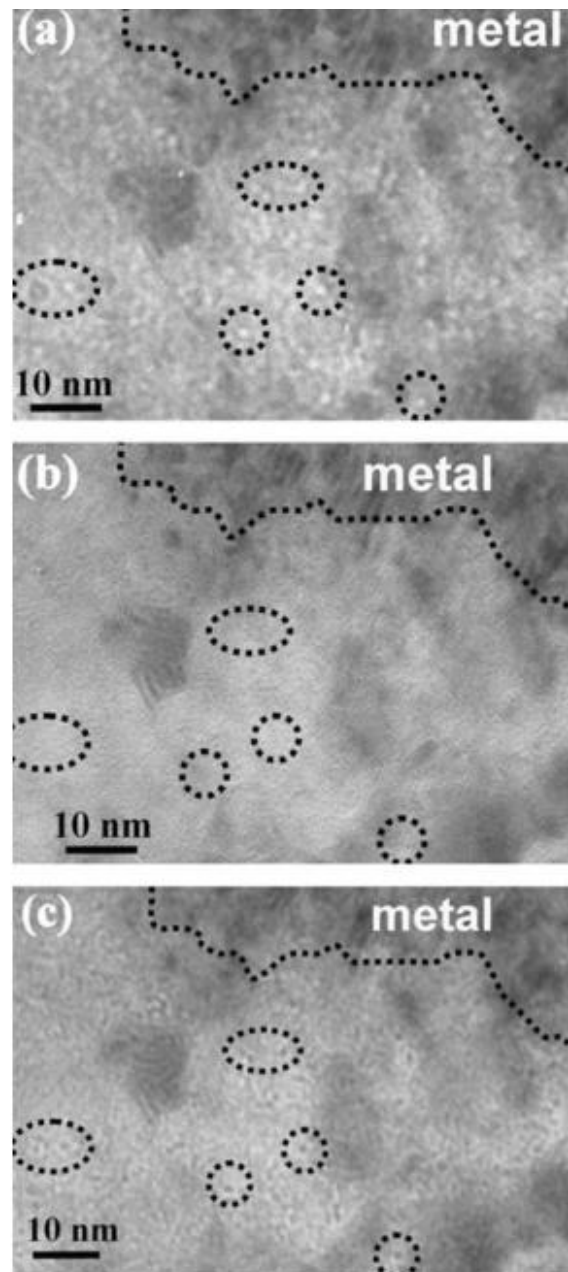


Figure 2-8: Through-focal imaging of fine pores (circled) at the metal/ oxide interface of pre-transition Zircaloy-4 recrystallized tube. The pores are invisible in (b), the in-focus image ($Df = 0$ nm), but show Fresnel contrast in (a), the under-focus image ($Df = -600$ nm), and in (c), the over-focus image ($Df = +600$ nm). The dashed line on the top indicates the metal-oxide interface⁷¹.

2.2.3 TKD vs ASTAR (Transmission Kikuchi Diffraction in SEM vs automated crystal orientation mapping in TEM)

Transmission Kikuchi Diffraction or Transmission EBSD was developed in recent years in order to improve the spatial resolution of conventional EBSD mapping^{125–127}. Instead of a bulk sample, by using a thin TEM foil mounted in the TKD holder (Figure 2-9) allowing electron beam to transmit through, the probed sample volume using a focused electron beam is much less. The EBSD detector below is collecting the Kikuchi patterns coming from the bottom surface of the TEM foil, which can avoid the problem of overlapping grains and result in much higher resolution maps^{63,128,129}. Another advantage of TKD is its ability to identify phases, especially the new ZrO suboxide phase predicted by modellers^{67,68}. TKD can also generate grain orientation maps, which is important to see the texture of the oxide^{63,128,129}. All of these features have made TKD suitable to study the nano crystalline microstructure of Zr oxide.

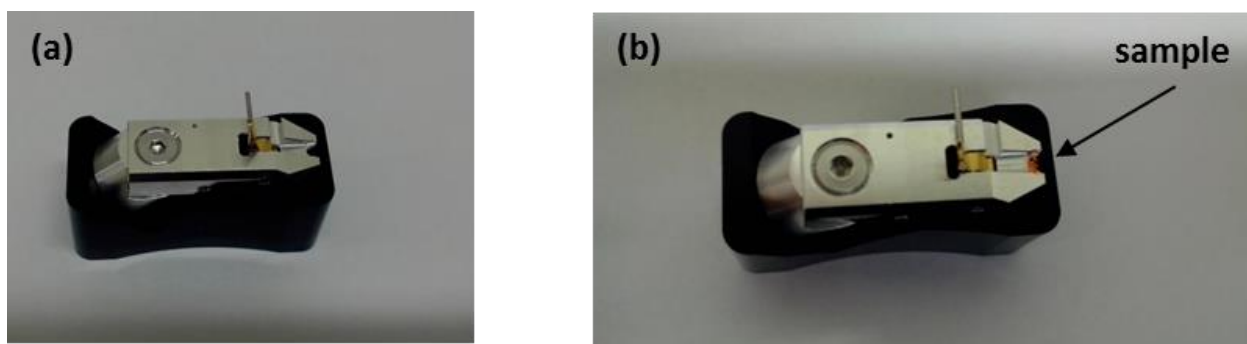


Figure 2-9: (a) Image of a TKD holder with the clamp in “open” position and (b) in the specimen.

TKD analysis was performed on an FEI Magellan FEG-SEM XHR 400L and a ZEISS Merlin SEM at 30 kV with a probe current of 1.6 nA. The step size for TKD was 10~15 nm. With an acquisition speed of 33.5Hz, the time to acquire a map time was ~70- 120 mins depending on the size of the map and step size chosen. In order to achieve optimal spatial resolution, the

TKD measurements were performed in transmission geometry, as seen in Figure 2-10. The sample was tilted at 20° away from the EBSD detector with a working distance of 2 mm (FEI Magellan) to 7.5 mm (ZEISS Merlin).

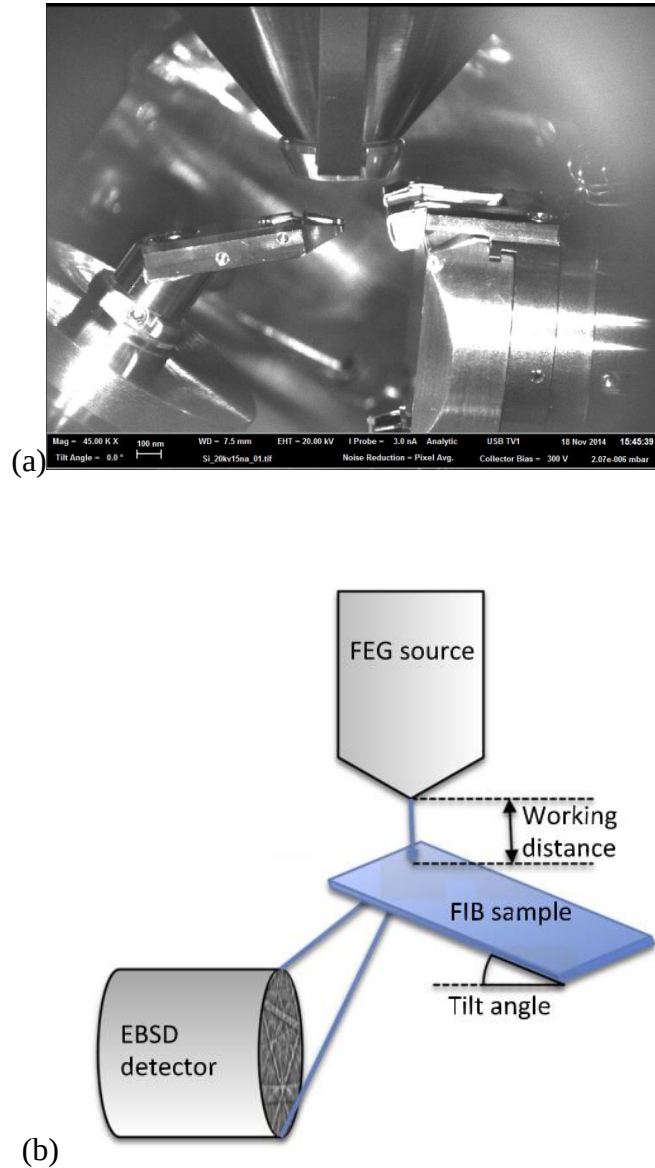


Figure 2-10: (a) In-chamber image of the TKD sample holder and sample geometry with regards to SEM column and EBSD detector. (b) Schematic diagram of experimental set up for TKD¹²⁹

The Kikuchi patterns were indexed using the AZtec software suite developed by Oxford Instruments. The crystal structures used for TKD and ASTAR analysis are shown in Table 2-1. To show how we verify the structure of these suboxide grains, the Kikuchi patterns

(EBSPs) from this region were matched using the AZtec software suite with the hexagonal ZrO phase predicted by Nicholls et al⁶⁸. Examples of matched EBSPs acquired from the suboxide region are shown in Figure 2-11, with the software providing consistent matching with a mean angular deviation of generally $\sim 0.5^\circ$. It worth mentioning that one has to bear in mind the tetragonal phase fraction is lower than the real value measured using synchrotron X-Ray Diffraction (XRD)¹³⁰. This is thought to be due to the transformation of stress-stabilized tetragonal grains to the equilibrium monoclinic phase during preparation of the thin FIB sample, also the possibility that the majority of the remaining small tetragonal grains is below the resolution of TKD⁶³.

Table 2-1: Reference crystal structure for monoclinic oxide, tetragonal oxide, suboxide and Zr metal for TKD and ASTAR analysis.

Phase	a (nm)	b(nm)	c (nm)	$\alpha(^\circ)$	$\beta(^\circ)$	$\gamma(^\circ)$	Ref
Monoclinic ZrO ₂	0.517	0.523	0.534	90	92.25	90	[¹³¹]
Tetragonal ZrO ₂	0.359	0.359	0.518	90	90	90	[¹³²]
Hexagonal ZrO (Suboxide)	0.531	0.531	0.320	90	90	120	[⁶⁸]
Hexagonal Zr	0.323	0.323	0.514	90	90	120	[¹³³]

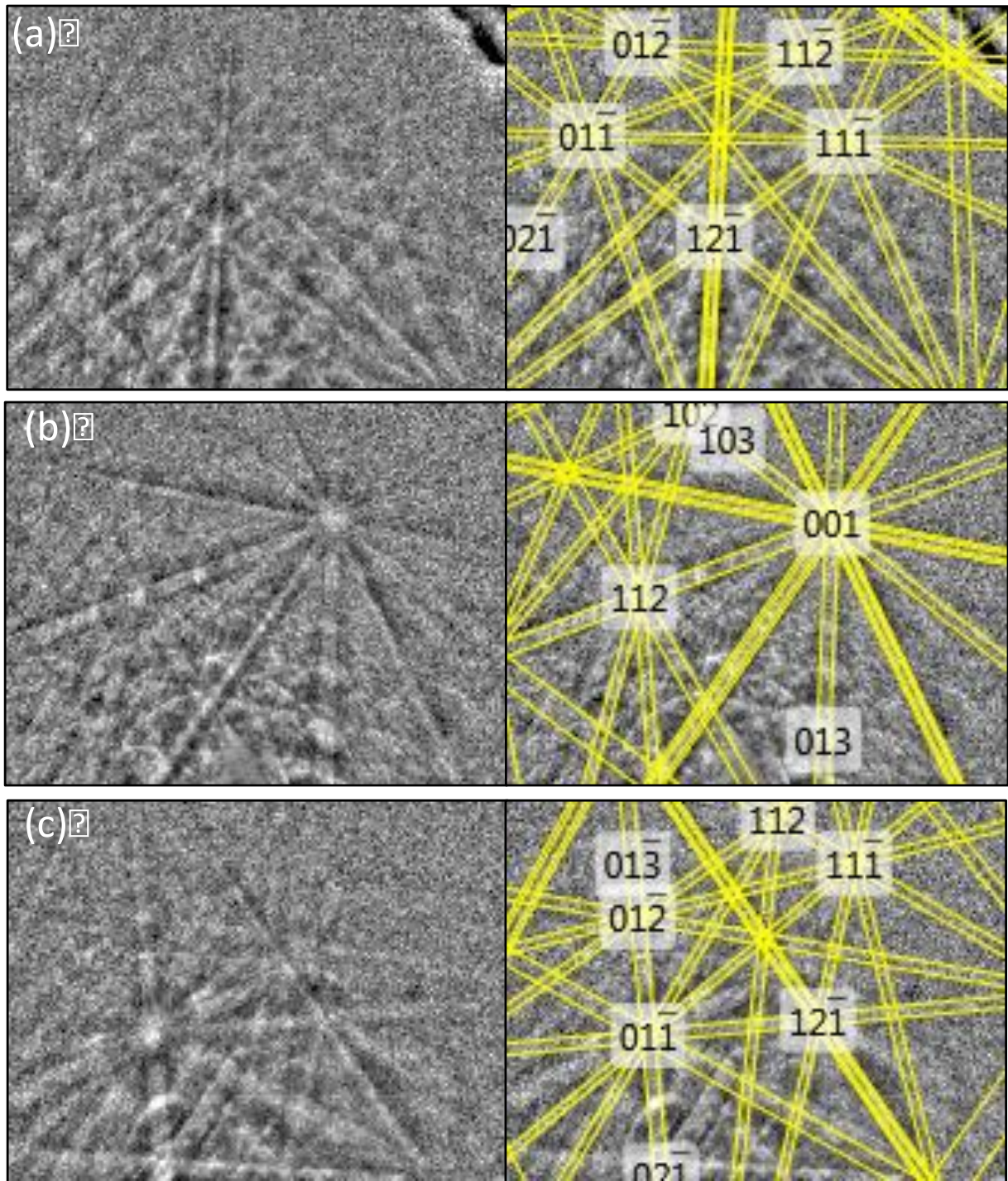


Figure 2-11: Selected electron backscattered patterns (EBSPs) from the suboxide region of the TEM sample and corresponding solutions using AZtec software and ZrO hexagonal phase (a) Mean angular deviation (MAD) = 0.45° number of matched bands = 7, (b) MAD = 0.59° number of bands = 7, (c) MAD = 0.57° number of bands = 8.¹²⁸

Automated crystal orientation mapping with TEM (ASTAR mapping) is a new diffraction based technique that has been developed recently^{134–138}. ASTAR mapping was performed in an FEI Tecnai F30 Field Emission Gun Transmission Electron Microscope (FEG-TEM)

operating at 300 keV with precession angle of 0.8° and 5 nm step size. By using precession, the quality of diffraction patterns improves. With the high speed CCD camera attached to the TEM, the diffraction patterns can be acquired (Figure 2-12). Later on, by using a NanoMEGAS ASTAR automated crystal orientation mapping system, these diffraction patterns are compared with the simulated diffraction patterns based on the crystal structure provided in Table 2-1.

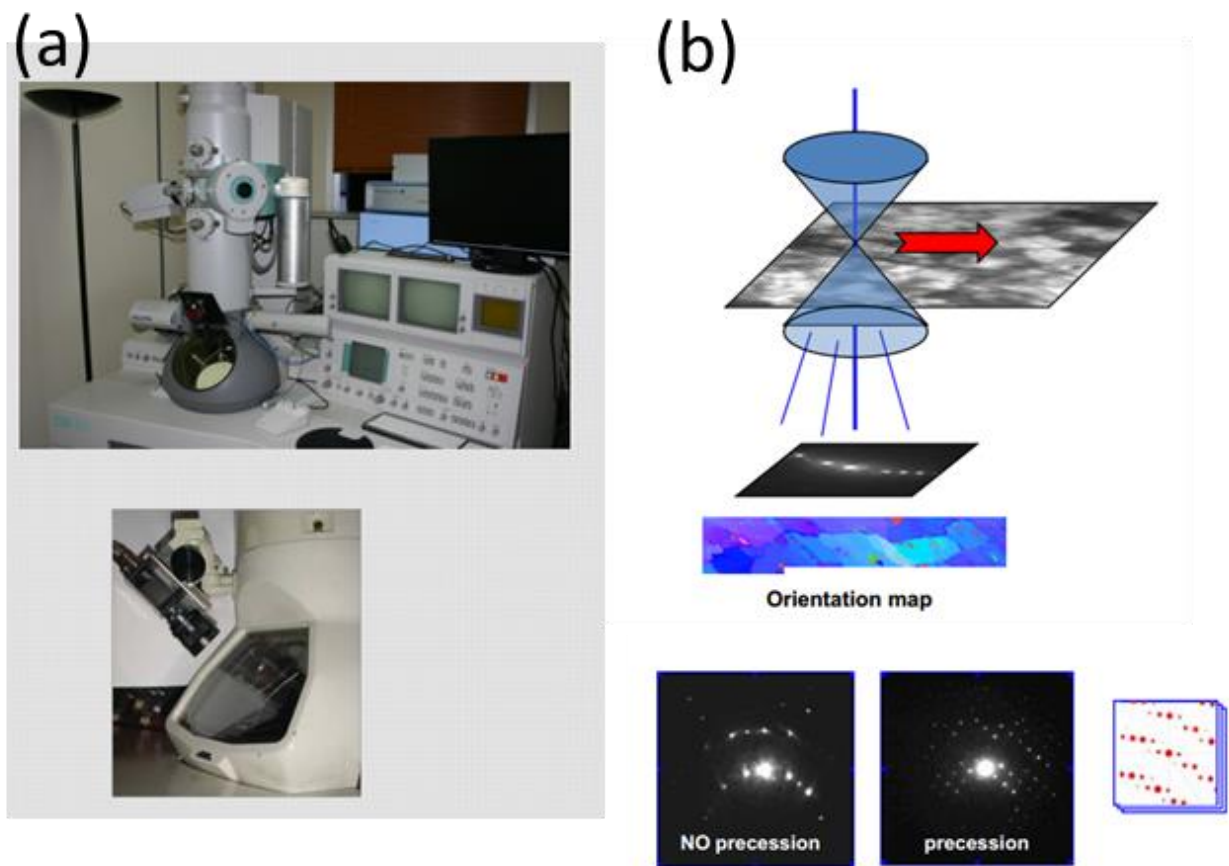


Figure 2-12: (a) Experiment setup of ASTAR mapping, (b) precession diffraction patterns comparison with normal diffraction patterns¹³⁹.

Comparing with TKD, ASTAR mapping has a higher resolution 5 nm vs 10-15 nm in TKD. However, the mapping takes a much longer time (6-12 hours) and since it is taking diffraction patterns over the whole FIB sample thickness, the ability to resolve overlapping grains

depends on whether the overlapping grains can provide different diffraction patterns and whether the NanoMEGAS software can produce a confident fit.

2.2.4 EDX vs EELS

Two analytical (S)TEM techniques have been used in this study: Energy-dispersive X-ray spectroscopy (EDX) and Electron Energy Loss Spectroscopy (EELS). Detailed analysis is shown from Chapter 3~5, here I discuss their principle and comparisons. Figure 2-13 illustrates the differences between EDX and EELS.

When an electron beam interacts with the thin foil, the majority of the beam passes through the sample without losing energy, however, some electron scattering happens. Some of this scattering leads to the inner shell electrons ejecting, which makes the outer shell electron jumps inward, emits characteristic X-rays, the process is shown in Figure 2-14 (a)^{140–142}. The X-ray will be received by an X-ray spectrometer on the TEM. In this study, EDX measurements were done on the JOEL 2100 microscope with a LaB₆ source and an Oxford instrument 80mm thin window EDX detector. The software used in this study is Oxford Instrument Aztec software for TEM. The EDX spectrum contains a wide range of energy, so it can cover many different elements at the same time which makes EDX a quick and easy way to get a chemical measurements or mappings of SPPs in the oxide. However, because the lighter elements such as oxygen have a lower energy and a high absorption in the detector, this has made the quantification not accurate.

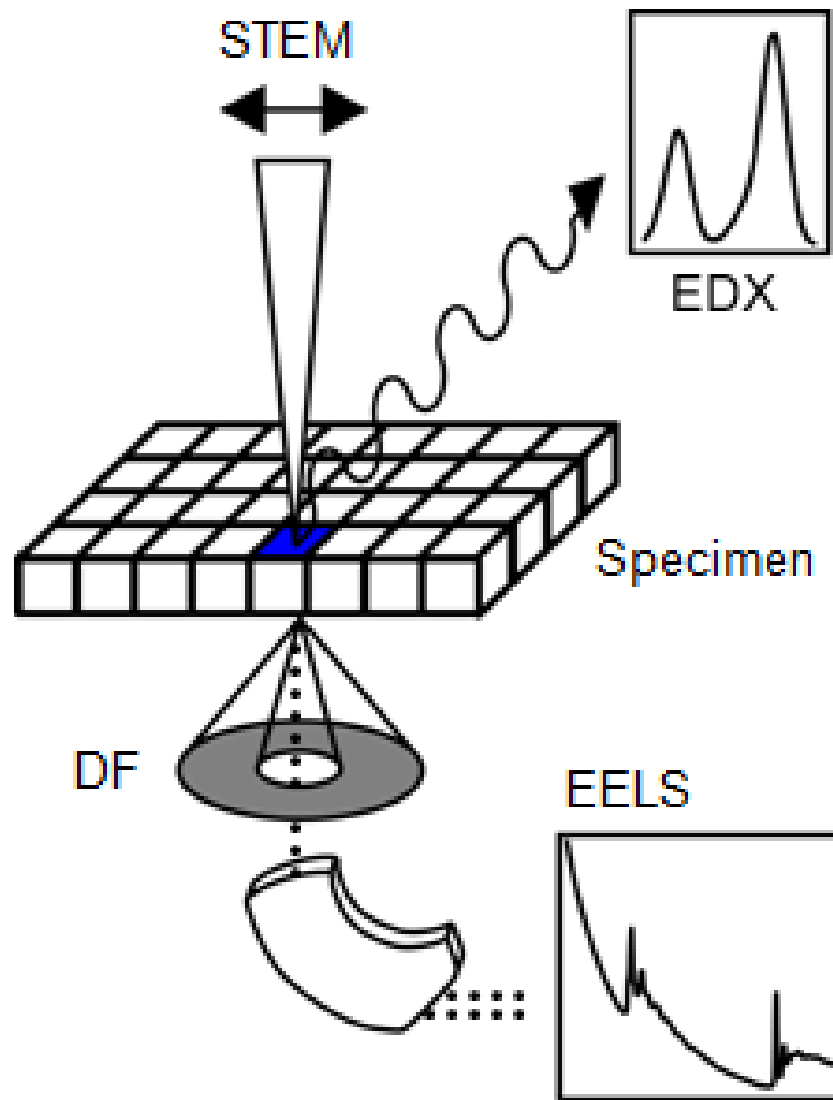


Figure 2-13: Simplified explanation of EDX vs EELS¹⁴³.

Another way to characterize the lost energy is by calculating how much electron energy is lost due to the inelastic scattering, this is called EELS^{66,142,144}. EELS signals will be received using an image filter as seen in Figure 2-15(a). The Gatan Image Filter (GIF) contains a magnetic prism which will differentiate different electrons based on their energy and project them into an EELS spectrum as seen in Figure 2-15(b) which contains the smaller range of energy to up to 2 kV however with much more energy resolution comparing with EDX. Figure 2-15(b) contains three parts: the zero loss part represents those electrons which did not lose any energy when interacting with the sample, the low loss part represents electrons which lost

energy less than 50 eV, this represents the plasma resonance of the valence electrons, which is also called Plasmon and can be used to understand the electronic state; the core loss part is above 50 eV peak, this represents the electrons that have excited the inner shell electrons thus can tell people about the chemical information of the sample.

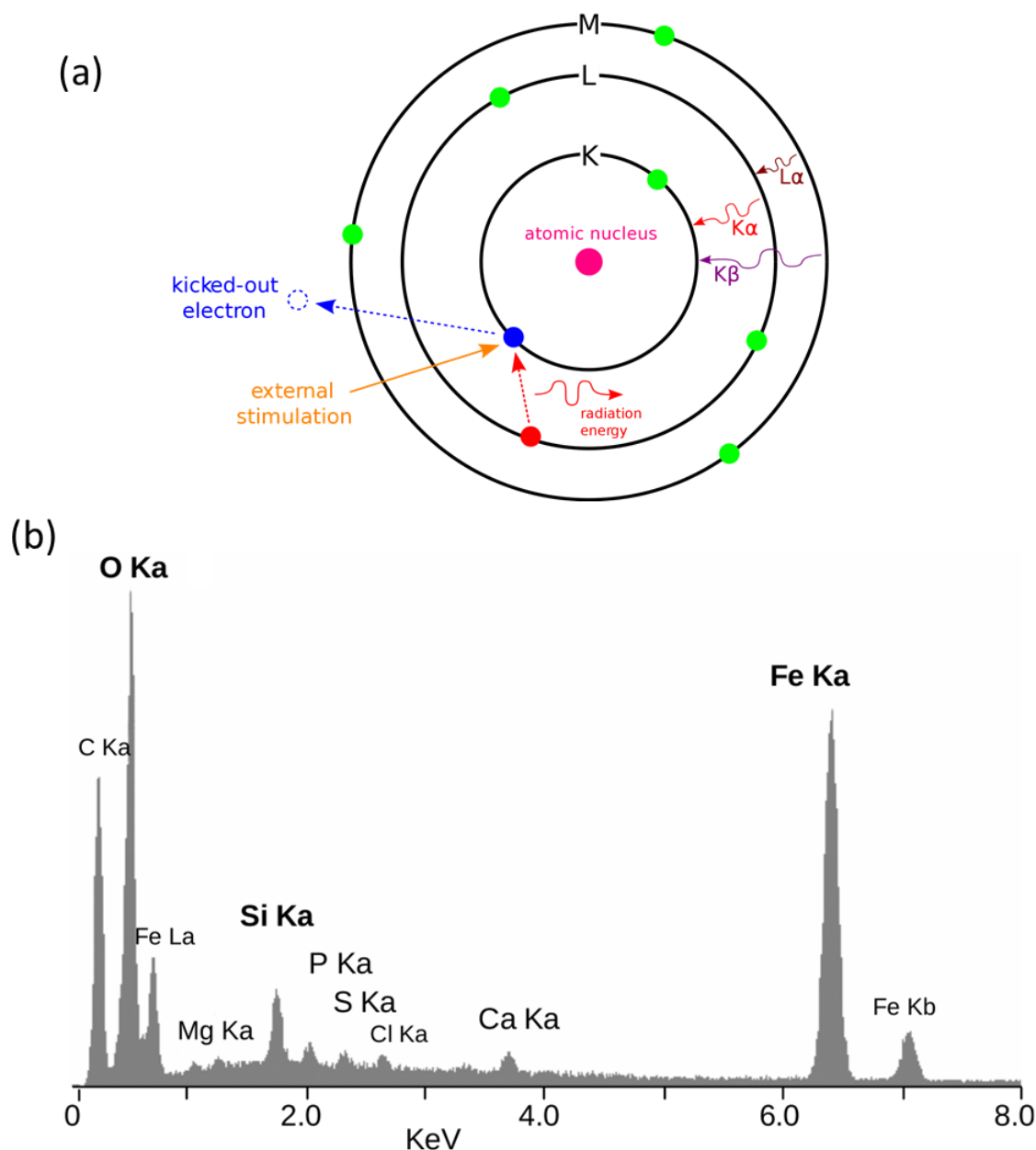
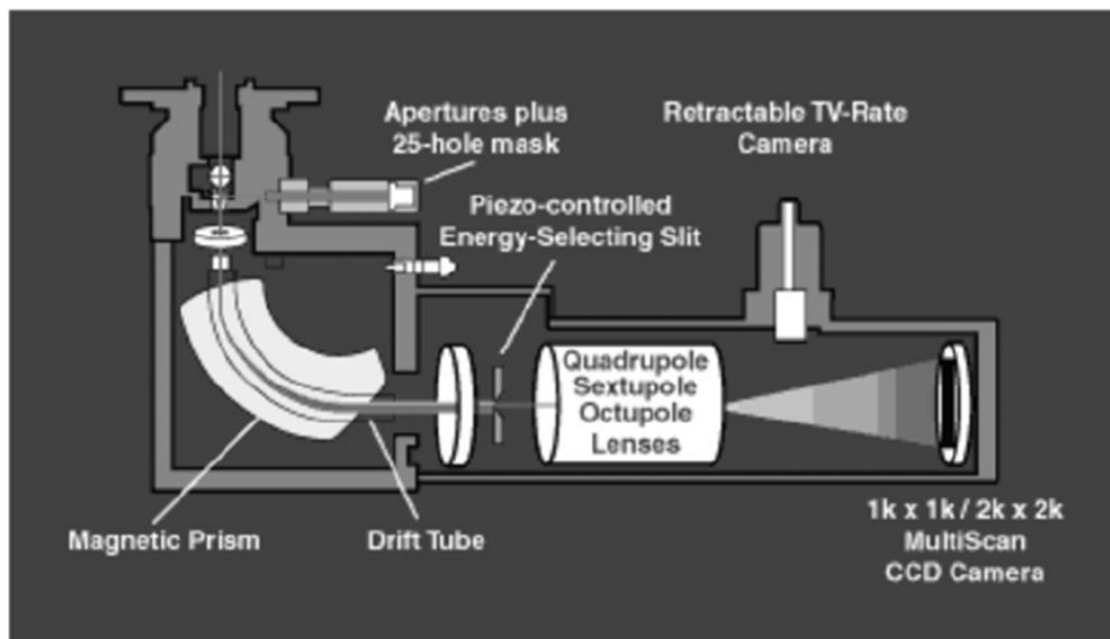


Figure 2-14: (a) electron interaction with an atom which creates the characteristic X-ray. (b) a typical EDX spectrum^{140–142}.

EELS spectrum imaging was performed on a JEOL ARM200F TEM operated at 200 kV and equipped with a Gatan image filter (GIF). The convergence half-angle α was 20 mrad and

collection half-angle β was 30 mrad with an energy dispersion of 0.25 eV per channel and a step size of 1~5 nm. The sample thickness after final thinning for EELS was estimated to be around 50 to 70 nm. Data analysis was mostly done using the Hyperspy toolbox¹⁴⁵, by using multivariate statistical analysis methods, such as principal component analysis (PCA) or independent component analysis (ICA).

(a)



(b)

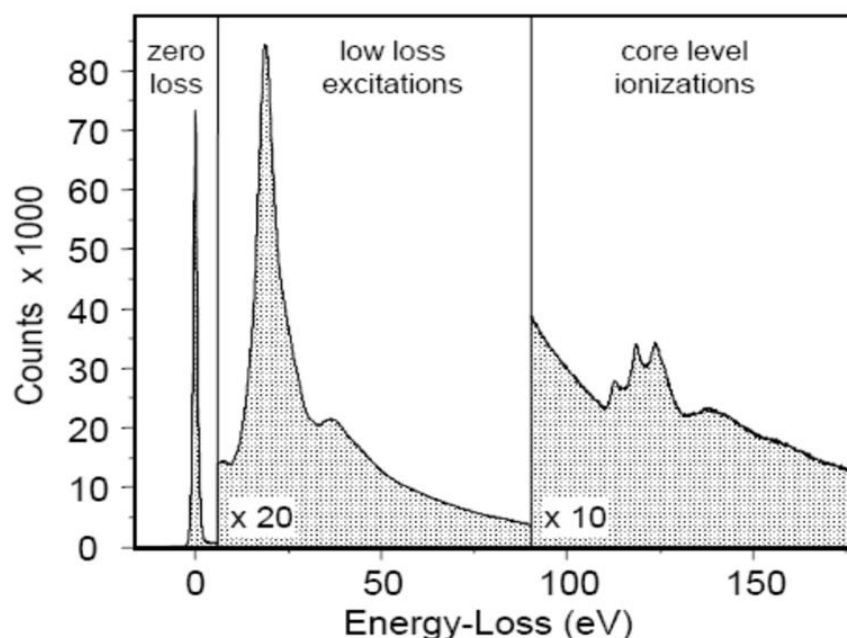


Figure 2-15: (a) Gatan Image Filter¹⁴⁶ (b) Schematic of an EELS spectrum⁶⁶

Due to its high sensitivity to light elements, one of the important uses of EELS in this study is on analysing the suboxide and oxygen saturated region at the metal-oxide interface, see Chapter 3.5. Low loss spectrum imaging combining with multiple linear least squares (MLLS) fitting^{147,148} allows a very quick mapping for different phases along a large area. Core loss around the metal-oxide interface region can give accurate measurements for oxygen content. The oxygen concentration was calibrated by using the starting point of the line in the ZrO₂ region using the method described by Ni et.al⁶⁰. By comparing the core loss spectrum of Nb and Zr-L edges, it is also possible to analyse the oxidation state of these elements (Chapter 3.4).

2.2.5 3D FIB slicing

3D FIB slicing is used to have a qualitative view of the metal-oxide interface evenness and crack distribution¹²¹. As seen in Figure 2-16 (a), a layer of carbon or Pt is deposited on top of a 10 μ * 10 μ m region. FIB sectioning was done using 700 pA beam current and a series of FIB SEM images were taken during the FIB sectioning Figure 2-16 (b). Due to the strong contrast in the SEM image, it was able to have a clear view of crack distribution (both parallel and vertical to the metal-oxide interface), big SPPs such as β -Zr and hydrides. Later on the 3D reconstruction was done using Software Avizo 6.1.

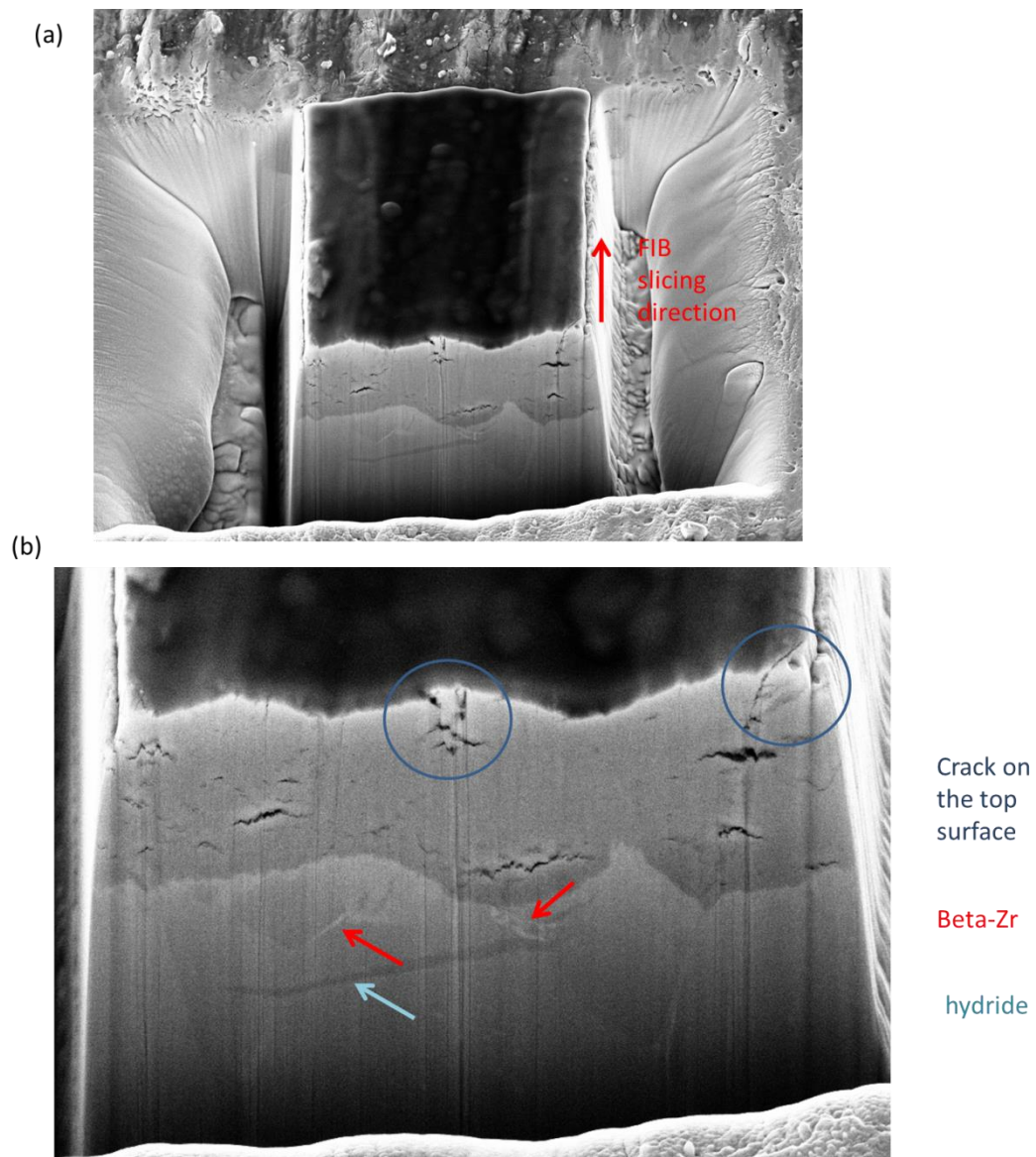


Figure 2-16: (a) FIB-SEM view of the 3D FIB slicing area and slicing direction. (b) SEM image of the oxide and metal in annealed Zr-1.0Nb alloy, showing cracks, SPPs and hydrides in the sample.

3 CHAPTER 3 ZR-1.0NB IN THE RECRYSTALLISED STATE (RXA ZR-1.0NB)

3.1 OXIDATION AND HPU DATA

In this chapter I report results on RXA Zr-1.0Nb samples from a set of WestinghouseTM developmental alloys as described in Chapter 2. The composition of this Zr-1.0Nb alloy was measured by EDF using inductively coupled plasma atomic emission spectrometry (ICP-AES) to be Zr-0.9Nb-0.01Sn-0.08Fe (wt%), and all samples were in the recrystallised (RXA) state with final treatment below the monotectic temperature to create β -Nb particles¹¹⁸.

Six samples were chosen for this study. Five of the six were chosen from bulk Zr cladding tube samples. They were oxidised in an autoclave at EDF under simulated Pressurized Water Reactor (PWR) water conditions at 360°C for up to 540 days, and some samples then received an additional exposure to deuterated water for a further 45 days. Details of the autoclave testing and oxidation kinetics are reported in a recent publication from the MUZIC consortium¹⁰⁹. The weight gain data in Figure 3-1 shows no obvious signs of transition after 360 days, but the HAADF image of the 360-day sample in Figure 3-3(d) reveals a first layer of cracks next to the metal-oxide interface which might suggest that transition has just started. Five samples were chosen to cover different stages in the oxidation profile, and at least two TEM samples have been made from each chosen sample. Their overview pictures are shown in Figure 3-3 (b)-(f). The first one is after 120 days which represents as early oxidation time and an average of oxide thickness of 2.2 μm . The second one had 180 days in the autoclave plus another 45 days in a different autoclave in deuterated water to make 225-day of oxidation in total, just before the first-transition. The third one had 360 days in the autoclave, which is at the first transition. The fourth sample has been through 540 days oxidation in the autoclave, and the SEM-FIB image in Figure 3-3 (e) shows a second layer of cracks at the metal-oxide interface suggesting that the second transition has just happened. The fifth sample had 540

days in the autoclave plus another 45 days in deuterated water to make 585-days of oxidation in total, and represents a post second transition sample.

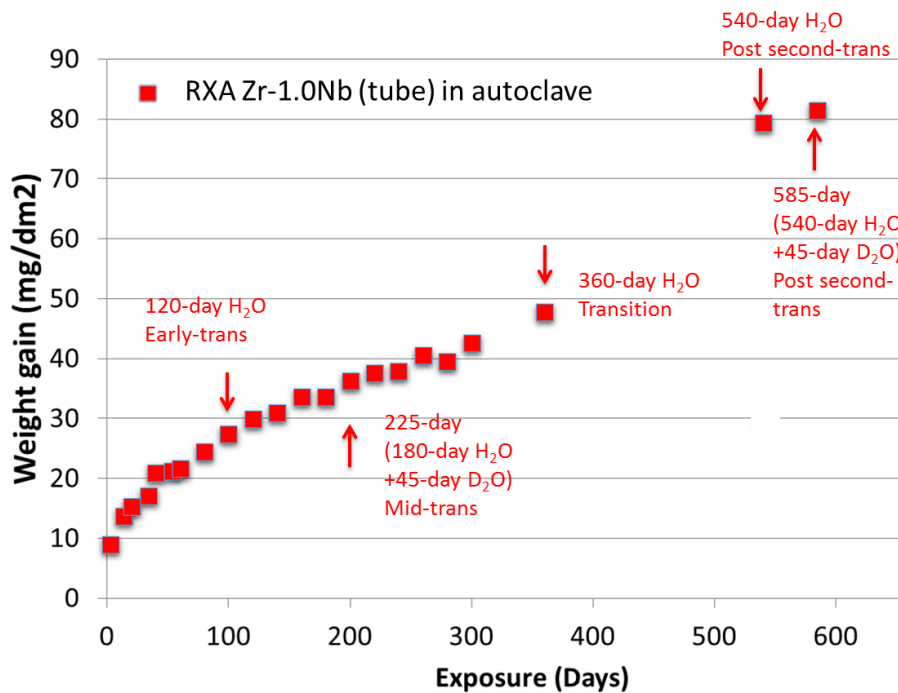


Figure 3-1: Weight gain data of RXA Zr-1.0Nb tubes, with the five chosen samples highlighted

A set of sheet shaped Zr-1.0Nb samples were received in the later stage of this study. These samples have a similar chemistry and manufacturing procedure to those described above. They were oxidised in static stainless steel autoclaves at Westinghouse™ in pure water at 360°C. The oxidation data was measured every 15 days up to 225 days, and the hydrogen content was measured by inert gas diffusion. Figure 3-2 shows the weight gain data and hydrogen content of these samples, the comparison of the tube and sheet samples are made in Chapter 2, Figure 2-2. I chose a 3-day sample from this set to represent the very beginning of oxidation. It would have been ideal to study all the samples from the second set of samples, but the time line of the project only allows me to select one sample to represent the very early stage of oxidation.

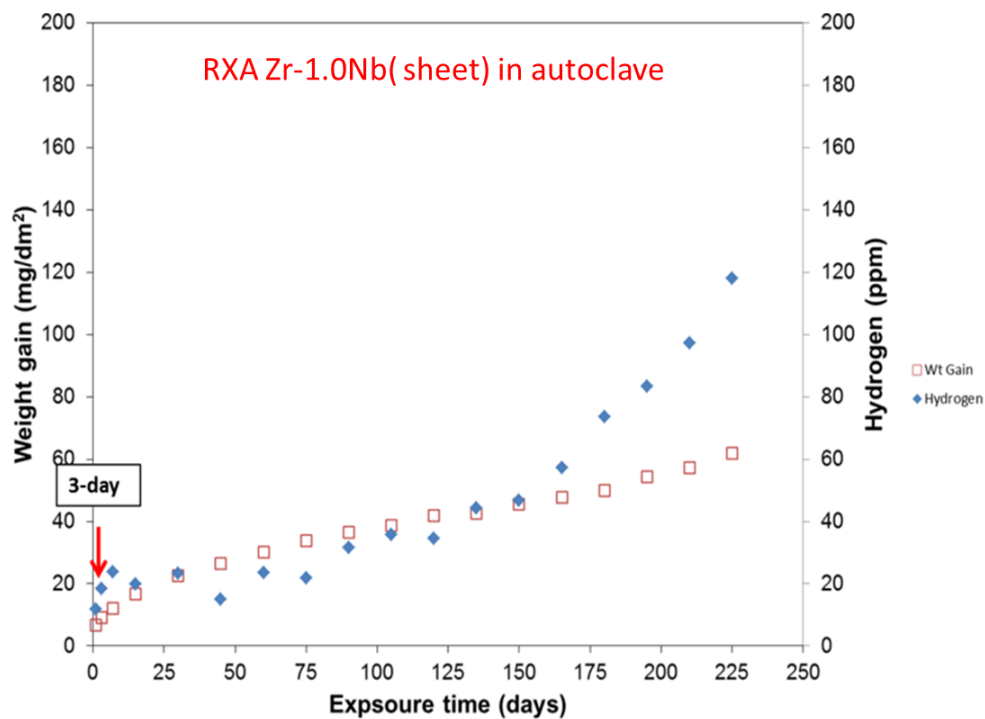


Figure 3-2: Weight gain and hydrogen content data of RXA Zr-1.0Nb sheets with the one chosen sample highlighted

3.2.MICROSTRUCTURAL ANALYSIS

3.2.1. (S)TEM overview

The 3-day sample represents the very beginning of oxidation where the sample has a very fast oxidation rate. It is interesting to see that the oxide thickness varies a lot in different regions. The TEM BF image in Figure 3-3(a) shows that on the right side of this region of the oxide, the oxide has uniform thickness of 0.65 μm . This oxide is very dense at most positions, with some micro cracks 100-150 nm in length parallel to the smooth metal-oxide interface. However, on the left part of this image, the oxide becomes uneven, with the thickness ranging from 0.85 μm to 1.3 μm . At around 400 nm from the top surface, there is a continuous layer of parallel cracks running over a 5 μm wide region.

The 120-day sample represents the early stage of oxidation. The STEM HAADF image in Figure 3-3 (b) shows that the majority of the metal-oxide interface is relatively flat, with an average oxide thickness of 2.2 μm . The equiaxed layer of the top surface is around 500 nm

thick. There are two 700-800 nm long parallel cracks near the metal-oxide interface, the right one associated with an obvious undulation some 500 nm high where the oxidation rate is locally much slower. The same area was used later for ASTAR analysis.

The 225-day sample represents a stage before the first transition. As seen in the STEM HAADF image in Figure 3-3 (c), some larger cracks can be seen near the metal-oxide interface, and the oxide has grown to a thickness around 2.5-2.7 μm . The equiaxed layer on the top surface is around 670 nm thick.

The 360-day sample is taken at approximately the first transition. The metal-oxide interface in Figure 3-3 (d) is relatively flat with more big cracks parallel to the interface. The oxide thickness has grown to around 3.2 μm . The equiaxed layer on the top surface is around 700 nm.

The 540-day sample is taken to be at the second transition. Figure 3-3(e) is a FIB-SEM image taken during sample making, and the oxide has an average thickness of 5.2 μm . The first 700 nm equiaxed oxide on the top surface is very porous which is shown in Figure 3-4(a) and (b), and is followed by two layers of cracks around 2 μm apart. This indicates that two transitions have occurred. However it worth mentioning that the two layers are not exactly parallel, which suggests that the local transition happens at different times in different locations.

The 585-day sample represents a stage post second transition. As seen from the STEM HAADF image in Figure 3-3 (f), after the second layer of cracks, another 900 nm of oxide has grown during the 45 days since the previous sample in (e). The oxide thickness is around 6.1 μm .

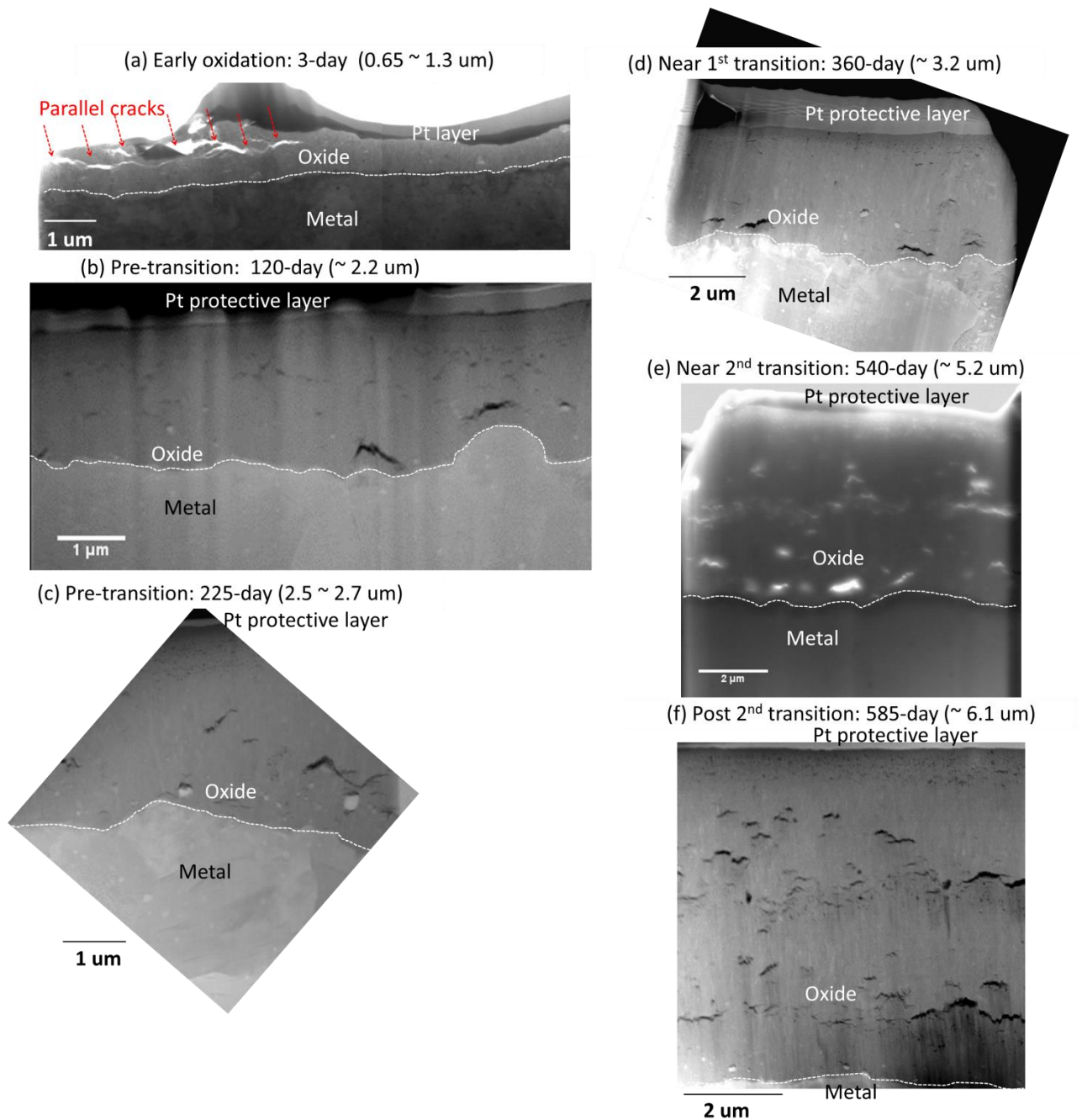


Figure 3-3: Oxide microstructure images for the RXA Zr-1.0Nb samples used in this study. (a) TEM BF image of 3-day Zr-1.0Nb, (b,c,d,f) STEM HAADF images of the four selected Zr-1.0Nb samples after 120-days, 225-days, 360-days and 585-days, respectively; (e) FIB-SEM image for the 540-day sample.

Detailed TEM BF microstructural analysis was carried out on these samples. Figure 3-4 shows a few examples of the typical features that are found in all these microstructures. A periodic pattern of equiaxed-columnar grain structure is observed in all the samples.

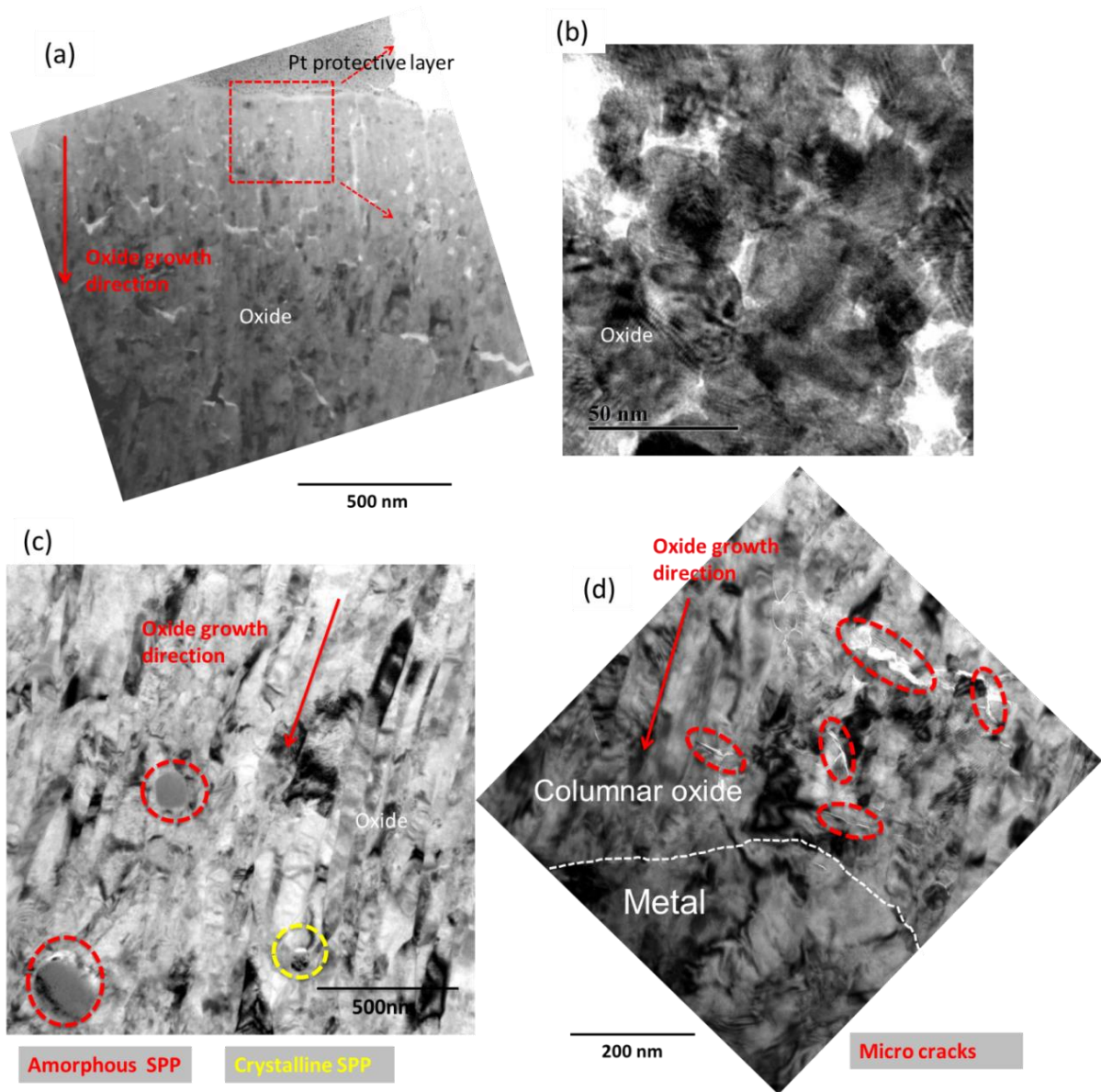


Figure 3-4: TEM BF images of the typical oxide microstructure: (a) Top oxide of 360-days sample showing micro cracks; (b) higher magnification image of (a) showing the equiaxed grain structure; (c) typical columnar oxide grain structure as seen in the 225-days sample.

As seen in Figure 3-4 (a), the top part of all the oxides is very porous, and there are macro-cracks around 60-100 nm in length parallel to the metal-oxide interface. The grain structure at the top surface is equiaxed and around 20-30 nm in diameter. (b) shows that the grain boundaries are very porous. In the post-transition sample, equiaxed grains were also observed near the two layers of cracks. The equiaxed grain layer thickness also increases with oxidation time, starting from 150 nm in the 3-days sample, to 500 nm in the 120-days sample, and up to

650-750 nm in the 225-days, at-transition and post-transition samples. Similar observations on equiaxed oxide growth have also been reported by Ni et. al⁶⁶.

Under the equiaxed layer in the pre-transition samples, and between the two layers of cracks in the post-transition samples, there are larger columnar grains around 50 nm wide and 350-450 nm in length as seen in Figure 3-4 (c). These columnar grains are very well organised, all lined up in the direction of oxidation. There are both amorphous and crystalline SPPs with crescent shaped cracks on the top scattered in the columnar oxide region. Nano porosity along these columnar grain boundaries will be covered in Chapter 3.3 in detail, but there are also much smaller micro-cracks or flake-like porosity 40-50 nm in length cutting through the columnar grains or located near the metal-oxide interface as seen in (d). There are also larger parallel cracks lying at the metal-oxide interface as in all the other pre-transition samples.

It is the first time that a very early day sample has been reported. For the 3-day sample, which is in a fast oxidation stage, the TEM BF overview of the 650 nm thick oxide in Figure 3-5 (a) shows that the oxide consists of equiaxed oxide throughout the top 150 nm (see a higher magnification image in (b)), with a grain size of around 20-30 nm. Below this is a layer of columnar oxide grains for another 500 nm before the metal-oxide interface. It is also noticeable that the average grain size of the columnar grains in this sample is only 26 nm, as seen in (c), much smaller than the 50 nm grain size seen in other later oxidation stage samples. A higher magnification image is shown in Figure 3-13, together with porosity along the grain boundaries. There is also an amorphous SPP around 300 nm away from the metal-oxide interface as circled in (a). As mentioned before, at most locations this sample is rather dense, but there are some 100 nm parallel cracks in the middle part of the oxide and some micro-cracks cutting through columnar oxide grains.

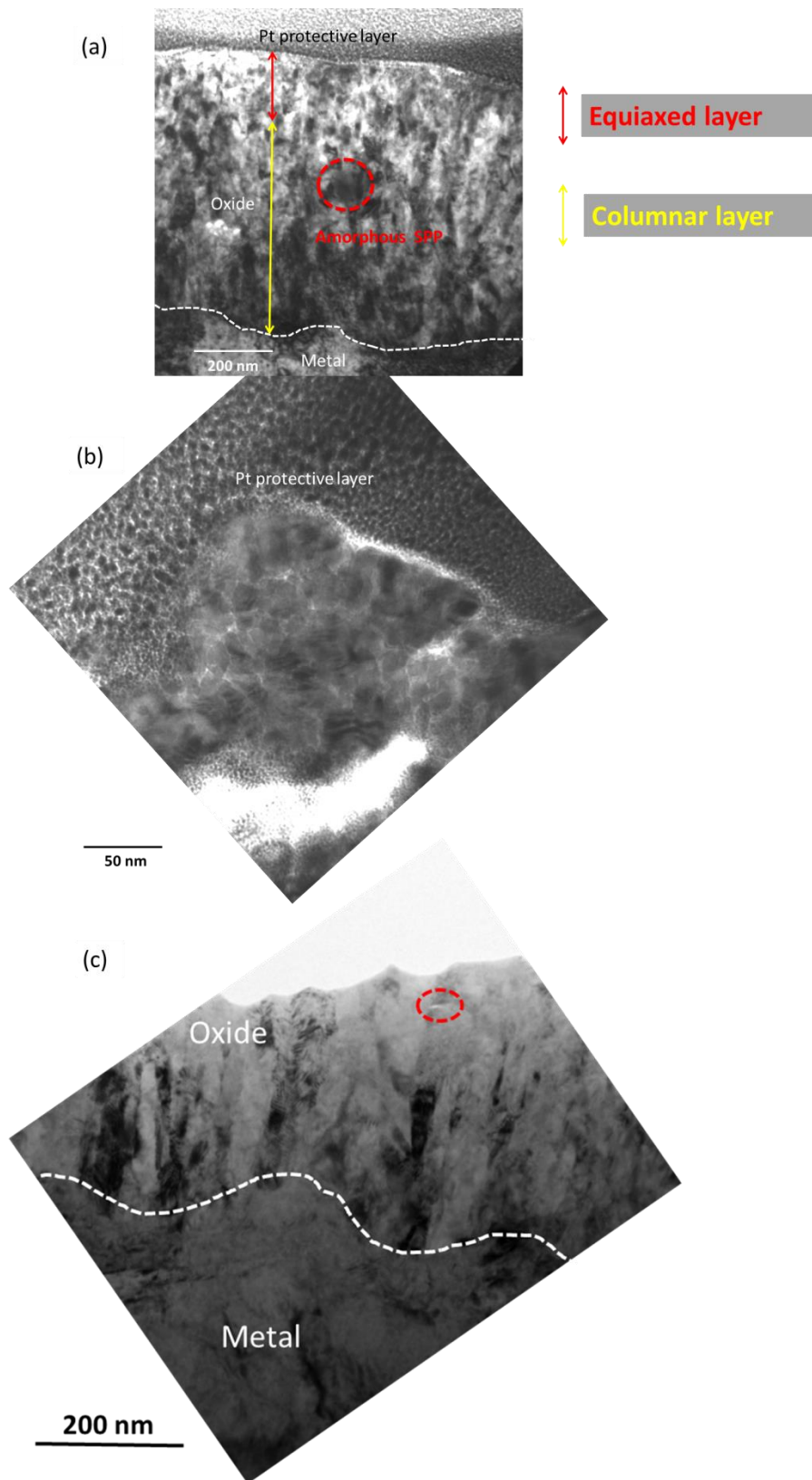


Figure 3-5: TEM BF images for oxide microstructure of the 3-days sample: (a) Overview image; (b) higher magnification image of cracks and the equiaxed grain region; (c) higher magnification image of columnar oxide region with a micro-crack circled.

Figure 3-6 shows some rare cases of features observed in the oxide region of these samples. Figure 3-6 (a) and (b) are SEM images of the 120-day sample, which are taken during FIB sample preparation. (b) is a higher magnification image of the dotted area in (a). It is easy to see a Y shaped crack running from the top of the sample surface which is intact and covered with the Pt protective layer. The crack continues through the whole of the 2 μm oxide and finishes at the metal-oxide interface with a parallel crack and a protrusion of the oxidation into the metal underneath. This is interesting because normally a vertical crack throughout the oxide is related with faster oxidation rate, however in this case, the undulation suggests that the area is oxidising at a slower rate. Comparing this type of large vertical crack, at a higher number density, there are vertical cracks from the sample surface about 400 nm in length, as Figure 3-6 (c) shows. These types of cracks provide the best paths for oxygen towards the metal-oxide interface. Since this type of cracking is observed very rarely, we do not believe that they are general features of FIB-prepared TEM samples. Other authors have observed similar vertical cracks¹⁴⁹. (d) shows at the top of the oxide, an example of a hole with diameter of 30-50 nm, surrounded by equiaxed oxide grains. This feature is observed in several samples. This might just be a few grains dropping out of a poorly bounded equiaxed region.

3.2.2. TKD analysis

Figure 3-7 and Figure 3-8 show examples of using TKD analysis to study the oxide microstructure. This technique allows for simultaneous acquisition of phase and orientation information as described in Chapter 2.

Figure 3-7 (a) shows the TKD map from a 225-day pre-transition sample. The entire oxide thickness is not shown as approximately half of the oxide was lost during FIB thinning, therefore the first layer of equiaxed grains is not visible. Figure 3-7 (b) shows the entire oxide

from the 360-day sample. Figure 3-7 (c) shows the whole oxide from the 585-day sample which I believe has gone through two transitions from previous observations (Figure 3-3).

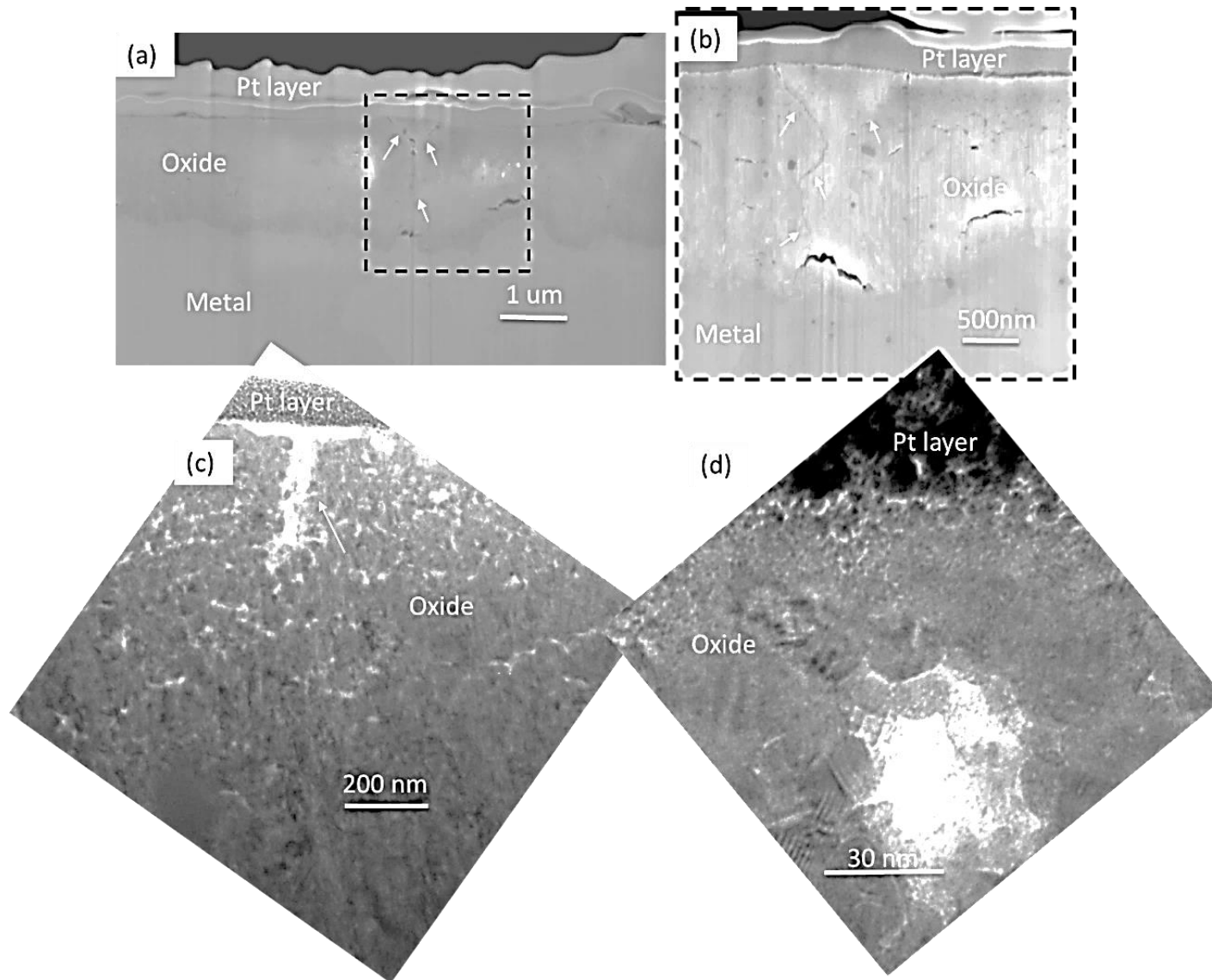
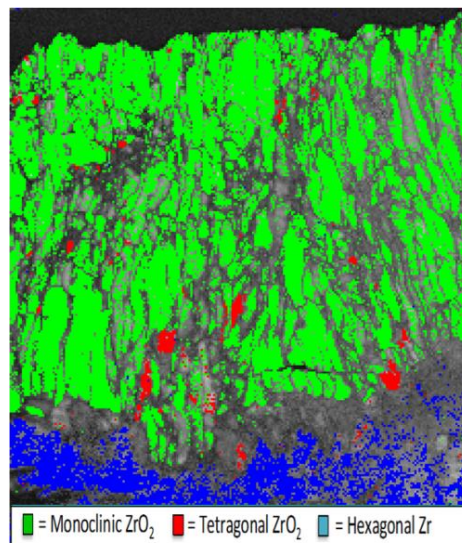


Figure 3-6: Uncommon features observed in the RXA Zr-1.0Nb samples: (a-b) FIB-SEM images showing connected cracks from the top surface towards the metal-oxide interface in 120-day sample. (c) TEM BF images showing a vertical crack from the sample surface about 400 nm. (d) TEM BF images showing a hole surrounded by equiaxed oxides.

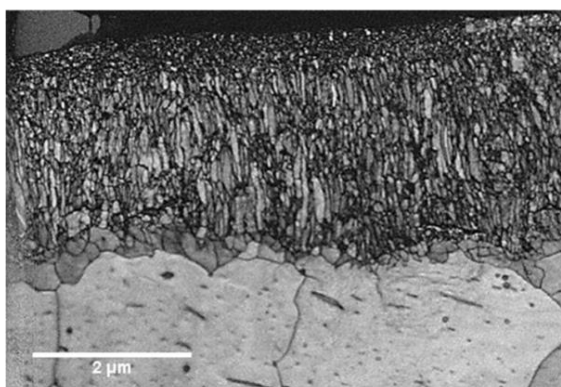
(a-1) Zr-1.0Nb 225-day



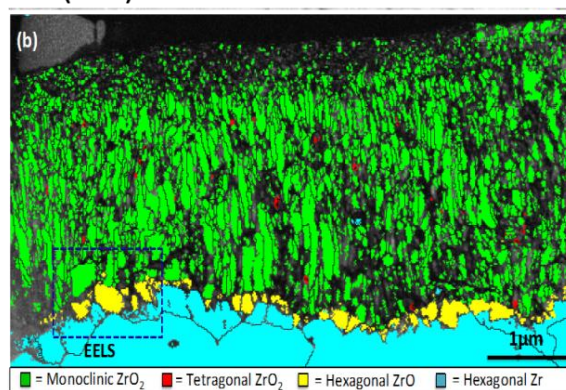
(a-2)



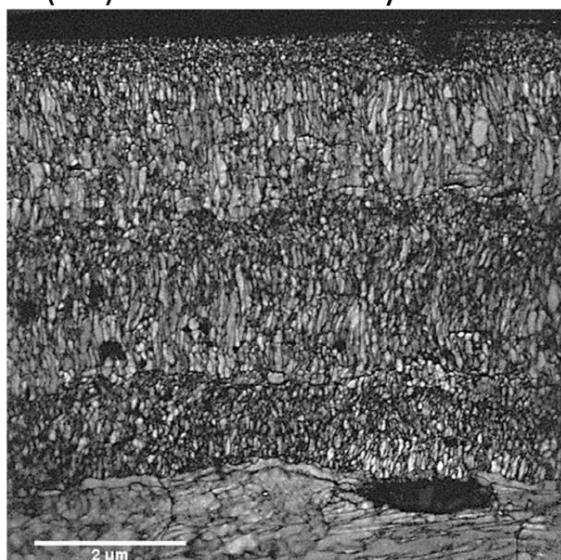
(b-1) Zr-1.0Nb 360-day



(b-2)



(c-1) Zr-1.0Nb 585-day



(c-2)

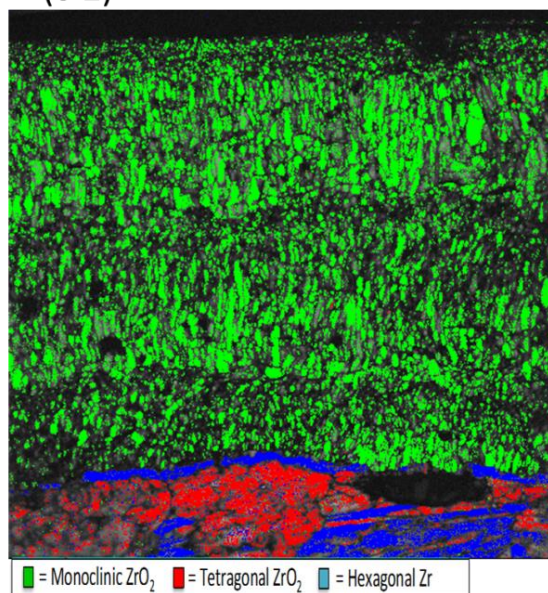


Figure 3-7: TKD mapping results for (a) pre-transition 225-day sample, (b) 360-day sample, (c) post-transition 585-day sample, including the band contrast map(left column) and phase map(right column).

The band contrast images from the TKD analysis shown in Figure 3-7 highlight the typical oxide microstructure, and agree well with the previous TEM analysis. As seen in (b) and (c) which show the whole oxide thickness, the oxide starts with small equiaxed grains around 20-30 nm in diameter, and this layer is around 700 nm in thickness. Under the equiaxed layer, there are large, elongated columnar grains towards the metal-oxide interface, oriented parallel to the oxide growth direction. These columnar grains are around 50 nm in width and 350-450 nm in length. There are scattered parallel cracks in the pre-transition samples which break up the columnar grains. Layers of lateral cracks appear to be correlated with the transition, which is estimated to occur at about 360 days. In the 585-day post transition samples, two layers of cracks can be clearly seen, suggesting two transitions have happened. The 900 nm thick layer under the second layer of cracks is full of many disorganised oxide grains which are smaller and shorter than those columnar grains higher up, only around 150-200 nm in length. This may be associated with fast oxide growth after the second transition. Comparisons of columnar grains in 360-day and 585-day above and below the second layer of cracks are shown in Figure 3-8. The phase maps shows that most of the columnar oxides have been identified with the monoclinic-ZrO₂ (m-ZrO₂) structure. There are a few tetragonal-ZrO₂ (t-ZrO₂) grains, around 20 nm in size and scattered in the equiaxed oxide from the top surface throughout the oxide thickness, while at the metal-oxide interface there are more and larger tetragonal grains. In the pre-transition samples, the TKD mapping detects around 2.7% tetragonal grains in the 225-day sample, and 0.7% in the near-transition 360-day sample, while in post-transition 585-day sample the fraction drops to 0.1%. It worth mentioning that the tetragonal phase fraction measurements in TKD are lower than the value of ~3%-5% measured on this alloy at a similar exposure time using synchrotron X-Ray Diffraction (XRD)^{109,129}. This is thought to be due to the transformation of stress-stabilized tetragonal grains to the equilibrium monoclinic phase during preparation of the thin FIB samples, and

also the possibility that the majority of the remaining small tetragonal grains are below the resolution limit of TKD¹²⁹.

At the metal-oxide interface, blocky grains are clearly visible. In the 360-day sample in (b) for example, some of the grains at the interface are identified as the hexagonal ZrO phase with P-62m symmetry and lattice parameters $a=5.31 \text{ \AA}$ and $c=3.20 \text{ \AA}$ ⁶⁸, while other grains match Zr metal with P 63/m symmetry and lattice parameters $a=3.23 \text{ \AA}$ and $c=5.14 \text{ \AA}$. The patterns were also checked against the orthorhombic ZrO phase predicted as a potential alternative structure by Nicholls et al⁶⁸, however there was no match to any of the interfacial grains.

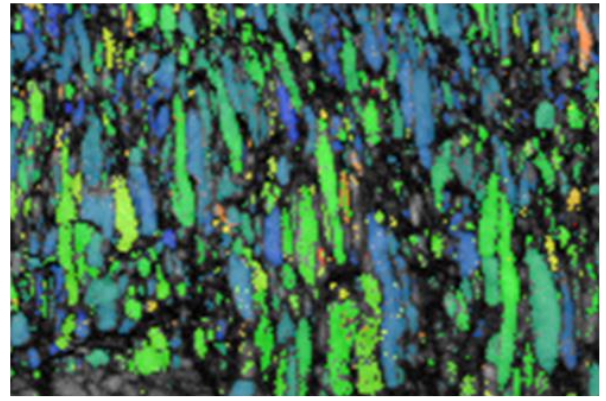
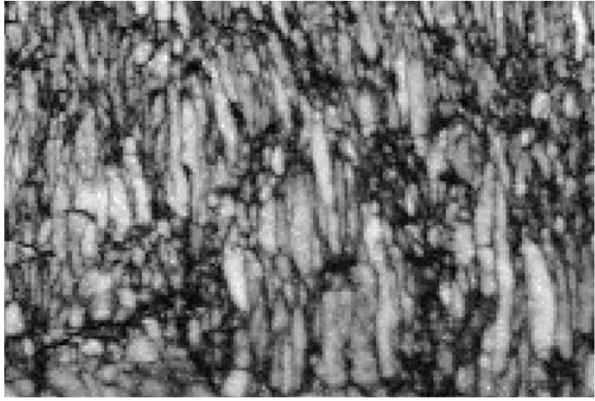
These ZrO grains are generally equiaxed and vary in size from ~50-300 nm. The orientation map indicates that most (but not all) of the suboxide grains inherit the orientation of the metal grain on which they form. Several examples of this epitaxial growth of suboxide are circled in Figure 3-9. It must be made clear that in the initial TKD analysis of the 225-day and 585-day samples, we did not include the ZrO suboxide phase in the indexing procedure, so for example in the phase map in Figure 3-7 (a-2) there is an empty area at the metal-oxide interface in 225-day sample, while in the 585-day sample the metal-oxide interface is matched incorrectly with hexagonal Zr metal. In both of these two cases, the interface is full of suboxide, as will be discussed later in Chapter 3.5 using analytical methods such as EELS.

The orientation maps of monoclinic oxide grains are shown in Figure 3-10. The grains are coloured by their deviation from the $(103\bar{1})$ fibre component that is often reported to be the preferred monoclinic oxide texture in order to minimise the mismatch stress at the metal-oxide interface¹²⁹. It shows that there is an increase in texture strength with increasing time of oxidation, possibly due to the growth of preferentially oriented columnar grains. In the pre-transition 225-day sample most of these grains are oriented from 15° to 20° away from the

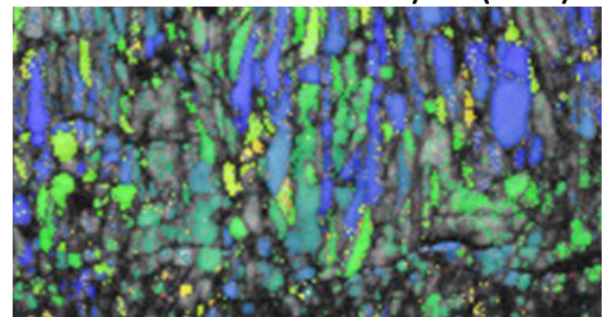
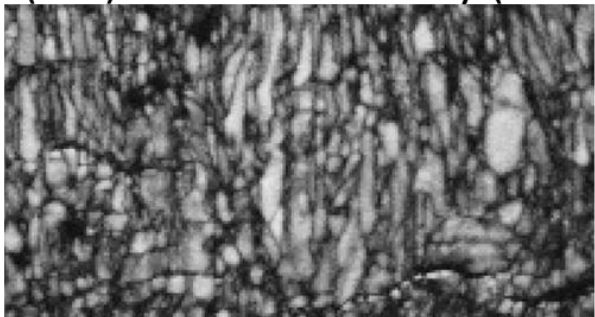
(103 $\bar{1}$) fibre component, while in the post-transition 585-day sample, these grains are only oriented from 5° to 10° away from the (103 $\bar{1}$) fibre component.

(a-1) Zr-1.0Nb 360-day

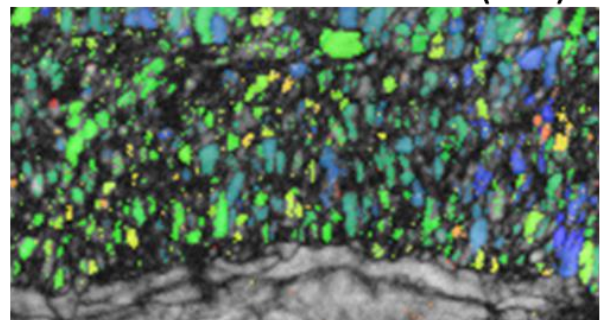
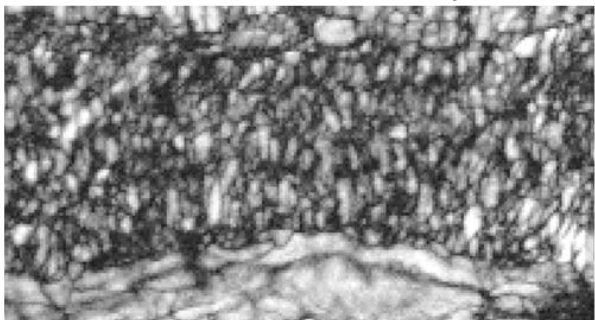
(a-2)



(b-1) Zr-1.0Nb 585-day (above 2nd transition cracks) (b-2)



(c-1) Zr-1.0Nb 585-day (below 2nd transition cracks) (c-2)



1 μm

1 μm

Figure 3-8: Higher resolution TKD mapping results (Pattern Quality and Misorientation maps) for (a) columnar grains in 360-day sample, (b) Columnar grains between 1st and 2nd transition cracks in 585-day sample, (c) Less organised grains between 2nd transition cracks and metal-oxide interface in 585-day sample.

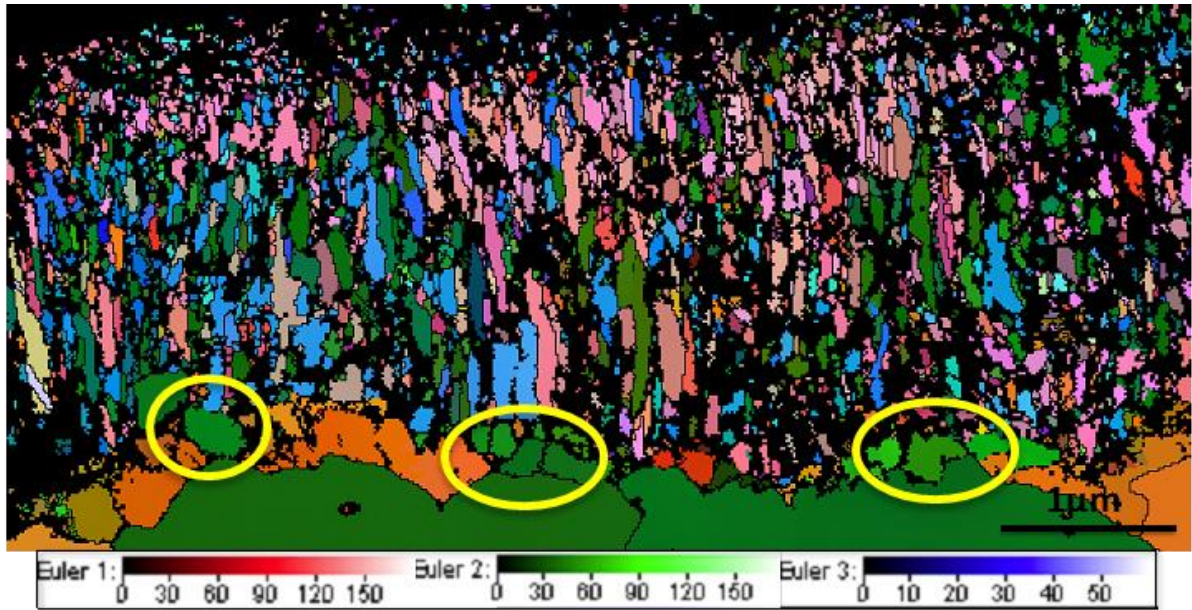


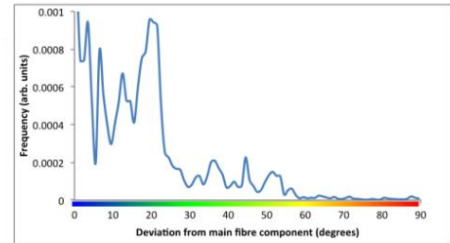
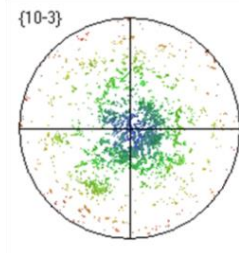
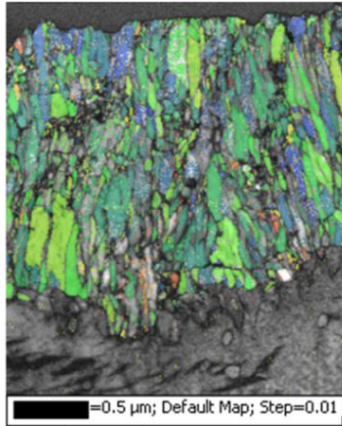
Figure 3-9: Euler angle map from TKD analysis of the TEM sample (grain boundaries $>10^\circ$ are highlighted). Circles show examples of epitaxial growth of the ZrO suboxide on the underlying metal.

3.2.3. ASTAR mapping

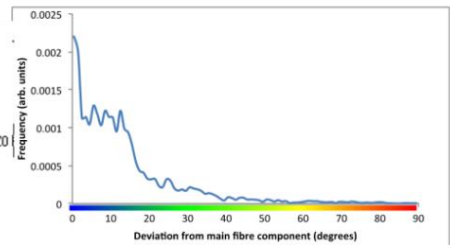
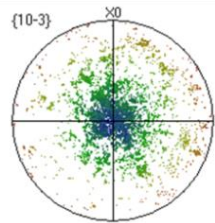
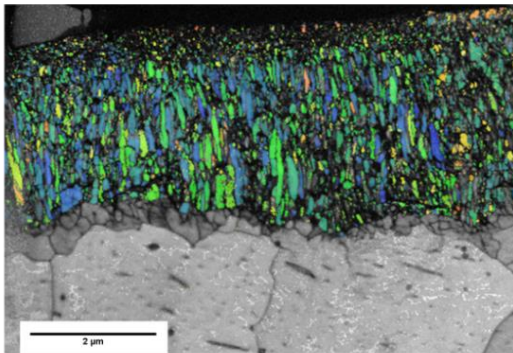
Figure 3-11 shows ASTAR phase maps of the TEM lamella for (a) the 120-day sample and (b) the 585-day sample. Columnar oxides with m-ZrO₂ structure are clearly seen, and scattered equiaxed t-ZrO₂ grains. The step size in ASTAR mapping is ~ 5 nm, and so we should be able to detect smaller t-ZrO₂ grains than by TKD. Tetragonal phase fraction in both samples is around 1%. In the 120-day sample, the top layer of t-ZrO₂ in (a) is considered to be a result of FIB damage¹⁵⁰. At the metal-oxide interface, there is a continuous layer of Widmanstätten-type suboxide with the hexagonal ZrO structure predicted with ab initio modelling⁶⁸, which agrees with Figure 3-7¹²⁸ using Transmission Kikuchi Diffraction but with a higher matching rate because of the better spatial resolution in ASTAR mapping. The undulating area under a parallel crack in (a) shows a more uniform saw-tooth shape with metal underneath intact, while other locations that have a flat metal-oxide interface show less well-defined saw-tooth suboxide grain structure. The same areas were analysed in EELS

mapping later. In the 585-day sample, there is also a continuous layer of suboxide around 50-100 nm in thickness.

(a) Zr-1.0Nb 225-day



(b) Zr-1.0Nb 360-day



(c) Zr-1.0Nb 585-day

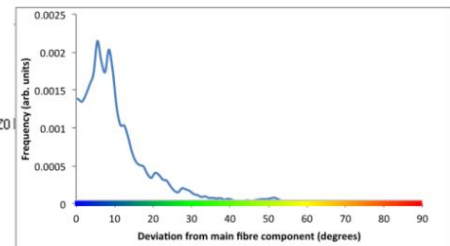
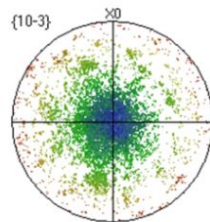
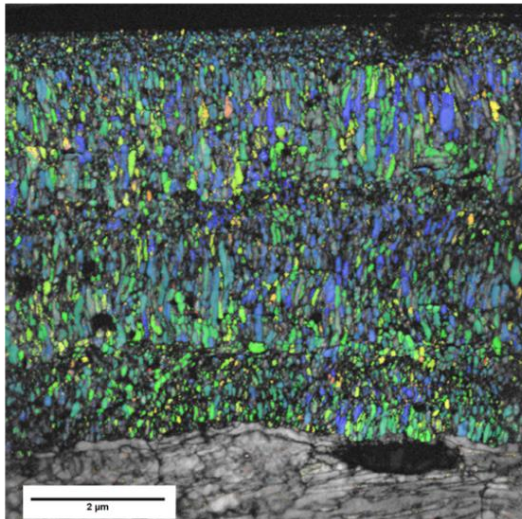


Figure 3-10: TKD mapping results for (a) pre-transition 225-day sample, (b) 360-day sample, (c) post-transition 585-day sample, including the texture component orientation map. Grain boundaries with misorientation $>10^\circ$ are highlighted).

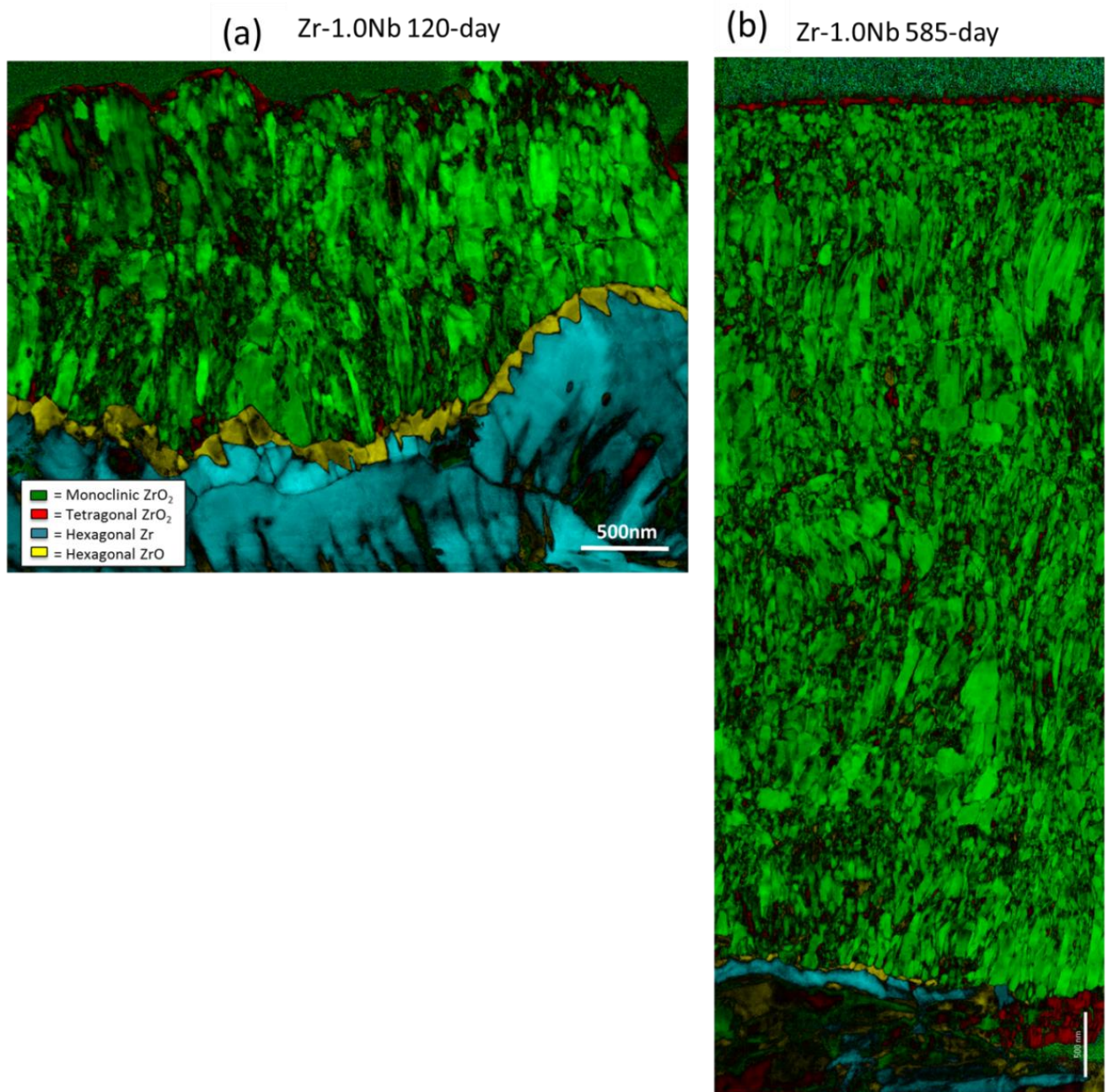


Figure 3-11: ASTAR phase map for (a) 120-day sample and (b) 585-day sample.

3.3.POROSITY IN THE OXIDE

By using Fresnel imaging in the TEM, different types of porosity can easily be identified⁷¹. I was able to look at the development of porosity at different stages of oxidation. Figure 3-12 shows examples in 225-day sample that the pores are invisible in the top in-focus images ($\Delta f = 0$ nm), but show Fresnel contrast in the middle under-focussed images ($\Delta f = -980$ nm) and

in the lower over-focussed images ($\Delta f = +980$ nm). In this thesis, most of the times I used over-focused images to represent the porosity because the porosity is most easily seen in this condition.

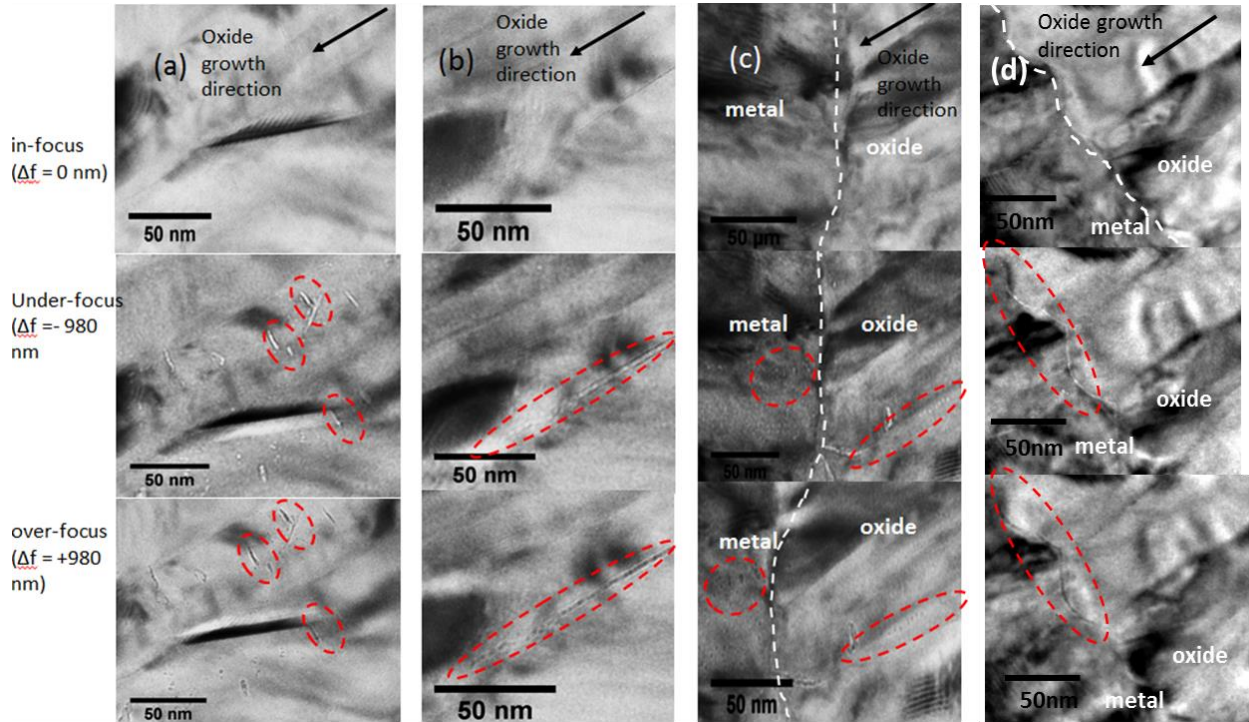


Figure 3-12: Through-focal imaging of fine pores (circled) close to the metal-oxide interface in the 225-day Zr-1.0Nb sample. Three different types of porosity are revealed at different locations: (a) 100nm from the metal-oxide interface: parallel interconnected pores; (b) 100nm from the metal-oxide interface: vertically interconnected pores along the columnar oxide grain boundaries; (c) near the metal-oxide interface: disconnected pores. (d) connected porosity under the columnar grains right at the metal-oxide interface.

3.3.1. Porosity in the early stage sample

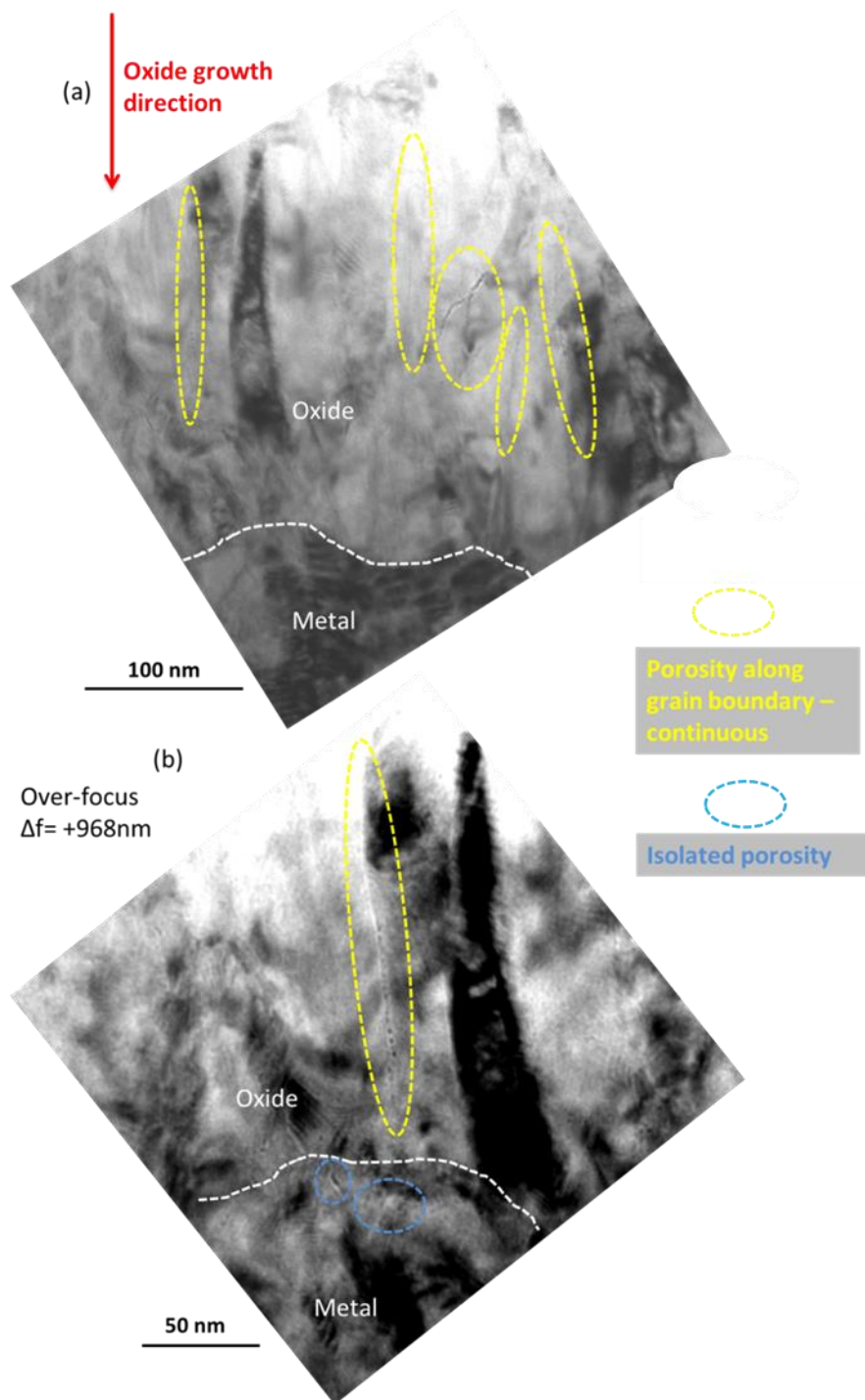


Figure 3-13 shows the porosity in 3-day early stage sample. As mentioned before, the top surface of the oxide has a 150 nm layer of porous equiaxed grains and then 650 nm of columnar oxide. These columnar grains not only have a smaller grain size (26 nm) comparing with columnar grains in later stage samples, but are also decorated with vertically connected

porosity along the grain boundaries as seen in (a). The higher magnification image in (b) shows that this connected porosity breaks up near the metal-oxide interface, eventually creates a sink in the metal underneath the columnar oxide.

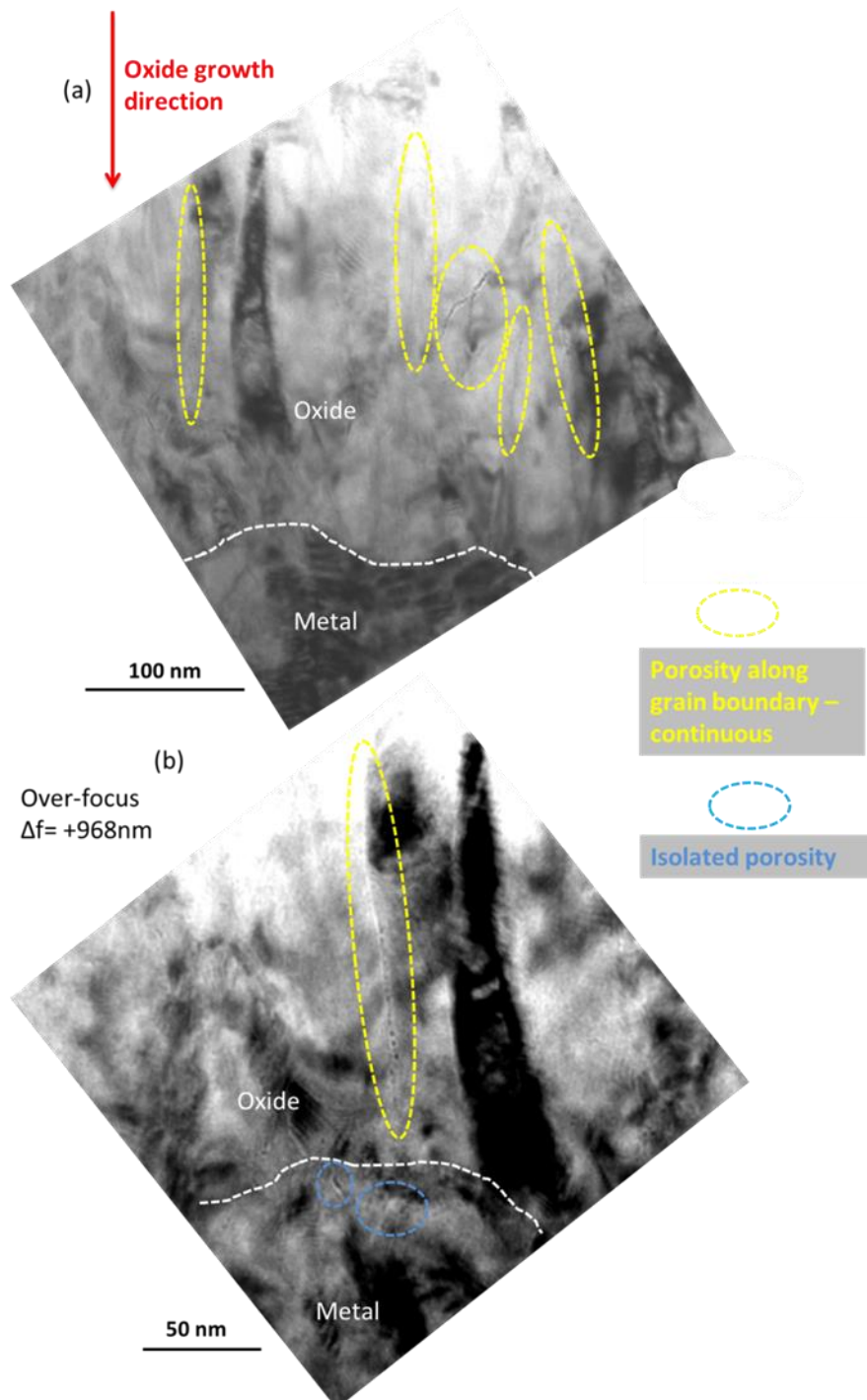


Figure 3-13: Over-focus images of 3-day Zr-1.0Nb: (a) a large amount of vertically connected porosity at columnar oxide grain boundaries; (b) Higher magnification image of the metal-oxide interface showing the connected porosity becomes disconnected closer to the interface.

Figure 3-14 show the porosity in the pre-transition 225-day sample. Figure 3-14 (a) show the general overview of the upper oxide, where the first 650 nm contains many parallel micro cracks around 60-120 nm long. Some small micro cracks around 200 nm in length start to appear parallel to the metal-oxide interface, lying between the equiaxed and columnar oxide grains. Like all the other samples I have studied, the outer equiaxed part is very porous, with individual pores around 10 nm in diameter at oxide grain boundaries, as seen in the STEM HAADF image in Figure 3-14 (b). The over-focus TEM BF image in (c) shows by dark contrast where the porosity is in this top oxide layer.

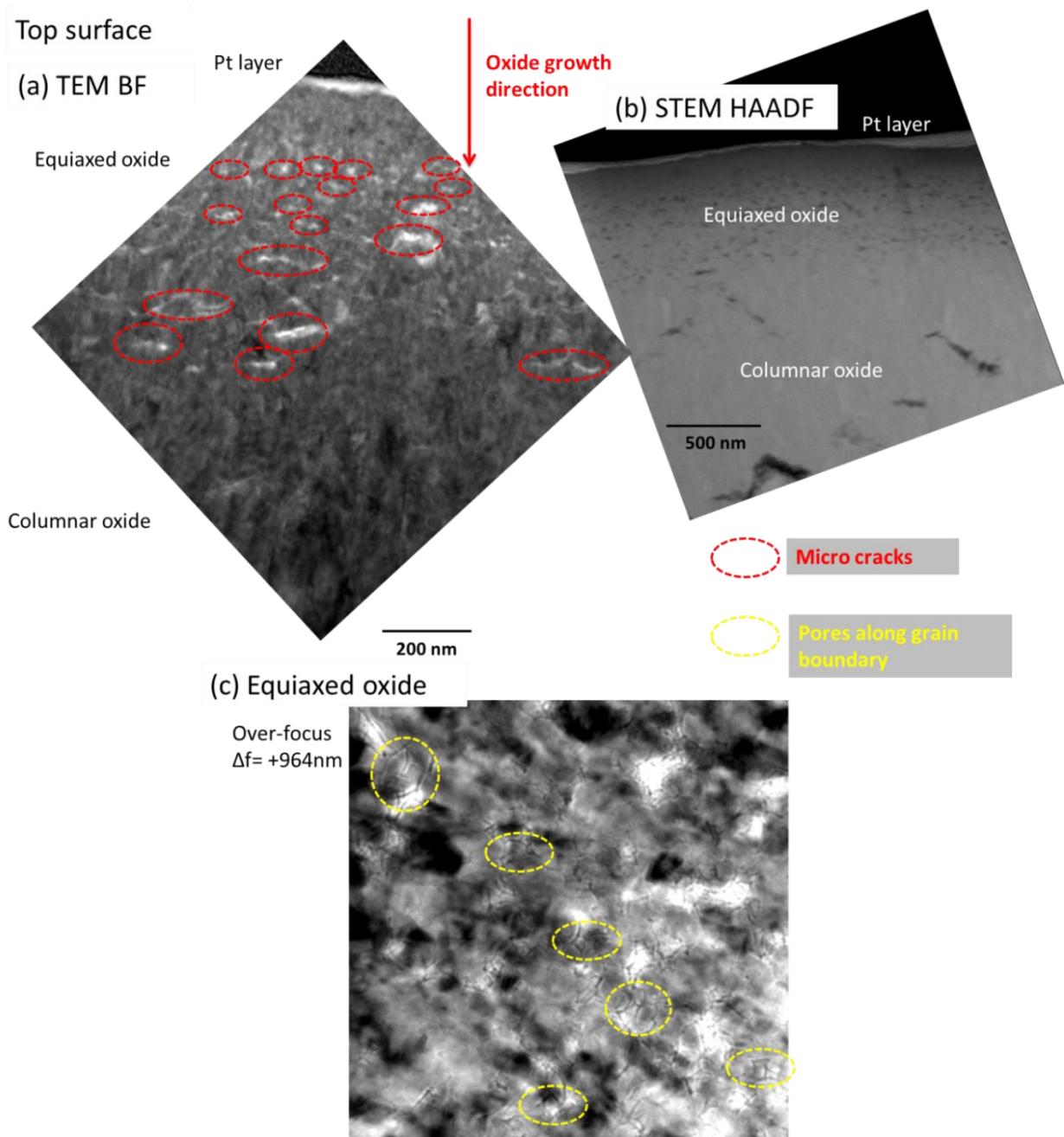


Figure 3-14: Porosity images of the top surface of the 225-day pre-transition sample: (a) TEM BF and (b) STEM HAADF images of overview of top surface oxide. (c) Over-focus image showing the top surface porosity.

A series of under- and over-focus images ($\Delta f = \pm 1400 \text{ nm}$) in Figure 3-15(a) show the porosity distribution in the middle part of this same oxide. Some of the columnar grain boundaries are decorated with continuous porosity, as shown by the higher magnification images in (b). In addition, near the micro cracks there are some parallel micro cracks 50-80 nm long cutting through the columnar oxides. Figure 3-15 (b) also shows a higher

magnification image of continuous porosity along a columnar grain boundary which in this case is around 240 nm long. There are also many individual pores inside the columnar grains, 3-5 nm in diameter, which suggests that migration through the bulk lattice is a possible path for oxygen transport, although not the fastest route.

Figure 3-16 (a) and (b) show two examples of the distribution of porosity near the metal-oxide interface. There are several different kinds of porosities, shown more clearly in the detailed higher magnification focal series images in Figure 3-17. In Figure 3-17 (a), ~100 nm away from the metal-oxide interface, there are some individual pores in the columnar oxide. Some of the individual pores are connected, especially identified by arrows, creating an interconnected array of flake-like porosity/micro-cracking around 10-15 nm in width that is parallel to the metal-oxide interface. In Figure 3-17 (b), near the metal-oxide interface, some of the columnar grain boundaries are seen to be decorated with vertically interconnected porosity. Towards the end of this vertically connected porosity, the pores gradually become disconnected as we move closer the metal-oxide interface, showing as disconnected individual pores. These can be inside columnar grains or along the grain boundaries. This kind of individual porosity is also found at the metal-oxide interface and in the suboxide region underneath, as seen in Figure 3-16 (a) which may act as an oxygen sink for the local oxidation process. At the end of the columnar grains, as seen in Figure 3-16 (b), there is also continuous porosity that lies at the interface underneath the columnar grains. This kind of complex interconnected porosity seems likely to play an important role in the rate determining oxygen diffusion process.

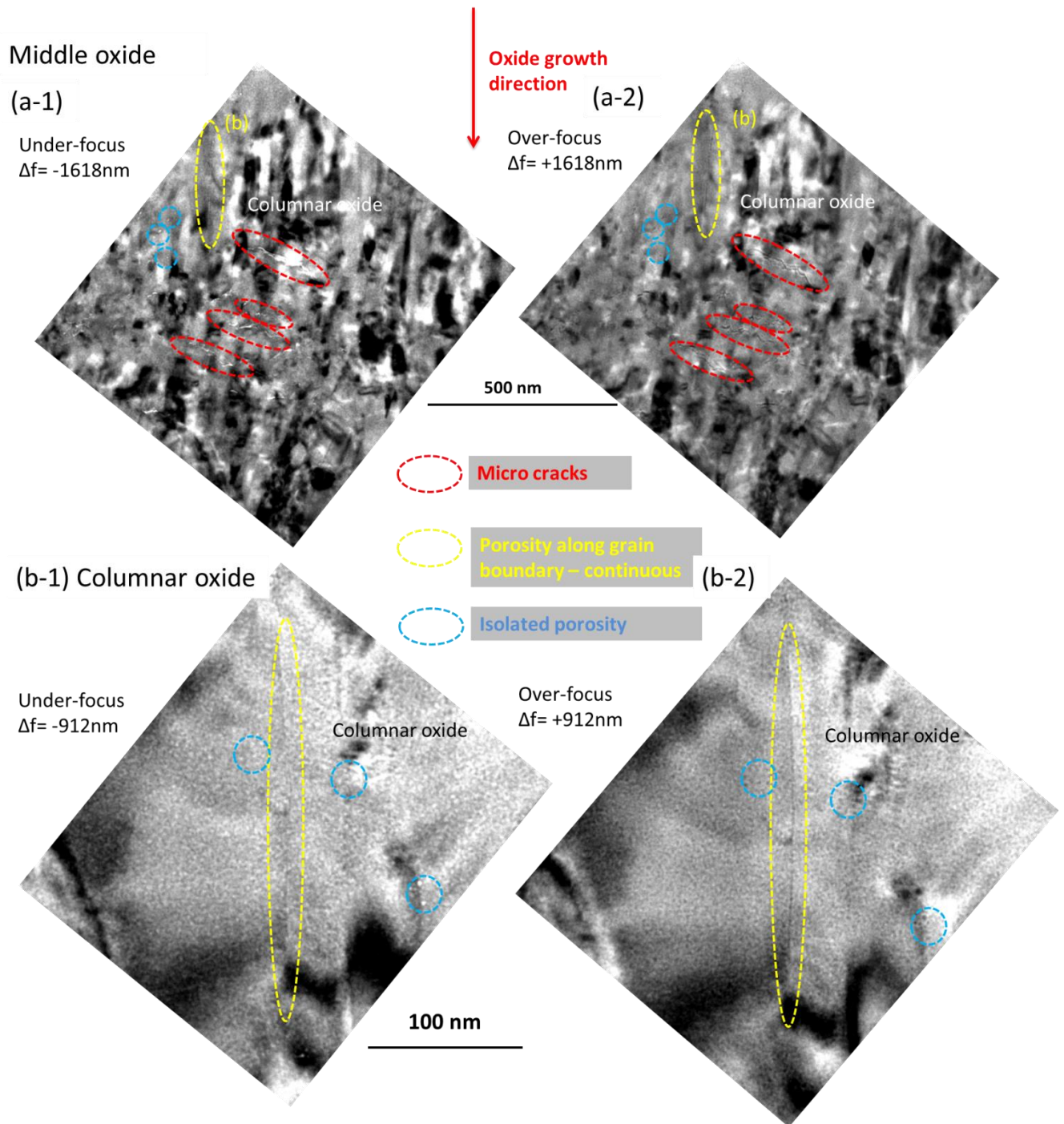


Figure 3-15: Porosity images of 225-day pre-transition sample: Middle oxide. (a) Through-focal images of middle oxide with area (b) in a higher magnification image showing columnar grain boundary porosity and individual porosity.

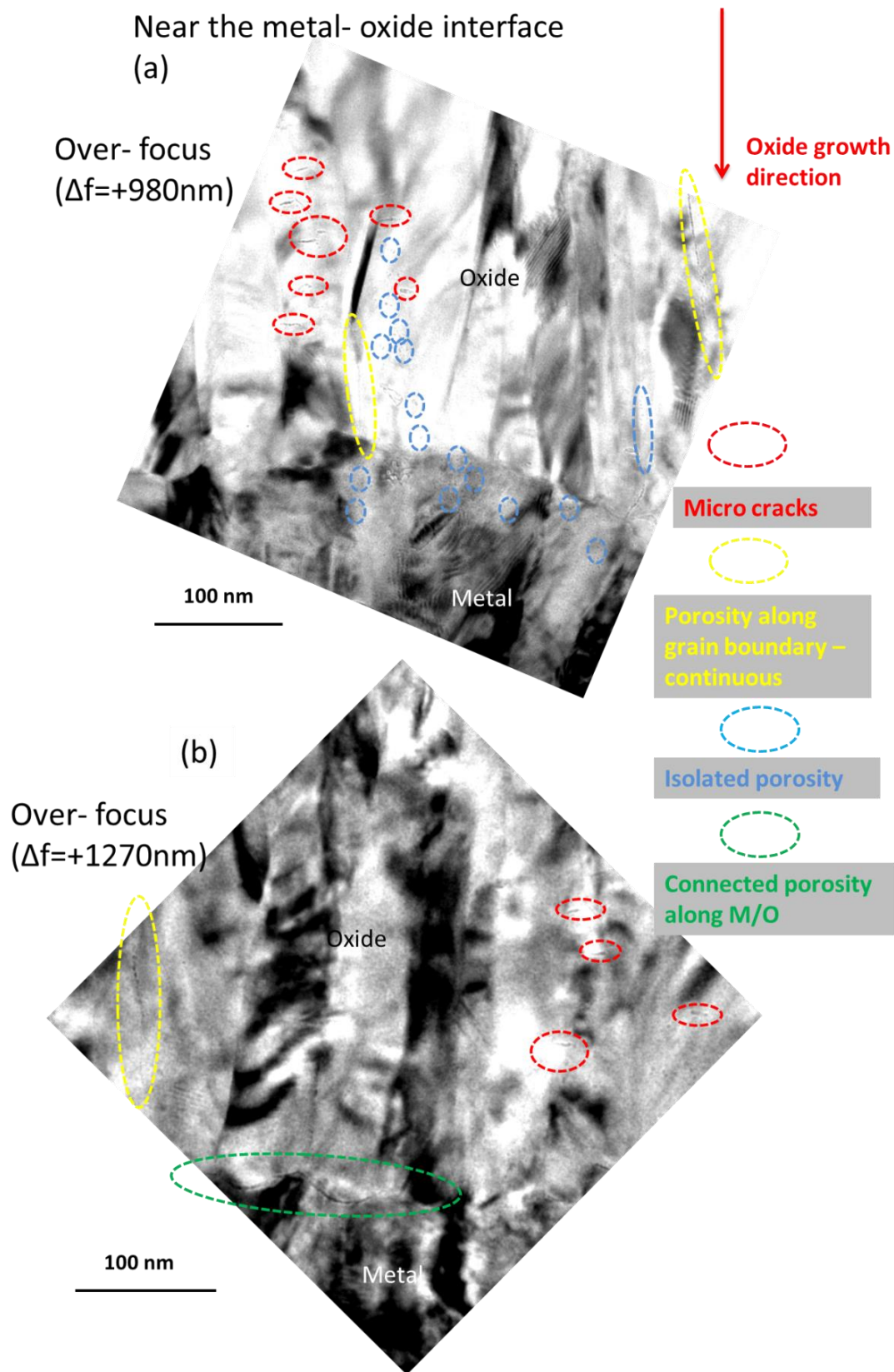


Figure 3-16: Porosity images of 225-day pre-transition sample: near the metal-oxide interface. Higher magnification through-focal images of these four types of porosities are shown in Figure 3-17.

100 nm from the metal-oxide interface

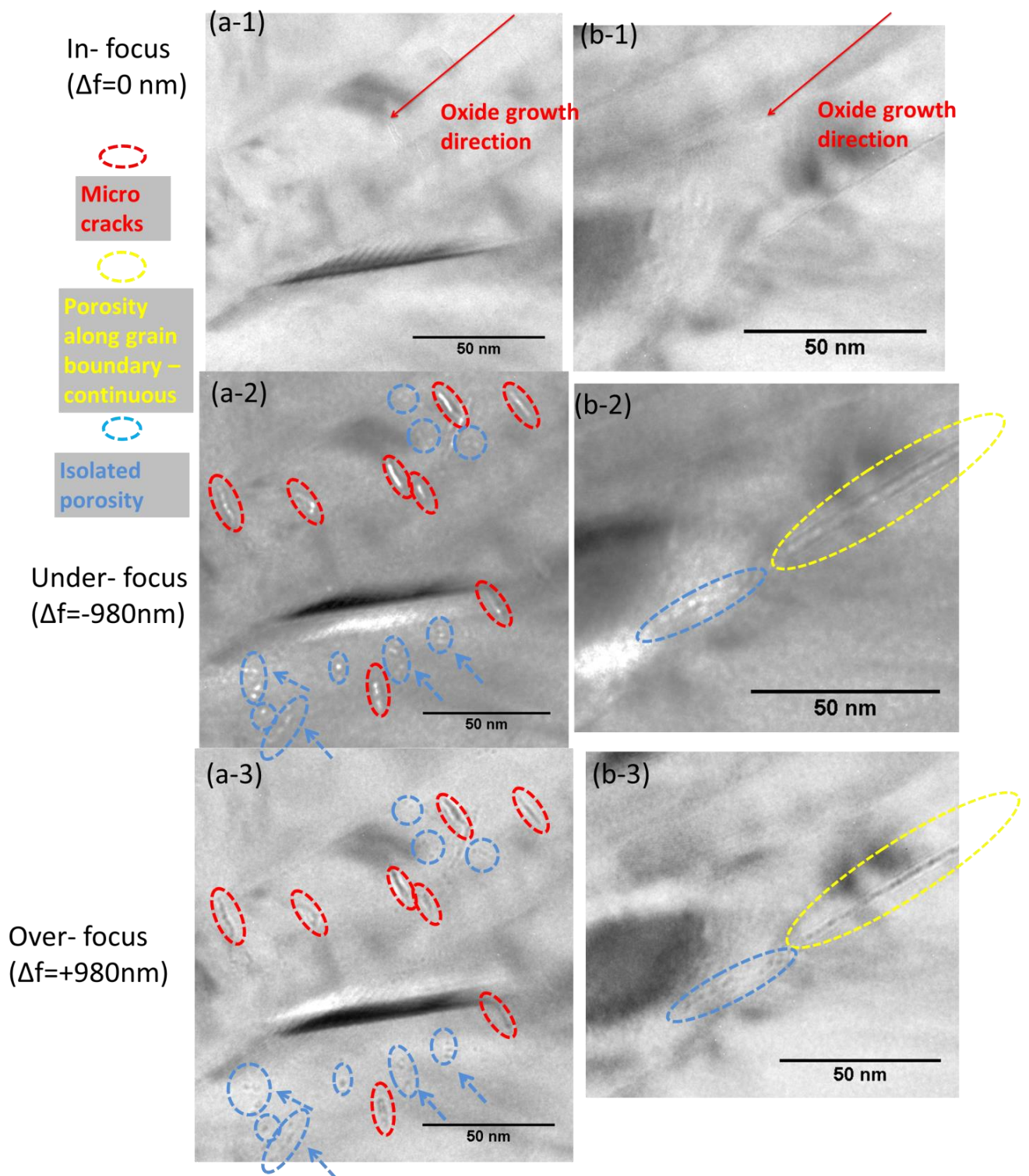


Figure 3-17: Through-focal imaging of fine pores (circled) 100 nm from the metal-oxide interface in the 225-day pre-transition sample. (a): individual pores some of which are interconnected to become micro cracks; (b) vertically interconnected pores along the columnar oxide grain boundaries which gradually become disconnected.

3.3.2. Porosity in samples close to transition

Figure 3-18 shows through-focal images of the 360-day sample which is near the first transition stage. Besides similar porosity to that seen in the equiaxed oxide, the columnar grains in this sample are decorated with more continuous porosity along columnar grain boundaries as shown in (a). There are two amorphous SPPs in this region of the oxide (as pointed by arrows), the top one is round with diameter 85 nm, the bottom SPP is elliptical and 75 nm in width and 95 nm in length and also has a crescent shaped crack on the top. It is noticeable that the vertical porosity is connected to the edges of the SPPs. There are also individual 2-4 nm pores and lateral 30 nm micro cracks in the columnar oxide grains.

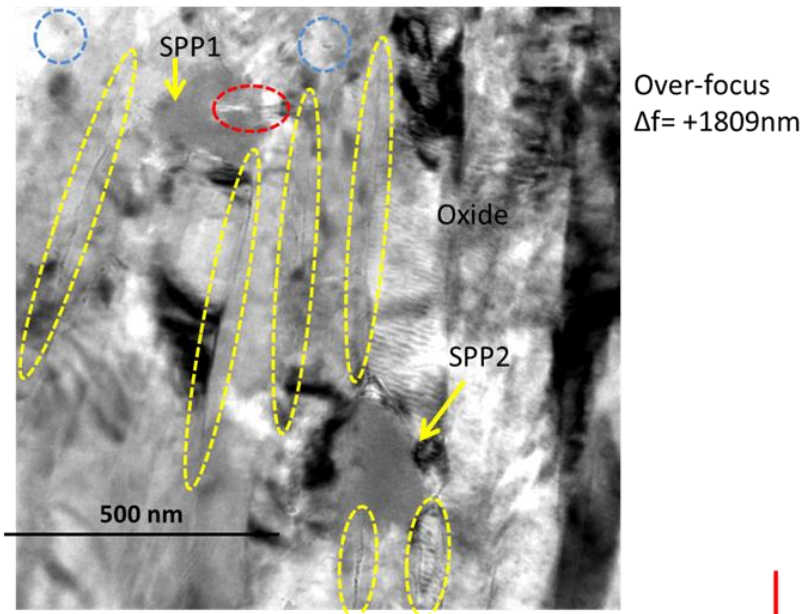
At this stage in the oxidation process, there are more micro-cracks near the metal-oxide interface as seen in Figure 3-18 (b) comparing with samples in the pre-transition stage. There is one big parallel crack 900 nm in width and 100 nm in length lying around 200 nm from the metal-oxide interface. In the region 1 μm from the metal-oxide interface, there is an intensive network of micro-cracks around 500 nm in width as circled in (b). They are likely to provide an easy way for the oxygen to get down to the metal.

3.3.3. Porosity in second-transition samples

Figure 3-19 shows through-focal images of the 540-day sample. Besides similar porosity as seen in the equiaxed oxide, the columnar grains in 540-day sample are decorated with more continuous porosity along grain boundaries as shown in (a) comparing with the pre-transition samples. There are also 50-150 nm micro cracks parallel to the metal-oxide interface, plus macro-cracks around 300 nm in length. There are also large numbers of individual pores inside columnar grains. Closer to the metal-oxide interface, as shown in Figure 3-19 (b) around 500 nm above the interface, there are more micro cracks around 100 nm in length which are interconnected, but less grain boundary porosity is seen. There is still a lot of

individual porosity at this location. Similar features have been observed in the 360-day sample as well.

(a) Columnar oxide



(b) Metal-oxide interface

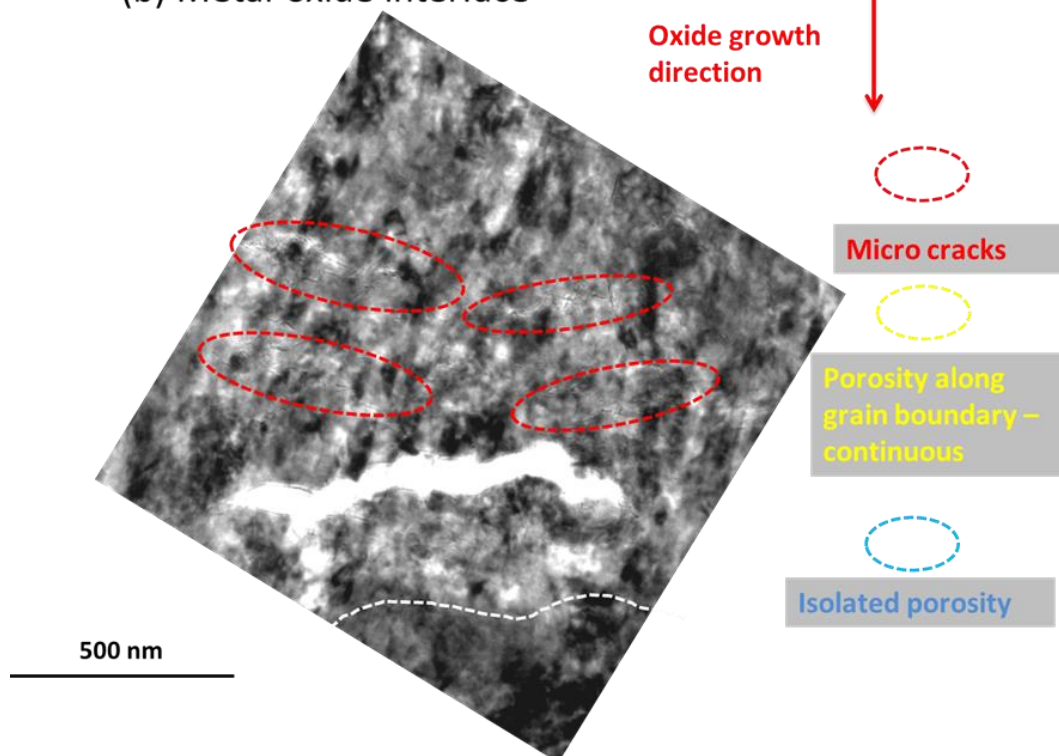
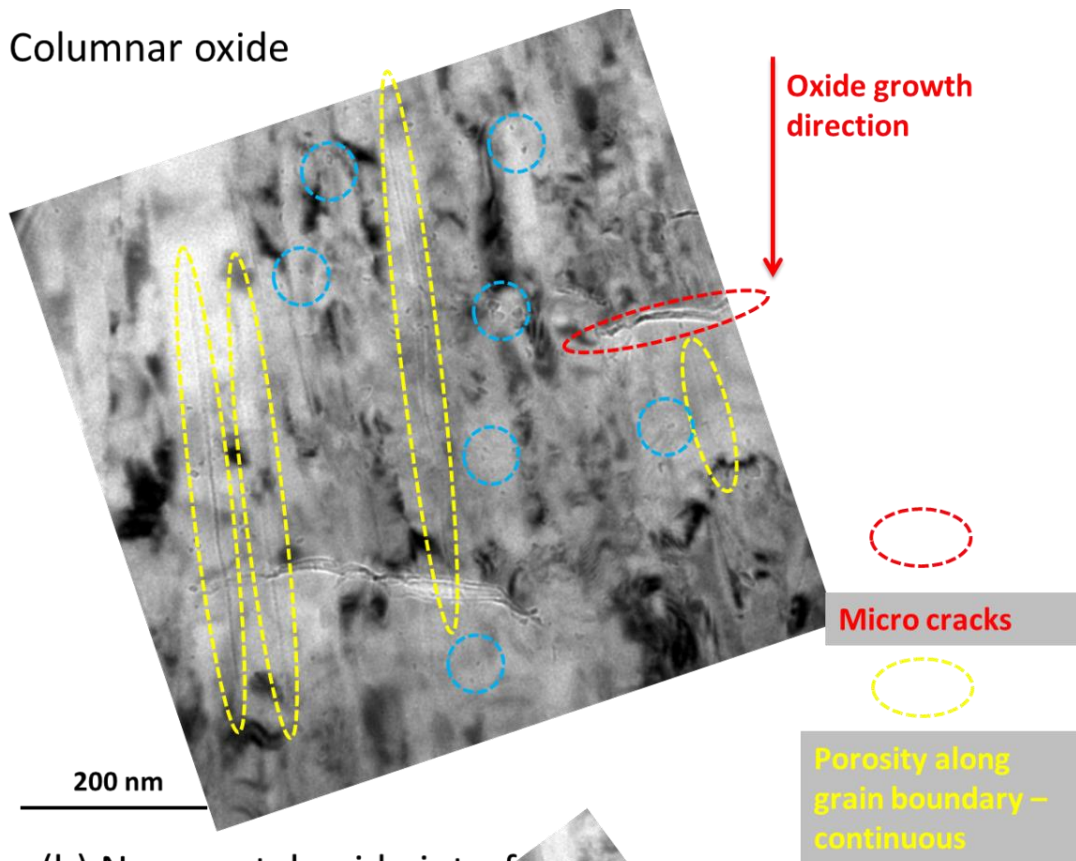


Figure 3-18: Over focus images of fine pores (circled) in the 360-day Zr-1.0Nb sample. Different types of porosity are revealed at different locations: (a) in the columnar oxide, (b) intensive network of connected porosity around 500 nm above the metal-oxide interface and a huge crack at around 200 nm above the metal-oxide interface.

(a) Columnar oxide



(b) Near metal-oxide interface

Over-focus
 $\Delta f = +1350\text{nm}$

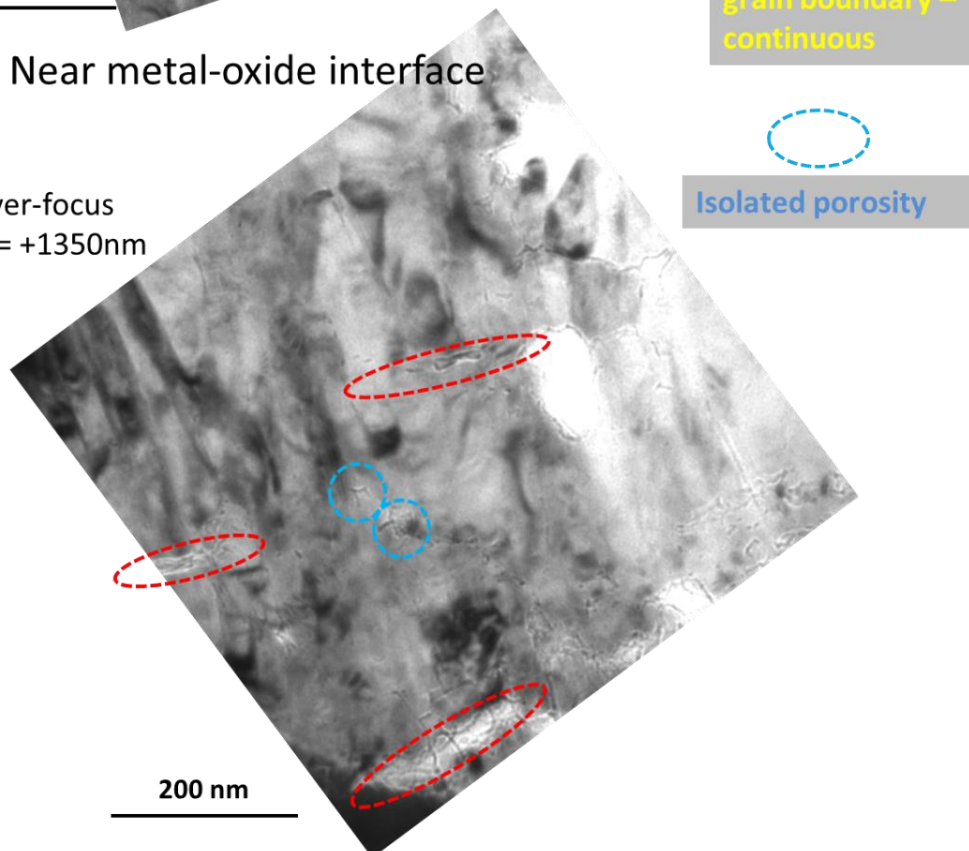


Figure 3-19: Images showing porosity in the 540-day sample: (a) over-focus image of vertically connected columnar grain boundary porosity, individual pores and parallel micro-cracks; (b) over-focus image of an area near the metal-oxide interface showing interconnected micro-cracks and individual pores.

3.3.4. Porosity in post-second-transition samples

Figure 3-20 shows over focus images of the 585-day post-second-transition sample. Between the two layers of cracks, there are columnar oxide grains. (a-1) and (a-2) shows over-focus images of vertically connected porosity along the columnar oxide grain boundaries. The location shown is above the second transition crack, around 2.1 μm away from the metal-oxide interface. It worth pointing out that at the lower part of (a-1), closer to the metal-oxide interface, the porosity becomes discontinuous.

Figure 3-21(a) shows an under-focus image around first-transition cracks of a region that is full of interconnected micro cracks and porosity between equiaxed grains. (b) shows the over-focus image of an area near the second-transition cracks. Under the second layer of cracks, there is a 500 nm thick layer of porous material, with many individual pores and some parallel micro cracks around 100 nm in width. It is followed by columnar grains down to the metal-oxide interface. This columnar oxide region contains some vertical porosity as seen in (c), some of the vertical porosity becomes discontinuous closer to the metal-oxide interface. Also, at the metal-oxide interface, there is continuous parallel crack lying right at the interface.

3.3.4. Porosity development with oxide growth

By looking at these samples at different oxidation stages, it is possible to speculate about the relationship between the development of porosity and the mechanism and rate of oxide growth.

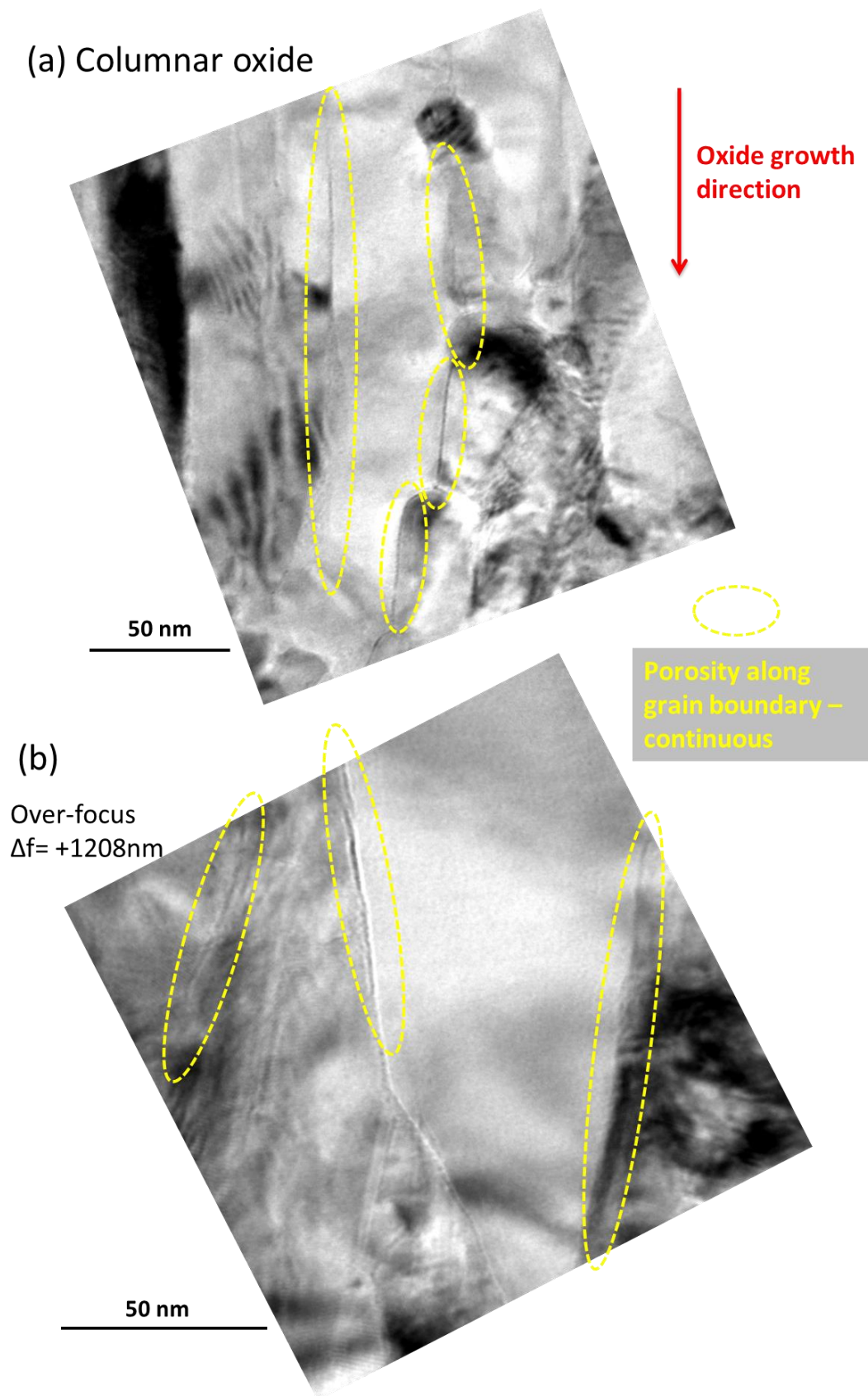


Figure 3-20: Images showing porosity in the 585-day sample: (a) and (b) Over-focus images of interconnected porosity along columnar grain boundaries.

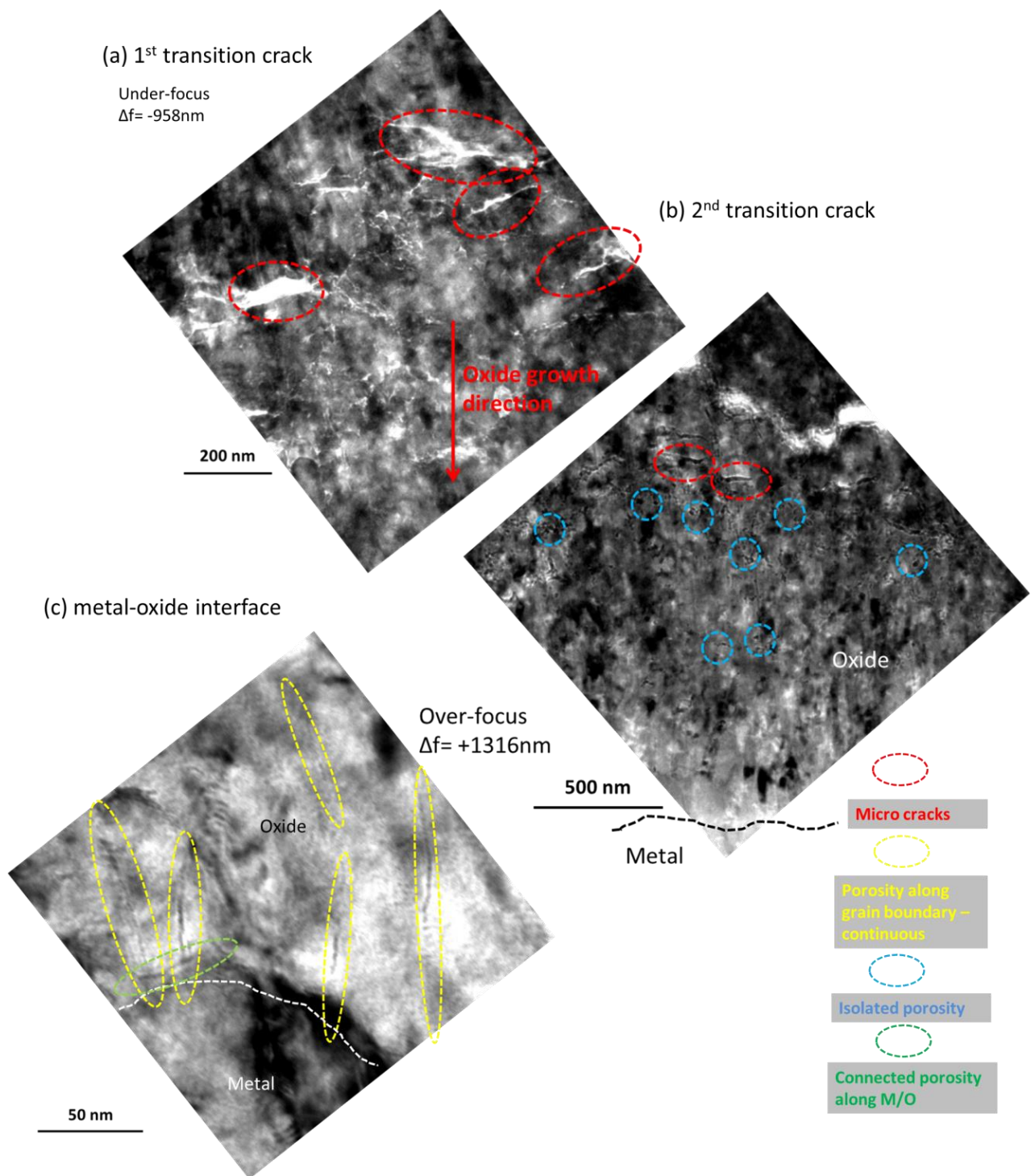


Figure 3-21: Porosity images of the 585-day post-second-transition sample: (a) Under-focus image of area near first-transition cracks; (b) Over-focus image of area near second-transition cracks; (c) Over-focus images of area under a second-transition crack above the metal-oxide interface, showing examples of vertical continuous porosity along columnar grain boundaries and continuous parallel porosity along the metal-oxide interface.

In all these samples, the outer oxide has a very porous equiaxed grain structure of thickness from 150 nm towards 650 nm before columnar oxide grains start to grow (Figure 3-14). In the pre-transition samples, some of the columnar grain boundaries are decorated with vertically connected porosity which becomes discontinuous closer to the metal-oxide interface, before it becomes individual pores either inside the oxide grains or underneath them (Figure 3-16 and Figure 3-17). Some of these individual pores seem to connect together to become micro cracks around 50-100 nm in length, and some of these also lie right at the metal-oxide interface (Figure 3-16(b)). When transition happens, as shown in the 360-day and 540-day samples, the individual pores become more connected, the columnar grain boundaries have more vertically connected porosity (some of which is connected with SPPs) (Figure 3-19 and Figure 3-20). Also there are more micro cracks, which can become an interconnected network of macro-cracks before the much longer transition cracks develop. After transition, the cycle begins again by forming isolated porosity in new columnar oxide grain. In the second-transition samples, we see more and more connected porosity, suggesting that there are more pathways for water to penetrate to the metal-oxide interface. This model of gradually increasing porosity as the oxide thickness increases provided more data on one series of samples on different oxidation stage to support the model proposed by Ni et al⁶⁶.

3.4. SECOND PHASE PARTICLES

Second phase particles (SPPs) have been studied in great detail because they are proposed to offer cathodic sites for hydrogen penetration and also become oxidised and may release aliovalent elements which can affect the local electronic conductivity in the oxides.

3.4.1. SPP morphology

Two types of SPPs are observed in these samples, which are β -Nb and $\text{Zr}(\text{Nb},\text{Fe})_2$ Laves phase particles. The latter have a bigger size and a lower density. Laves phase SPPs also tend to become amorphous once incorporated into the oxide, as will be described below. Near the

metal-oxide interface, most SPPs remain metallic and they often have crescent-shaped voids on the top^{61,64}, which indicates the delayed oxidation of the SPPs and generation of local stress differences between the SPPs and the oxide due to the P-B ratio of 1.6.

β -Nb SPPs are found in either the crystalline or amorphous states, and can be associated with both micro cracks and big cracks. Figure 3-22 shows examples of β -Nb SPPs in the oxide. (a) shows examples of amorphous β -Nb SPPs; the two elliptical amorphous β -Nb SPPs 60 nm in length and 40 nm in width are around 670 nm away from the metal-oxide interface. There is another smaller (20 nm in diameter) round β -Nb SPP 863 nm away from the metal-oxide interface. No other amorphous β -Nb SPPs have been found below this layer, i.e. in the area below 670 nm all the β -Nb SPPs tend to remain crystalline, as seen in Figure 3-22 (b), (c) and (d). It is often found that β -Nb SPPs are associated with parallel cracks as seen in (b). In this case, the β -Nb is around 100 nm above the metal-oxide interface, and the SPP is round with 48 nm in diameter. The parallel crack next to the SPP is 318 nm in length and 65 nm in width. (c) shows a common morphology for a crystalline β -Nb SPP 45 nm in diameter with a crescent shaped crack on the top. (d) shows a crystalline β -Nb right above the metal-oxide interface which shows a slight sign of a crack on top, but still remains round.

$\text{Zr}(\text{Nb,Fe})_2$ Laves phase SPP are more often seen in the amorphous state, but have crescent shaped cracks on the top if they remain crystalline. Figure 3-23 shows four examples of $\text{Zr}(\text{Nb,Fe})_2$ Laves phase SPPs. All of these SPPs contain Cr as well. (a) is an amorphous SPP with an elliptical shape, 90 nm in length and 55 nm wide, with a crescent shape crack on the top. Another amorphous SPP is round and 80 nm in diameter. (c) shows an SPP that is 130 nm in width and 110 nm in length, and the top 70 nm is amorphous and the bottom 40 nm still remains crystalline. (d) shows a crystalline SPP that is 220 nm in width and 120 nm in length, with a big crescent shaped crack on the top.

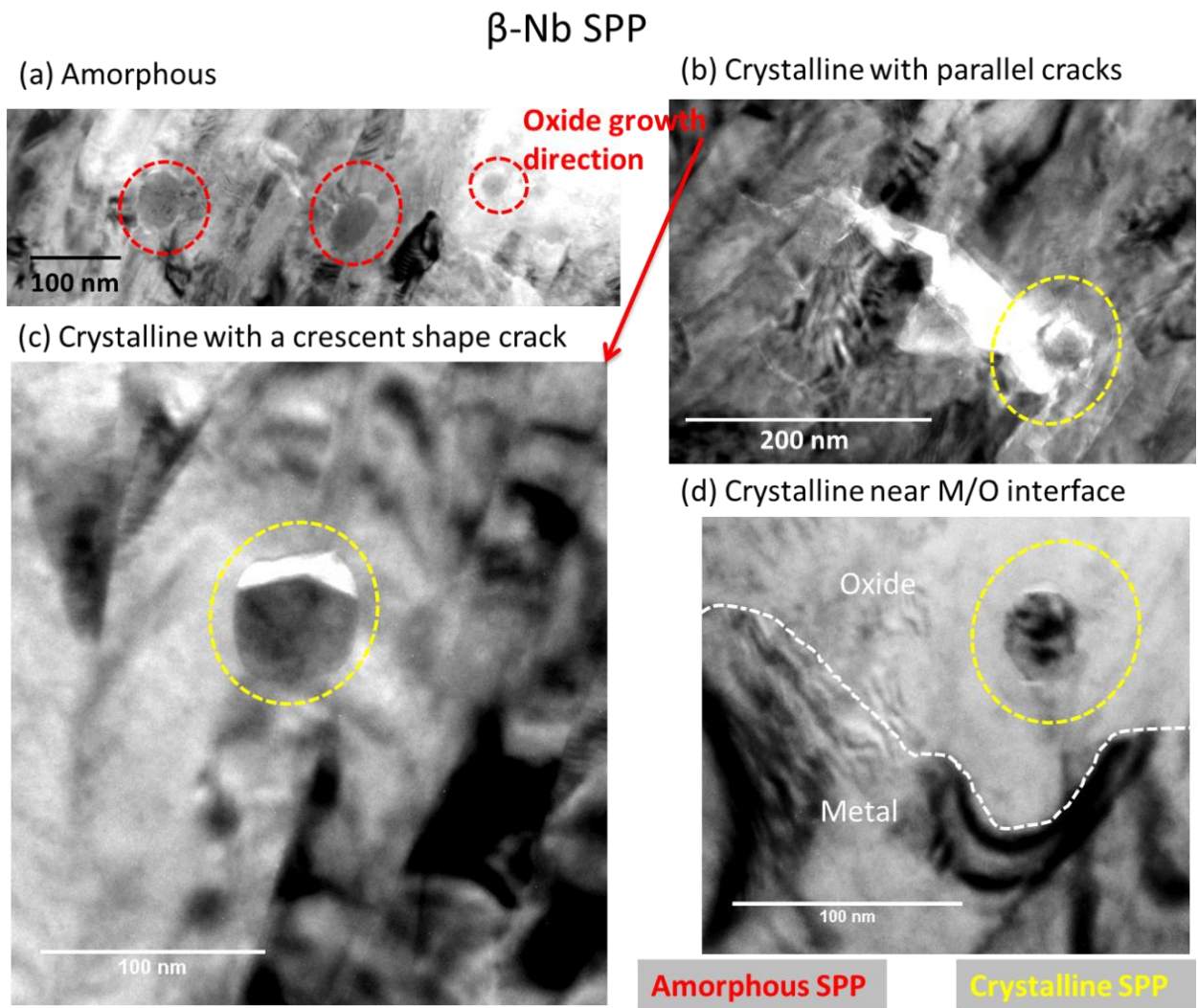


Figure 3-22: β -Nb SPPs in the oxide: (a) three amorphous SPPs around 670-863 nm above the metal-oxide interface; two are elliptical and one is round; (b) crystalline SPPs with a parallel crack next to it; (c) commonly observed crystalline β -Nb with a crescent shaped crack on top; (d) crystalline β -Nb near the metal-oxide interface.

3.4.2. The state of SPPs with distance to metal-oxide interface

Compared with the bulk metal, SPPs have a delayed oxidation process, which results in them either remaining crystalline or becoming amorphous in the oxide as the oxygen content increases. Here I discuss their crystalline/amorphous state with regards to their distance from the metal-oxide interface and so time in the oxide.

$\text{Zr}(\text{Nb,Fe})_2$ Laves phase SPP

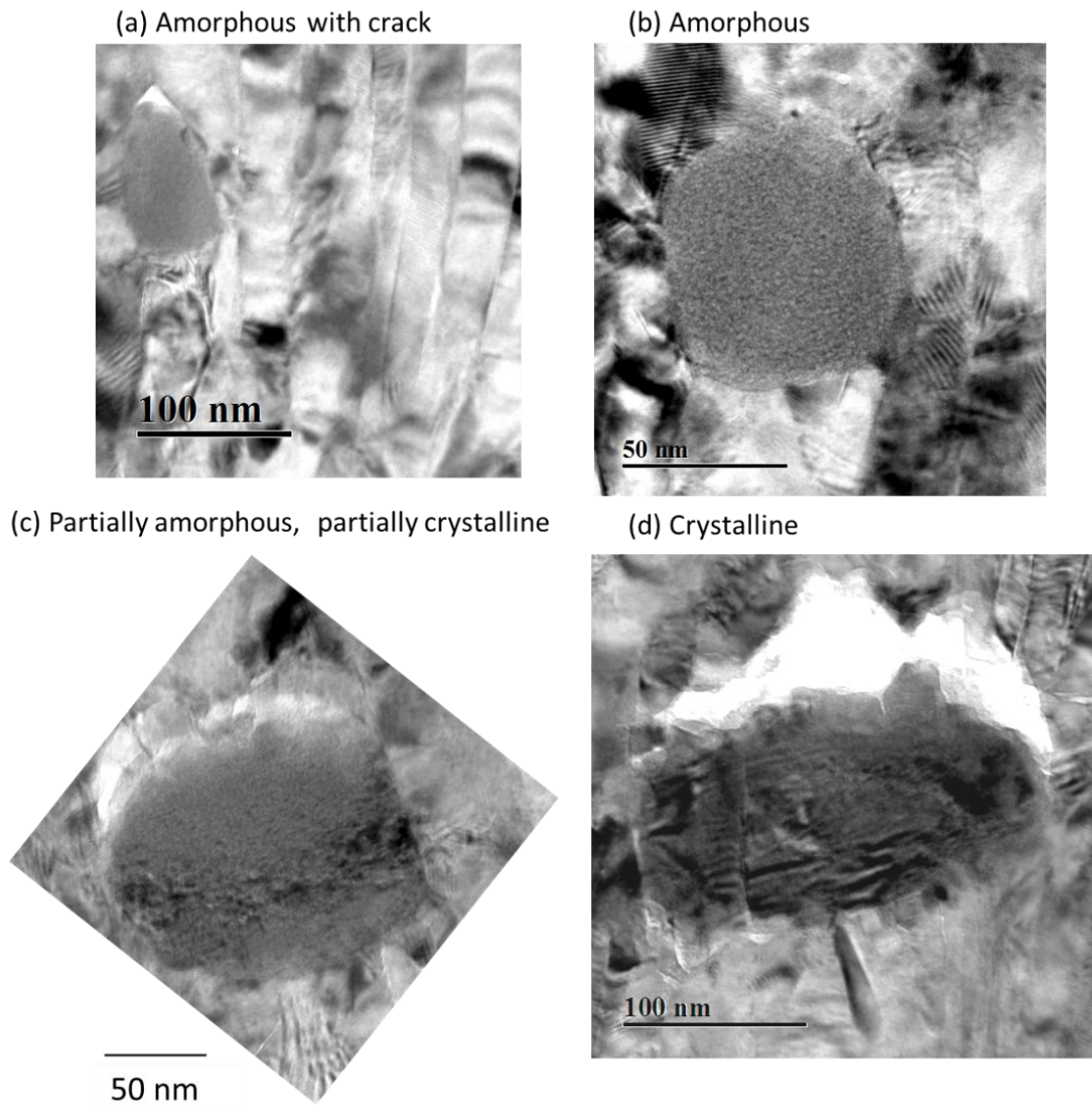


Figure 3-23: Examples of $\text{Zr}(\text{Nb,Fe})_2$ Laves phase SPPs: (a) amorphous with crescent shaped crack on top; (b) fully amorphous and incorporated into the oxide; (c) partially amorphous and partially crystalline with crescent shaped crack on top; (d) crystalline with crescent shaped crack on top.

In the pre-transition samples, as shown in Figure 3-24, the furthest I can find a crystalline Laves phase SPP above the metal-oxide interface is 545 nm as seen in Figure 3-24 (a). This SPP has a large size of 90 nm and presumably will take longer time to oxidise. β -Nb SPPs as seen in (b) have a smaller size of 40 nm. Above about 670 nm, the β -Nb SPPs are amorphous/invisible, which I will discuss later using EELS means that they are partially/fully oxidised.

It is noticed that β -Nb SPPs have different shapes when oxidising. As seen in Figure 3-24 (a), there is a small (20 nm in diameter) round β -Nb SPP 260 nm away from the metal-oxide interface. About 120 nm above the metal-oxide interface, there is another round 40 nm β -Nb SPP that is crystalline and has crescent shaped crack on top. However, when the SPPs become amorphous, again in (a) around 670 nm away from the metal-oxide interface, they become elliptical, 60 nm in length and 40 nm wide. Similar observations are seen in the 225-day sample in Figure 3-24 (b). There are several round β -Nb SPPs 40 nm in diameter distributed in the region from 80 nm to 740 nm above the metal-oxide interface. The top one at 740 nm above the metal-oxide interface is round and 40 nm in diameter, and has a crescent shaped crack on top. Another round SPP 30 nm in diameter and 240 nm above the metal-oxide interface, connects with a parallel crack around 250 nm in length and 70 nm wide. In 225-day sample in Figure 3-24 (c), the top one is connected with a parallel crack 280 nm in length near the crack and SPP is full of micro cracks, some of which cut through columnar oxide grains. Figure 3-24 (d) shows the STEM HAADF image of the 3-day sample. There are three crystalline SPPs in the oxide and one right at the metal-oxide interface. The top two SPPs are β -Nb, one is 30 nm in diameter and another 50 nm in diameter. The bottom two SPPs are Laves phase SPPs around 80 nm in diameter.

When the oxidation rate slows down for the 360-day sample, the delayed oxidation/amorphousation of SPPs is more obvious. As seen in Figure 3-25, β -Nb SPPs start to become amorphous at 1.5 μm , while the Laves phase at 0.8 μm . They are both crystalline in the region between 1.2 μm down to the metal-oxide interface, which is much further compared to what I have found in the pre-transition samples. In the higher magnification TEM BF image in Figure 3-25 (c), there are three crystalline β -Nb SPPs at distances of 1.0 μm , 670 nm and 220 nm above the metal-oxide interface. They are all around 50 nm in diameter. In (d) there is one amorphous β -Nb SPP 1.49 μm above the metal-oxide interface

and also a metallic Laves SPP that is 220 nm in width and 160 nm in length 1.16 μm above the metal-oxide interface. In (e), there is one amorphous Laves phase SPP that is around 80 nm in diameter 1.27 μm above the interface. There is a partially amorphous and partially crystalline Laves phase SPP 160nm in width and 110 nm in length 0.8 μm above the metal-oxide interface. There is also another $\beta\text{-Nb}$ SPP 0.95 μm above the metal-oxide interface.

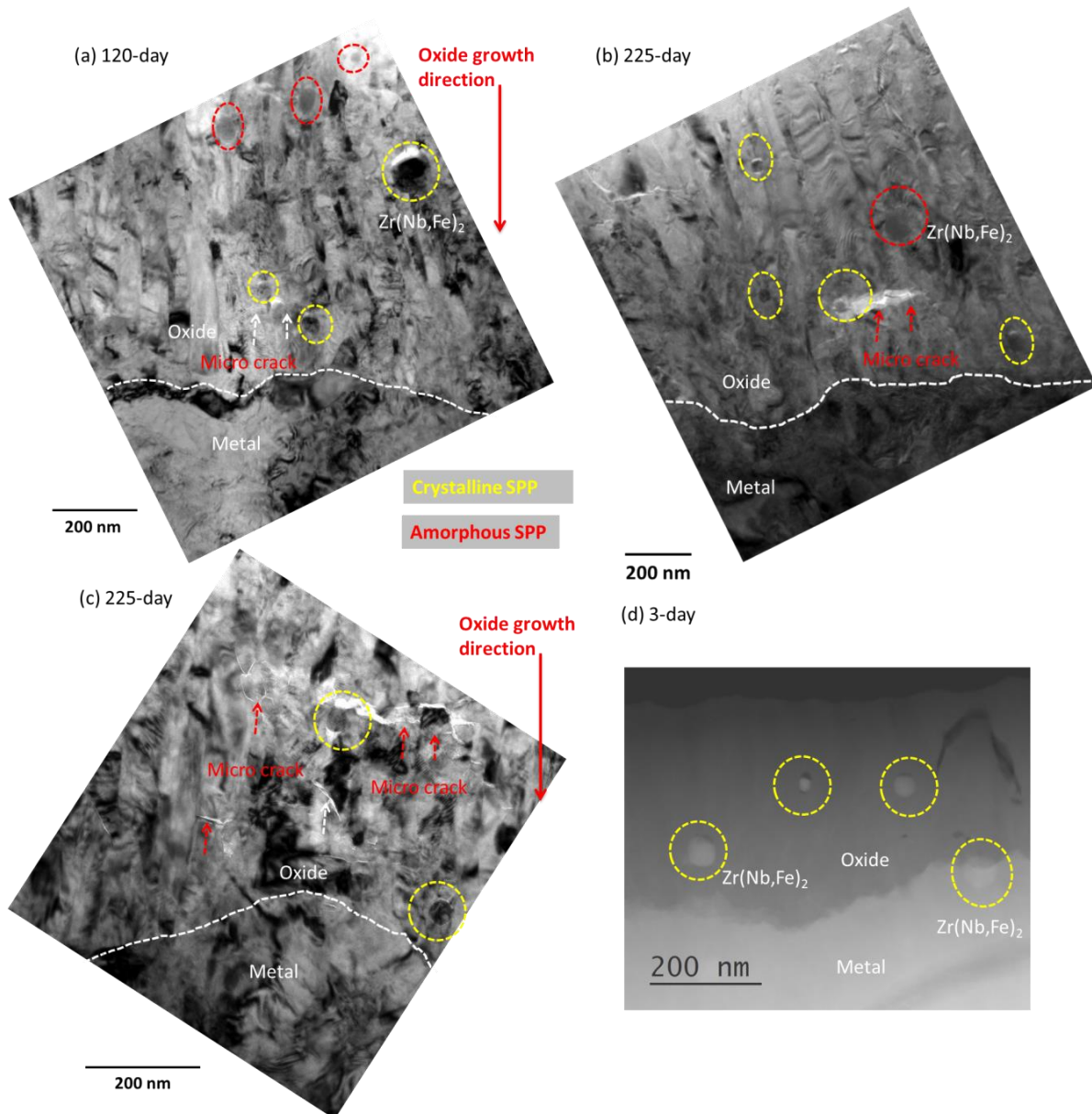


Figure 3-24: SPP distribution in relation to the metal-oxide interface: (a) 120-day sample; (b) and (c) 225-day sample; (d) 3-day sample. Unless highlighted as $\text{Zr}(\text{Nb},\text{Fe})_2$ Laves phase SPPs, all these SPPs are $\beta\text{-Nb}$. Amorphous SPPs are circled in red while crystalline SPPs are circled in yellow.

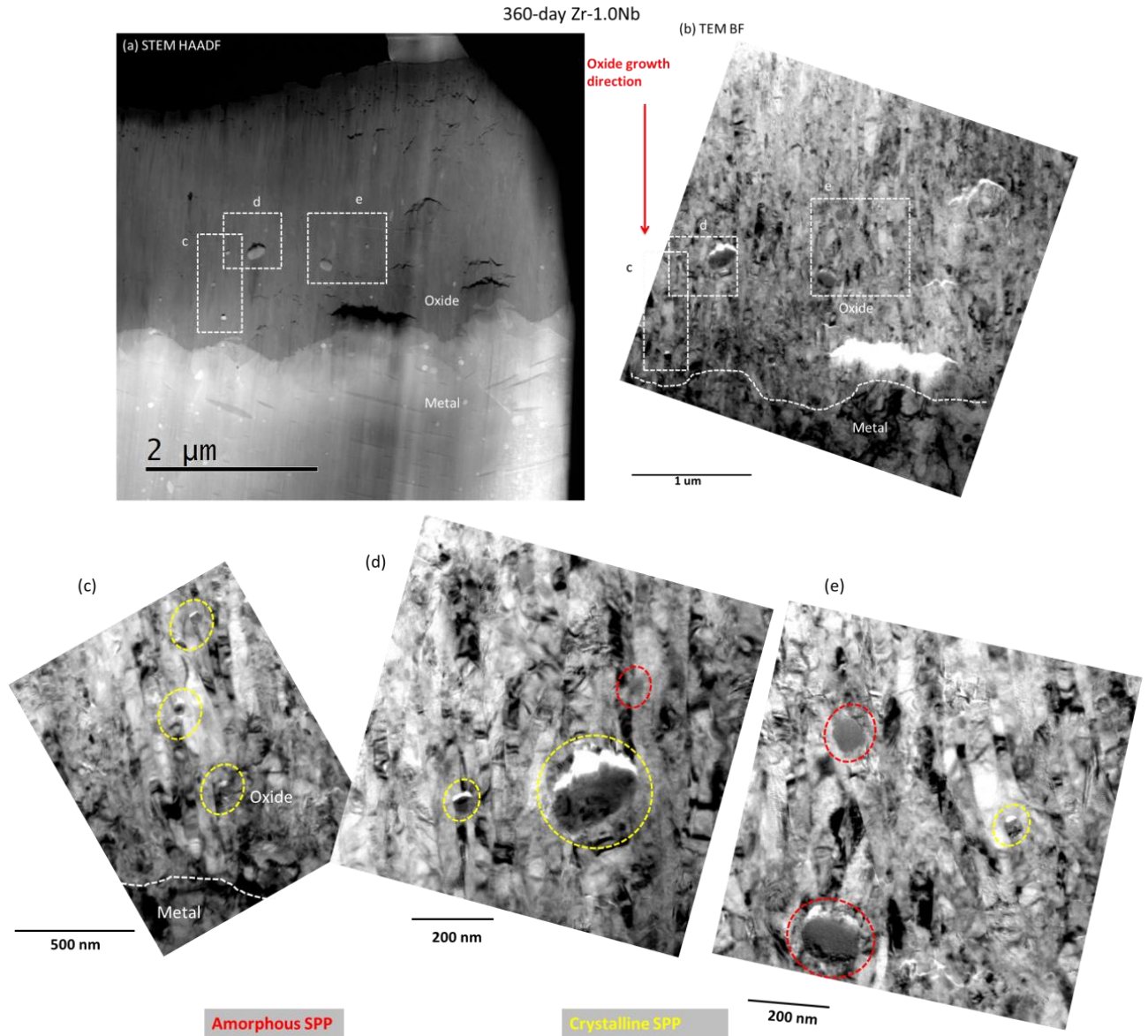


Figure 3-25: SPP distribution in 360-day sample: STEM HAADF (a) and TEM BF (b) image of the sample with positions of (c), (d) and (e) highlighted; (c) three crystalline β -Nb SPPs; (d) one amorphous β -Nb SPP, one crystalline β -Nb SPP and one crystalline Laves phase SPP; (e) one amorphous Laves phase SPP, one partially amorphous partially crystalline Laves phase SPP and one crystalline β -Nb SPP.

3.4.3. SPP type with distance to the metal-oxide interface

The same area in the 360-day sample as shown in Figure 3-25 has been analysed in EDX mapping in Figure 3-26. The Nb K map shows that the β -Nb SPPs have a relatively homogenous distribution from the surface towards the metal-oxide interface. The number density of SPPs is higher in the metal than in the oxide, due to the volume expansion of the oxide. There are several Laves phase SPPs at the top surface, but it is interesting to see that

there are almost none from the middle part of the oxide until near the metal-oxide interface. Previously in Figure 3-25 I showed that these Laves phase SPPs are either crystalline or partially crystalline or amorphous. The Laves phase SPPs at the interface have a much larger size than the ones at the top surface and still contain Cr, while the ones near the top surface (in contact with the oxide for longer) have lost all the Cr. There is thus clear evidence for changes in the SPP chemistry as they spend more time in the growing oxide. In

Table 3-1, I summarise the number of all SPPs (as represented in the Nb map) and Laves phase SPPs (as represented in the Fe map) in different regions, and also calculated the Laves phase SPPs fraction in all the SPPs. It is found that the top layer of oxide has the highest proportion of Laves phase SPPs 50%, while the number gradually drops to 14% in the columnar oxide region, where there are almost no Laves phase SPPs. Closer to the metal-oxide interface, the ratio of Laves phase SPPs seems to be similar to that found in the metal, around 20%. Because the Laves phase SPPs are not in a large number in these samples, so it is hard to draw a conclusion on why the distribution of these SPPs is different depending on their location.

A similar trend is seen in the 585-day sample. Figure 3-27 shows (a) the area mapped, and the individual high resolution EDX maps for Nb (b) and Fe (c). The Nb maps show all the SPPs, i.e. the combination of β -Nb and Laves phase particles. In the equiaxed layer at the top surface of the oxide, there are 12 SPPs in total, 6 of them being Laves phase. In the region

underneath the equiaxed layer and above the second transition cracks there are many β -Nb particles, but Laves phase SPPs are hardly seen. In the region around 1 μm above the metal-oxide interface, as previously described, there are many crystalline SPPs. Of the 26 SPPs in this area, 5 of them are Laves phase, and these are all of larger size in agreement with my previous observations. In the metal, there are 27 SPPs, 4 of them Laves phase. Table 3-2 summaries the number of all SPPs (as represented in the Nb map) and Laves phase SPPs (as represented in the Fe map) in different regions, also calculates the Laves phase fraction. Top layer of oxide has largest fraction Laves phase SPPs, 56%, while the number gradually drops to 15% near the first transition cracks. In the columnar oxide and two layers of transition cracks, and almost no Laves phase SPPs, as it gets closer to the metal-oxide interface, the ratio of Laves phase SPPs seems to be similar to the metal, around 15% to 19%. It also worth pointing out that the number density of SPPs is higher in the metal-oxide interface region and in the metal than in the oxide, due to the volume expansion when forming the oxide so that the area fraction of the SPPs is diluted.

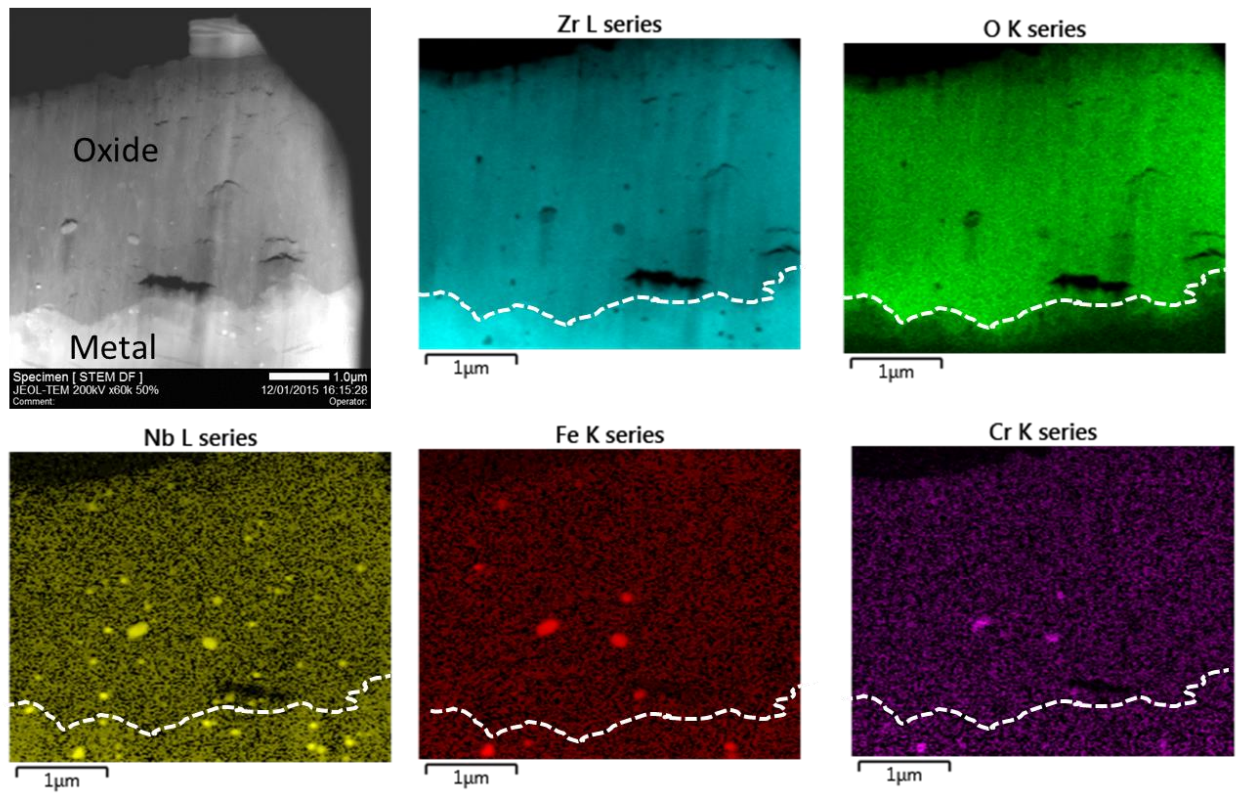


Figure 3-26: EDX map of SPP distributions in the 360-day sample: STEM HAADF (a) and elemental maps for Zr, O, Nb, Fe and Cr.

Table 3-1: numbers of all SPPs in the Nb map, Laves phase SPP number in the Fe map, the number density, and Laves phase SPP/all SPP ratio.

EDX map position	Nb map (n)	Fe Map (n)	All SPP number density (n/um ²)	Zr(Nb,Fe) ₂ number density (n/um ²)	Zr(Nb,Fe) ₂ /all SPP
Equiaxed	4	2	1.62	0.83	50%
Columnar grain	7	1	2.54	0.36	14%
Above the metal-oxide interface	20	4	4.20	0.84	20%
Metal	16	3	6.72	1.26	19%

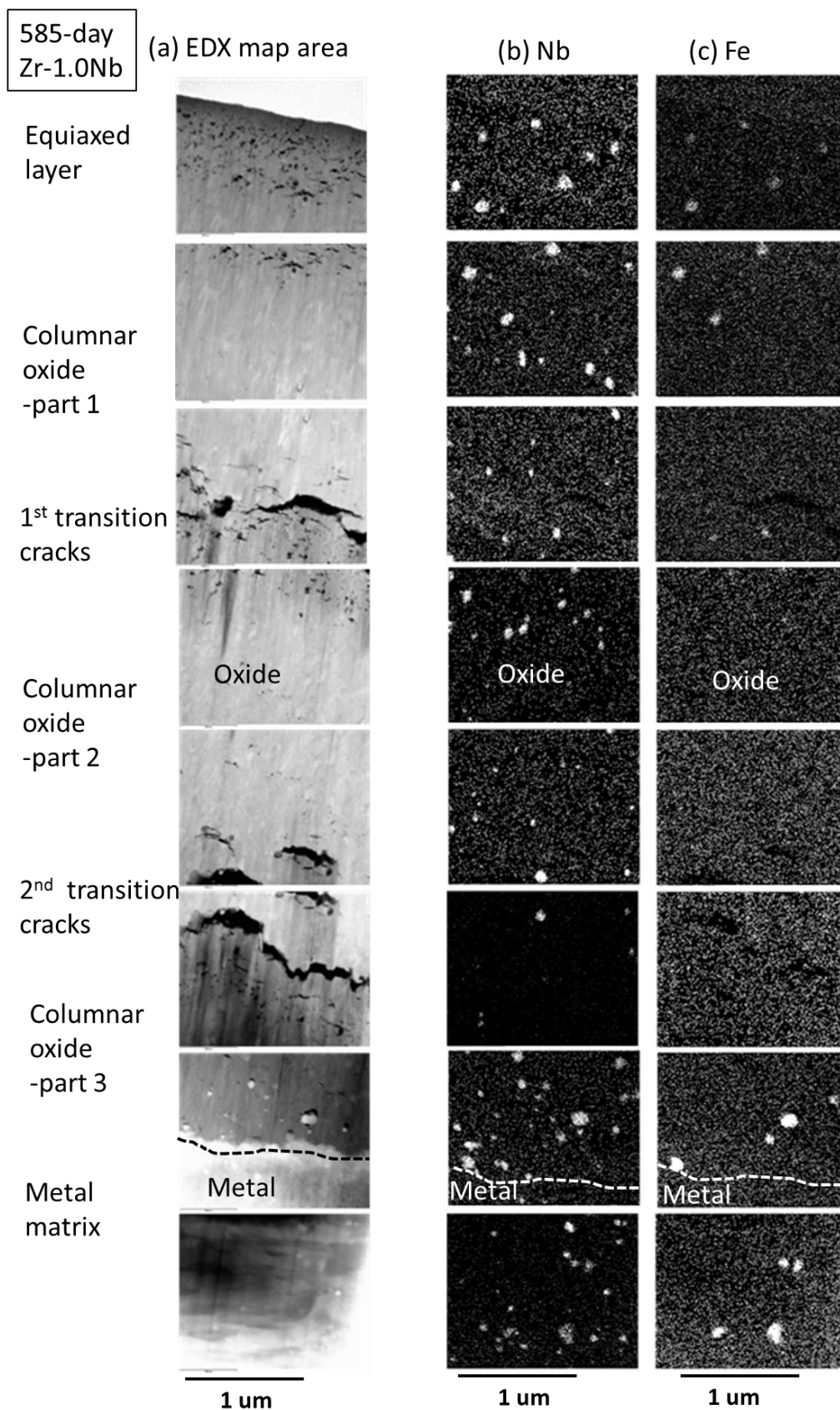
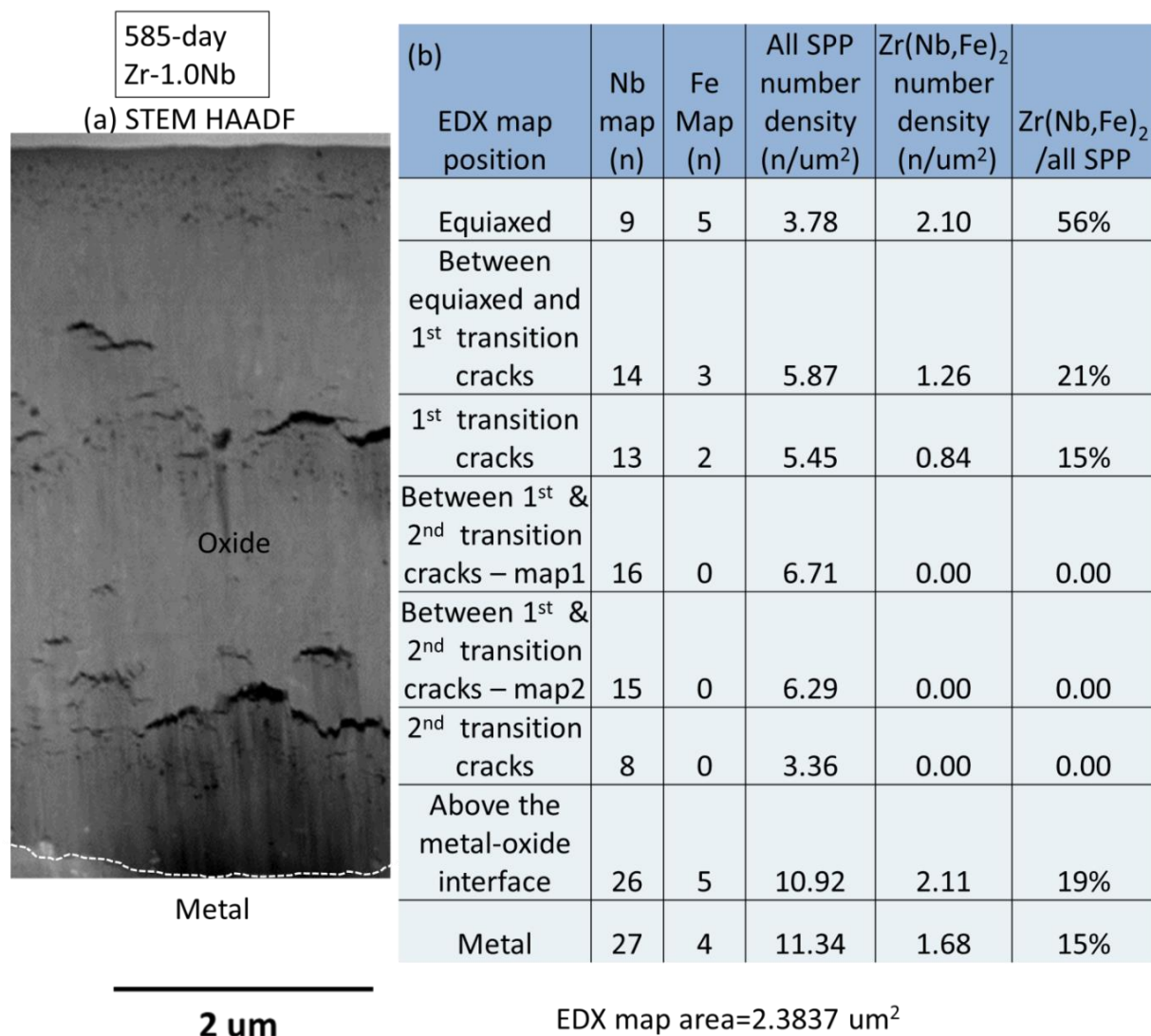


Figure 3-27: EDX maps of the SPP distribution in the 585-day sample: (a) STEM HAADF images of individual maps and elemental maps for Nb (b) and Fe (c).

Table 3-2: Number of SPPs in 585-day sample: (a) STEM HAADF image of the whole oxide, (b) table showing the number of all SPP in the Nb map, Laves phase SPPs in the Fe map, the number density of SPPs, and the Laves phase/all SPP ratio.



3.4.4. EELS analysis of the oxidation state in SPPs

EELS analysis was carried out on SPPs at different locations in the oxide from samples at different stages of oxidation. By using state-of-the-art microscopy, it is possible to combine low loss spectrum imaging, core loss spectrum imaging and line profiles to study the oxidation state in different types of SPPs.

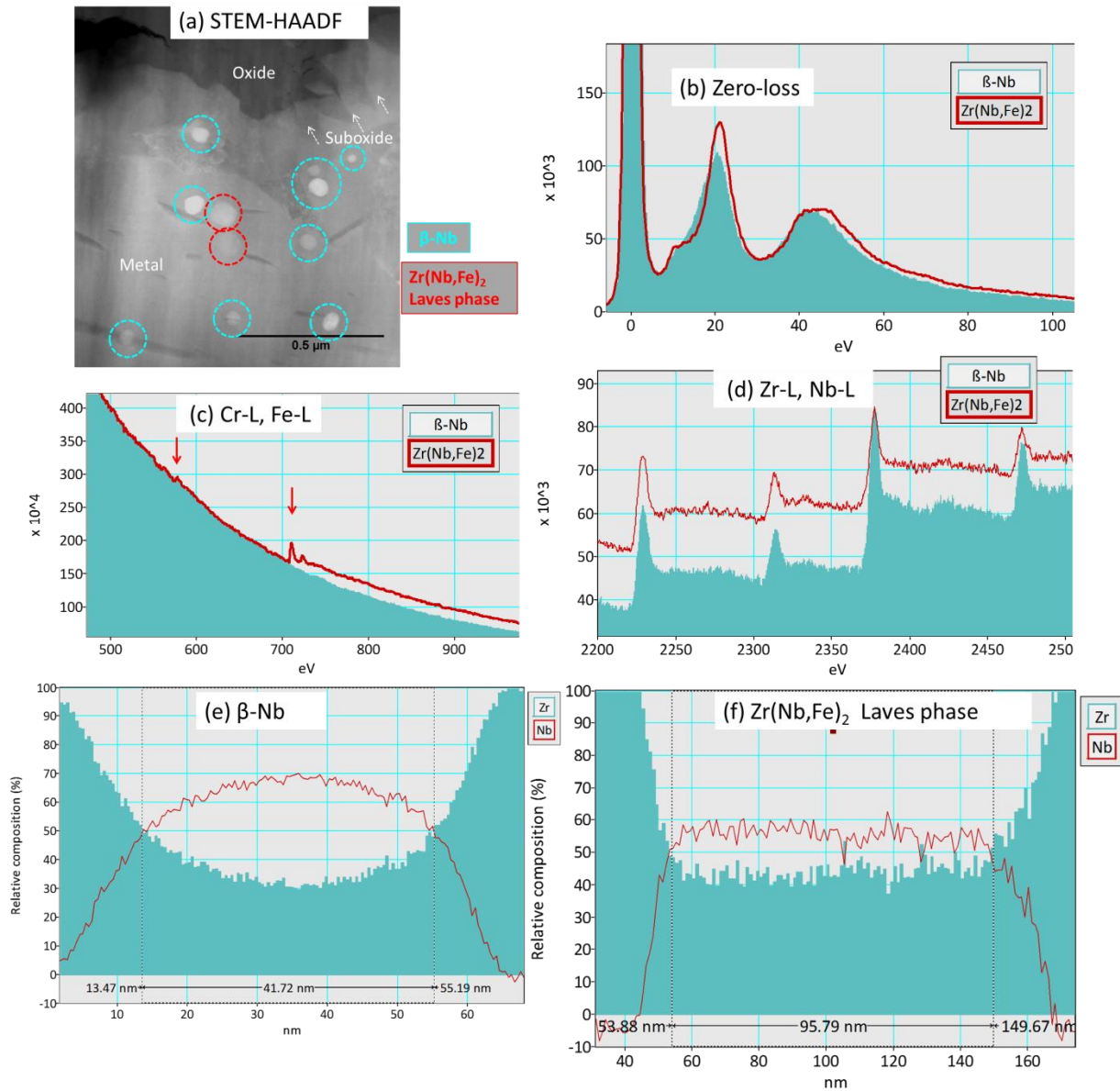


Figure 3-28: Example of EELS analysis of SPPs in the metal in 360-day Zr-1.0Nb sample: (step size 1 nm, channel per pixel: 0.25 eV) (a) STEM HAADF image shows the location of the β-Nb and Laves phase SPPs, (b) comparison of EELS spectrum of β-Nb SPP and Laves phase SPP over the range containing Cr-L and Fe-L signals, (d) comparison of EELS spectrum of β-Nb SPP and Laves phase over the range containing Zr-L and Nb-L signals, (e) concentration of Zr and Nb across a β-Nb SPP, (f) (f) concentration of Zr and Nb across a Laves phase SPP.

3.4.4.1. SPPs in the metal

The STEM HAADF image in Figure 3-28 (a) shows the distribution of SPPs in the metal of 360-day sample. The two Laves phase SPPs are quite large, 84 nm and 96 nm, while the β-Nb SPPs have sizes ranging from 27 nm to 65 nm, with an average diameter of 49 nm. We can often see saw-tooth shaped suboxide grains due to Z-contrast in the HAADF image.

Four β -Nb SPPs and two Laves phase SPPs in the metal have been analysed and their EELS spectra compared over different energy ranges. Figure 3-28 (b) shows the plasmon peaks from the β -Nb and Laves phase SPPs. (c) shows the comparison of EELS spectra over the range containing the Fe and Cr signals. It is clear that there is no Fe in the β -Nb SPPs, while the first Fe L peak in the Laves phase SPPs lies at 709.25 eV and the second peak at 722 eV. The Cr L peak is at 576.25 eV but it is not very strong. (d) shows a higher energy range for these two different types of SPPs and the Zr L and Nb L peaks lie at a similar position; the Zr L3 peak is at 2228.2 eV and Nb L3 peak is at 2376.9 eV. The concentration profile in (e) shows the β -Nb SPP contains 30% Zr and 70% Nb, a slightly lower Nb concentration than the 80 % Nb percentage in β -Nb by the phase diagram, possibly due to the small size of 41 nm which means the area contains a concentration from the Zr matrix. The concentration profile in (f) shows the Zr and Nb ratio in Laves phase SPP is 2:3 and that the size of the SPP is 96 nm.

3.4.4.1. SPPs in oxide in pre-transition samples

Figure 3-29 shows an example of three SPPs near the metal-oxide interface in the 120-day sample. They all show different oxidation states. The TEM BF image in Figure 3-29 (a) shows a parallel crack about 300 nm above the metal-oxide interface, and there are three SPPs near the crack, lining up along the oxidation growth direction. The top one (SPP1) is 700 nm above the metal-oxide interface and is an amorphous SPP 90 nm in length and 140 nm in width. Judging from the size, it is possible there are two smaller SPPs with 90 nm in diameter overlapping horizontally in the image to make the 140 nm width. The higher magnification image in (c) shows that it has also crescent shaped crack on the top. The second SPP (SPP2) is 470 nm above the metal-oxide interface, and is also 90 nm in diameter. The TEM BF image in (d) shows that interestingly the top 45 nm of this SPP is amorphous while the bottom 45 nm part still remains crystalline. It also has a crescent shaped crack on the top. There is a

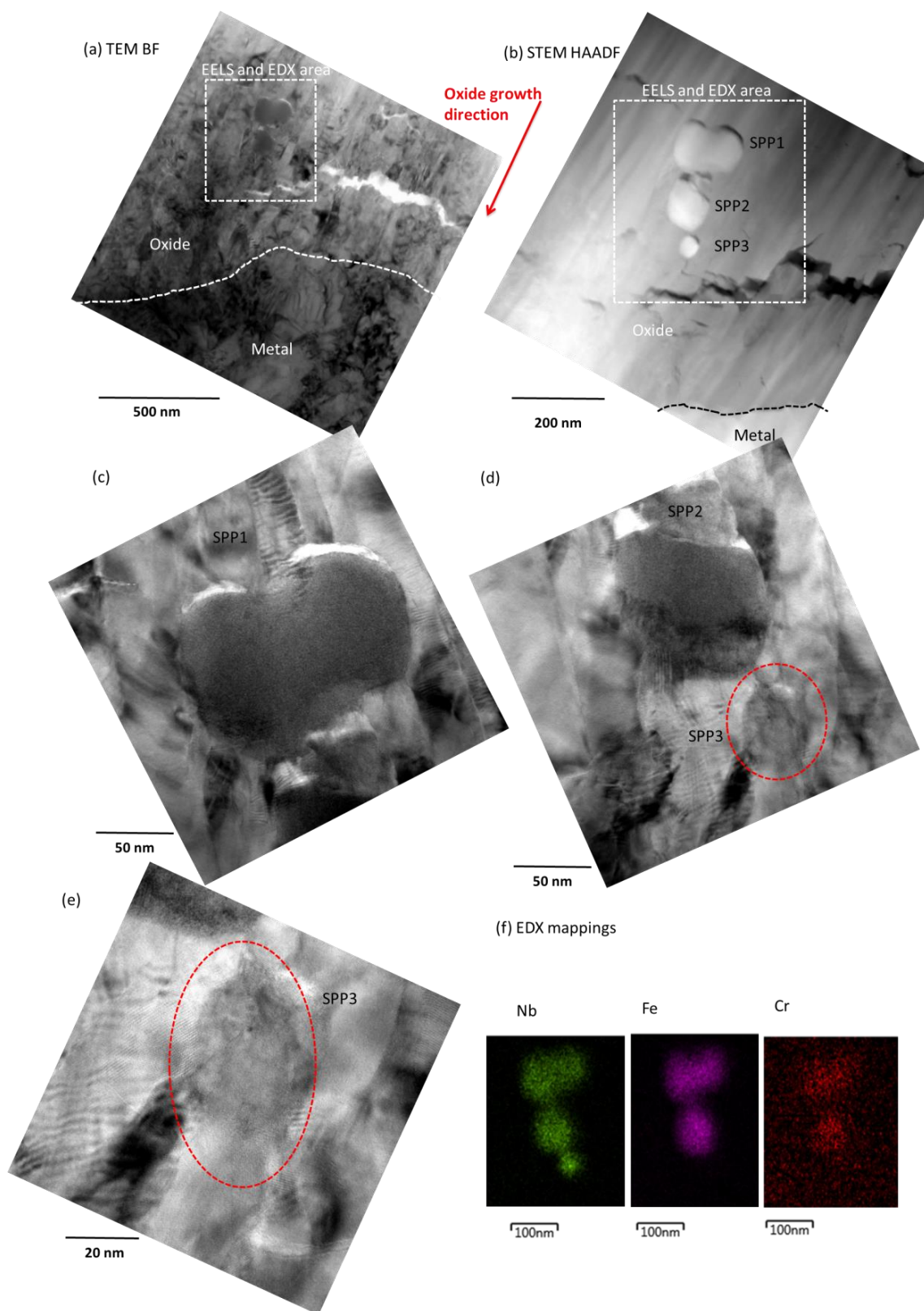


Figure 3-29: Three SPPs in the oxide on the 120-day sample: low magnification (a) TEM BF image and (b) STEM HAADF image of three SPPs, higher magnification images of (c) amorphous SPP 1; (d) half-amorphous and half-metallic SPP2; (e) metallic SPP3; (f) EDX maps for Nb, Fe and Cr in the three SPPs.

smaller SPP (SPP3) underneath these two. The TEM BF image in (e) does not show strong diffraction contrast, but STEM HAADF image in (b) shows clearly the metallic state of the SPP by brighter contrast (higher atomic mass). It is round 45 nm in diameter, and 330 nm above the metal-oxide interface. EDX maps in (f) shows that the top two SPPs are Laves phase SPPs containing Cr, while the bottom small one is a β -Nb SPP.

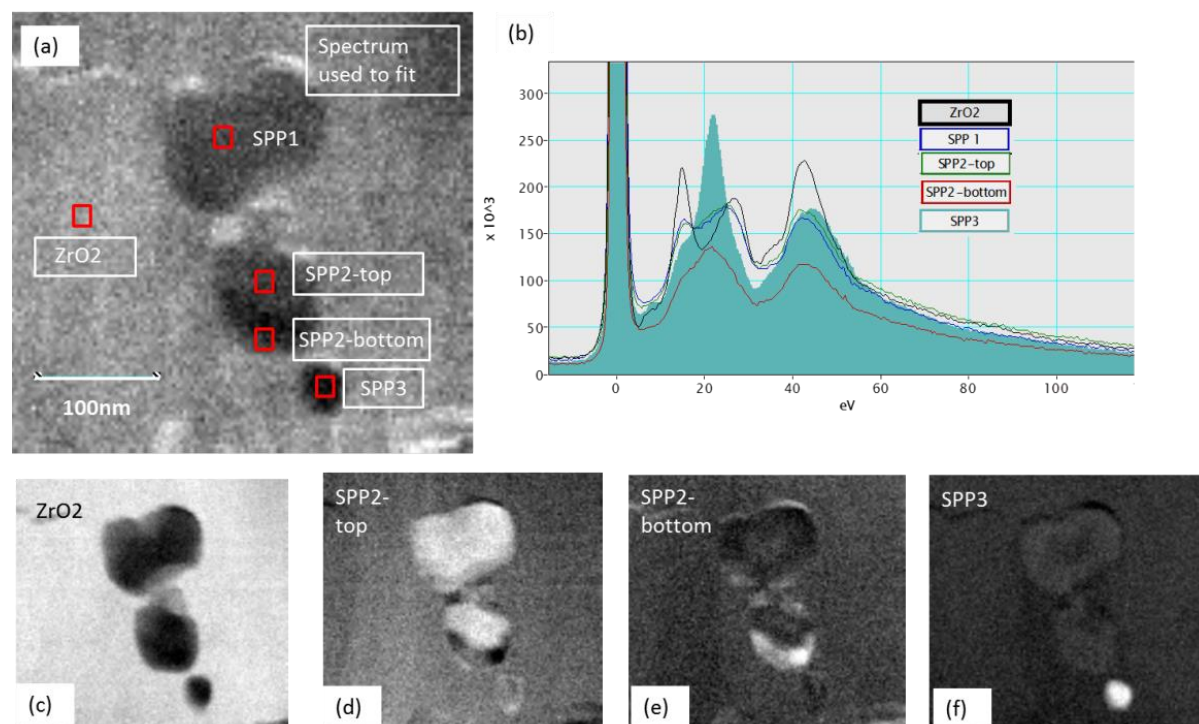


Figure 3-30: Multiple linear least squares (MLLS) fitting of low loss spectrum: (a) EELS low loss spectrum imaging map, showing the position from which each spectrum was taken. (b) low loss spectra comparison of ZrO₂ oxide, SPP1, SPP2-top, SPP2-bottom and SPP3. (c)-(f) MLLS fitting of ZrO₂, SPP2-top, SPP2-bottom and SPP3 respectively.

Both low loss and core loss EELS spectrum imaging was carried out on these three SPPs. I observed the low loss signals of the three SPPs also have their own signature peak shapes and position as shown in Figure 3-30 (b), while the position from which the spectrum was taken is marked in (a). The spectra from SPP1 and the top part of SPP2, which are both amorphous Laves phase SPPs, are very similar. However, the bottom part of SPP2, which is crystalline, has a different spectrum from SPP3 which is crystalline β -Nb. This may be due to the different compositions between SPP2 and SPP3. I chose the spectra from SPP2-top, SPP2-

bottom, SPP3 and ZrO_2 for the multiple linear least squares (MLLS) fitting of the low loss spectra, and the results of this fitting are shown in Figure 3-30 (c)-(f). The residual of this fitting mostly contains noise which suggests a good fitting. The fitting results show a clear difference between these different spectra, especially the top part and bottom part of SPP2, and it seems that the SPP2 has a more crystalline core at the bottom part.

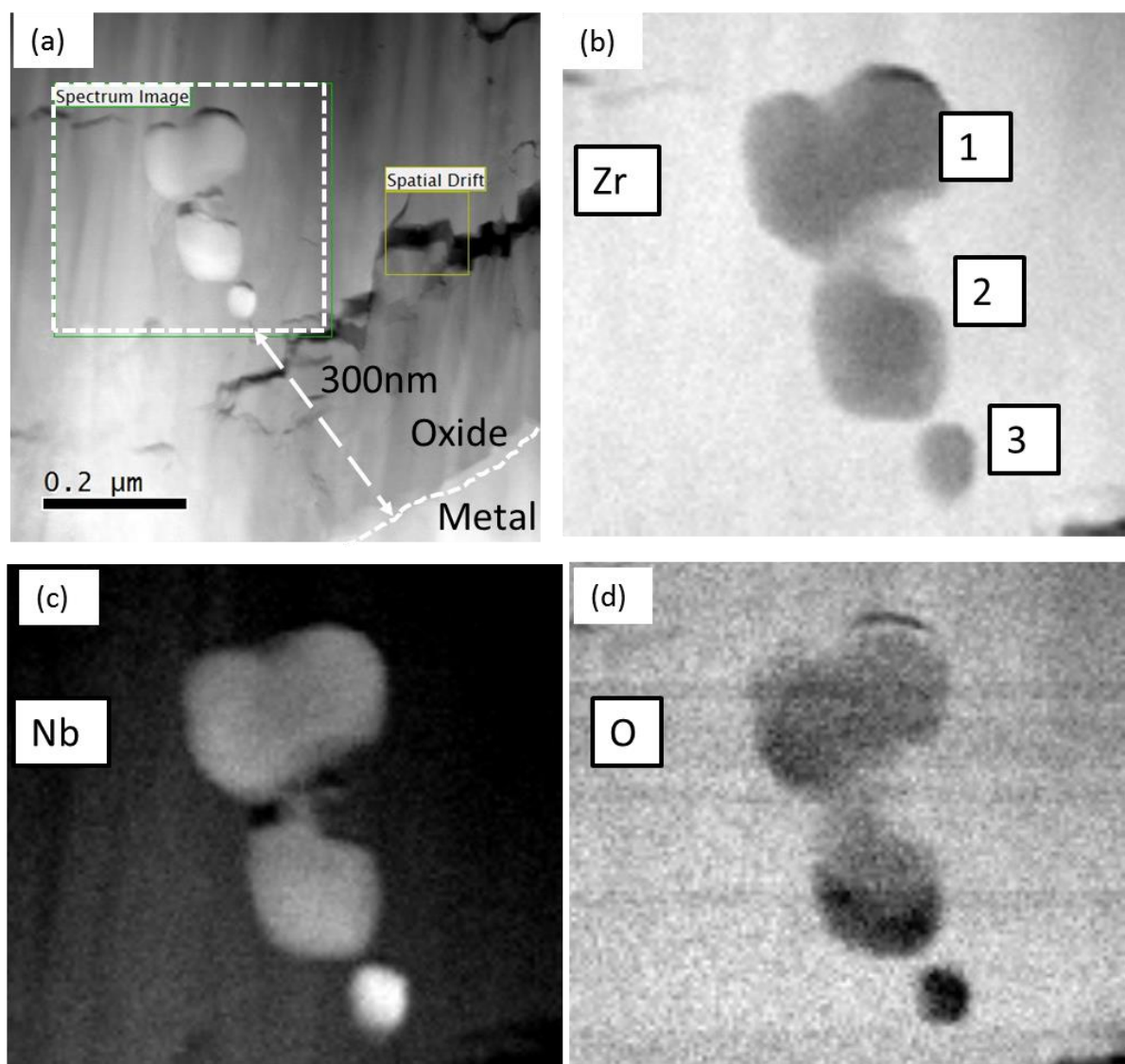


Figure 3-31: (a) STEM HAADF image of an area containing three SPPs in 120-day sample; (b)-(d) Core loss EELS maps of Zr, Nb and oxygen respectively. These three SPPs are labelled as SPP1, SPP2, SPP3 in (b). SPP1 is fully oxidised, SPP2 is partially oxidised and SPP3 is metallic.

Figure 3-31 (a)-(d) shows the EELS core loss results from the same SPPs. Figure 3 31 (b)-(d) show different oxidation stages for each of these three SPPs; SPP1 is fully oxidised, SPP2 is

partially oxidised with the bottom part remaining metallic, while SPP3 has the lowest oxygen content (metallic). This illustrates the gradual oxidation process of the SPPs as they move away from the metal-oxide interface during oxide thickening.

3.4.4.2. SPPs in oxide in at-transition samples

STEM HAADF images provide a good way to use z-contrast to distinguish oxidised and metallic SPPs, and EELS low loss spectrum imaging is an easy way to give an overview of SPP distribution. In the 360-day sample, 37 SPPs have been analysed in detail by EELS and here I discuss the characteristics of these SPPs in terms of their relative distance from the oxide-metal interface.

- *SPPs near the metal-oxide interface*

Several SPPs near the metal-oxide interface were chosen for analysis by EELS. They all remained in the crystalline state and their positions ranged from right above to 1 μm above the metal-oxide interface. Figure 3-32(a) and (b) show three examples of these metallic $\beta\text{-Nb}$ SPPs, at 1 μm , 670 nm and 220 nm above the metal-oxide interface. They are all around 50 nm in diameter and have a crescent shaped crack on top. By comparing the core loss spectrum from line profiles across these SPP with the reference spectrum from a $\beta\text{-Nb}$ SPP in the metal as shown in Figure 3-28 (d), it is possible to analyse the Nb and Zr oxidation states. Both SPP5 and SPP6 have similar peak shift as shown in (c). The Zr-L peaks in the SPP and oxide lie at 2229.9eV while in the unoxidised metal it is at 2227.9 eV. This suggests that Zr starts to oxidise in the crystalline SPPs near the metal-oxide interface. It is interesting to see that Nb L3 and L2 peaks also show a slight shift. In the higher magnification spectra comparison on the right, it is found that the SPP has the Nb-L peak at 2377.4 eV which is slightly different from the metallic Nb peak at 2376.4 eV, suggesting the Nb in the $\beta\text{-Nb}$ near the metal-oxide interface may be partially oxidised. In SPP4 as shown in (d), which is at the position further from the metal-oxide interface where I detected a crystalline $\beta\text{-Nb}$ SPP, the

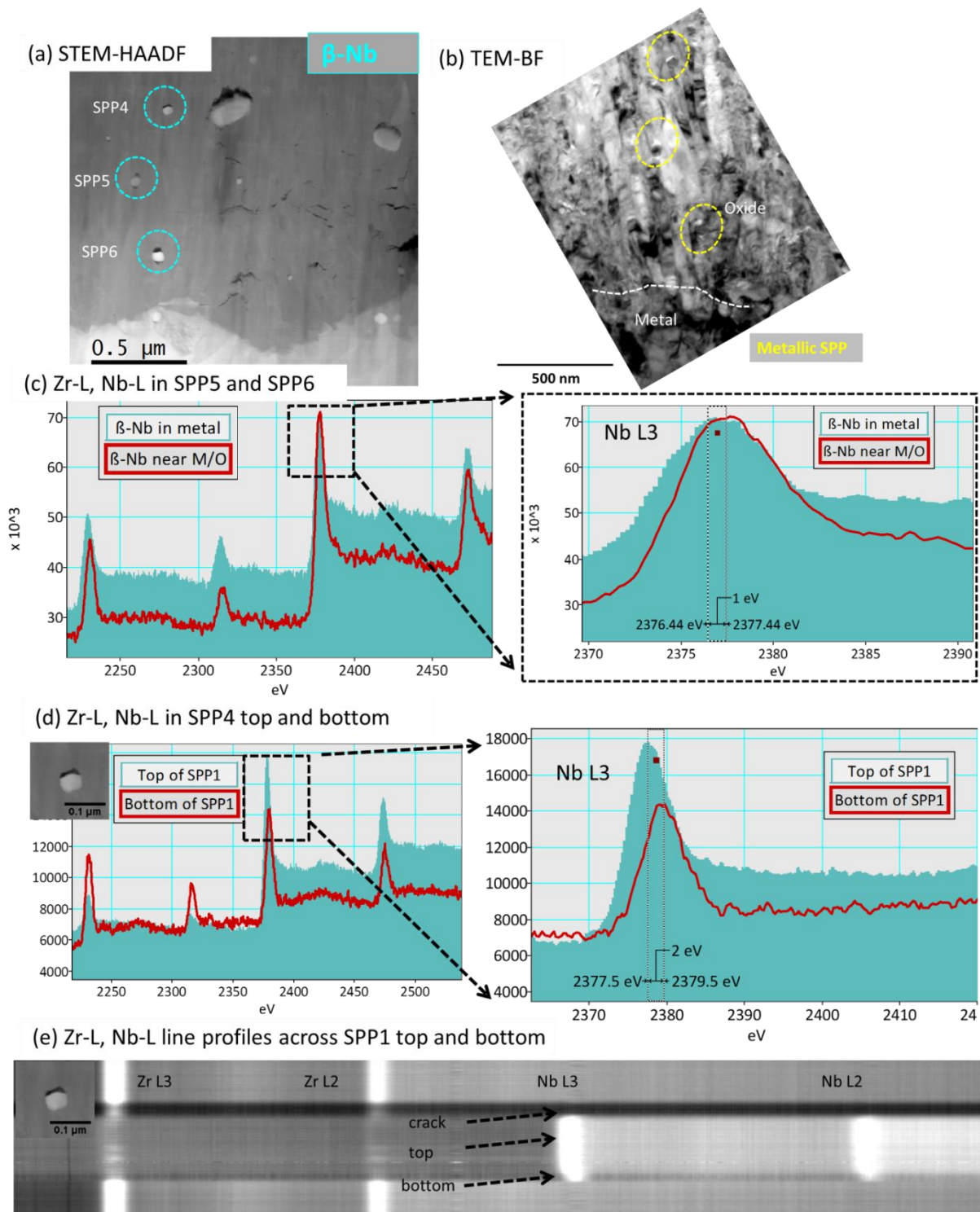


Figure 3-32: Example of EELS analysis of three β -Nb SPPs near the metal-oxide interface in the 360-day Zr-1.0Nb sample: (a) STEM HAADF image and (b) TEM BF image showing the location of the β -Nb SPPs, (c) comparison of EELS spectrum of β -Nb SPP5, SPP6 and β -Nb in the metal over the range containing the Zr-L and Nb-L signal, (d) comparison of EELS spectrum of β -Nb SPP4 top part and bottom part over the range containing Zr-L and Nb-L signal, (e) EELS line profiles of β -Nb SPP4 over the range of the Zr-L and Nb-L signal, shift in the bottom of SPP1 pointed with arrows.

Nb L3 peak in the top part of the SPP lies at 2377.5 eV which is close to that in SPP5 and SPP6. But in the bottom part of SPP4, the Nb L3 peak shifts to 2379.5 eV which indicates that it has been oxidised to a higher state, possibly Nb⁴⁺. This is a significant peak shift and similar observations are also seen in two other crystalline β -Nb SPPs and one amorphous β -Nb SPP as I will discuss later. This suggests that as a β -Nb SPP oxidises, the crack on the top of the SPP makes oxygen introduction to the SPP difficult, so the SPP starts to oxidise from the bottom (or from the outside surface of SPP).

Figure 3-33 shows an example of Laves phase SPP (SPP7) about 0.76 μm above the metal-oxide interface. This SPP is round and about 80 nm in diameter. The top of the SPP is connected with a parallel crack, so some part of the SPP has been preferentially milled during FIB process as seen from the STEM HAADF image (a). Diffraction contrast in the TEM BF image in (b) shows that the SPP is still crystalline. By comparing the core loss spectrum from line profiles across this SPP with the reference spectrum from a Laves phase SPP in the metal, as shown in Figure 3-28 (c) and (d), the results are shown in Figure 3-33 (c) and (d). The oxygen peak in the range shows that there is oxygen in the SPP, although it can be from the oxide surrounding the SPP or surface oxide created after final thinning. The core loss spectrum of the SPP in (c) shows the Fe-L3 and Fe-L2 peaks. Comparing with Fe in the Laves phase SPP in the metal, the Fe L3 peak in this SPP is shifted for about 1.25 eV, from 709.56 eV to 710.81 eV.

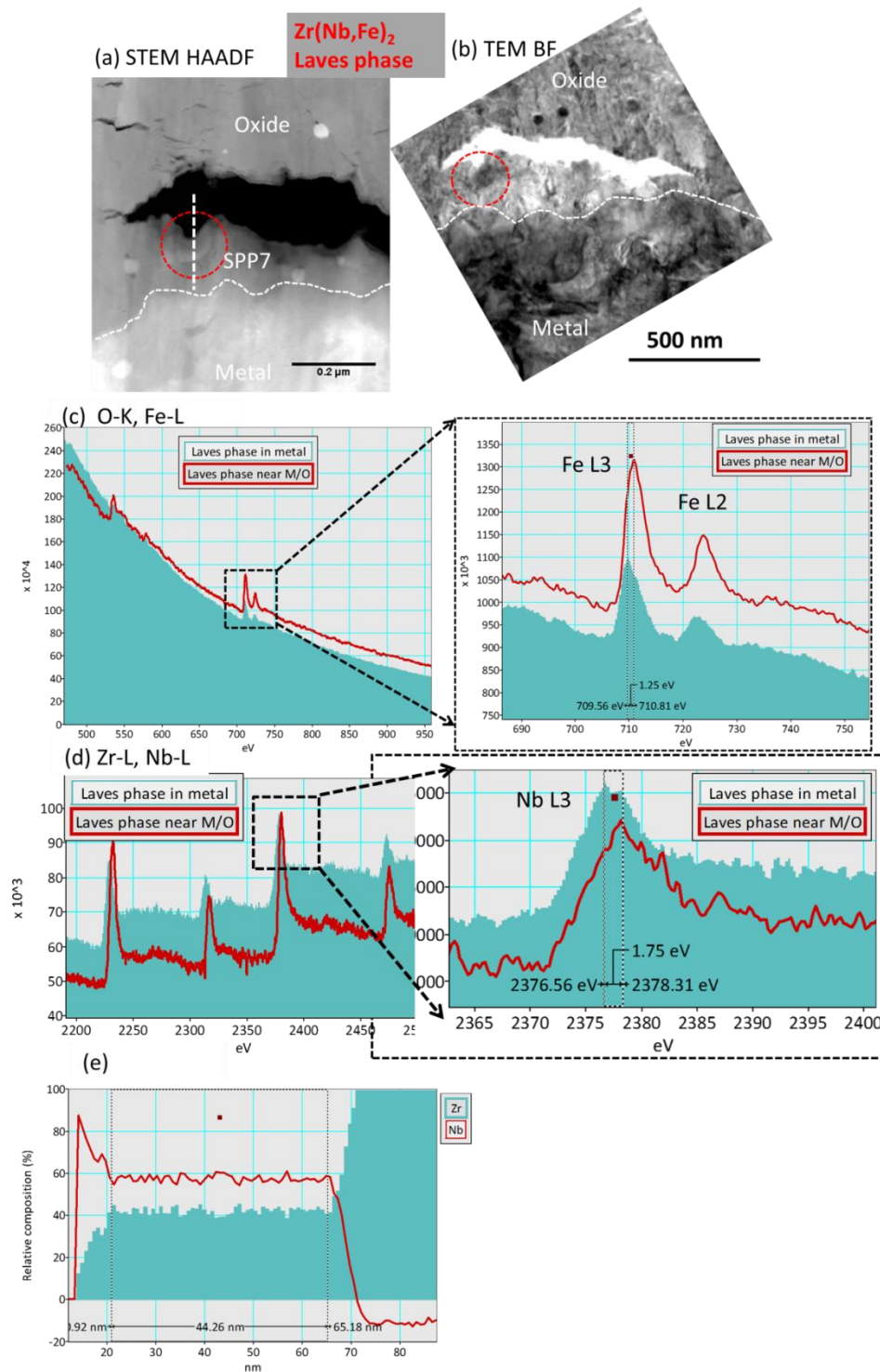


Figure 3-33: Example of EELS analysis of Laves phase SPP near the metal-oxide interface (SPP7) in the 360-day Zr-1.0Nb sample: (a) STEM HAADF image and (b) TEM BF image showing the location of the Laves phase SPP, (c) comparison of EELS spectra of Laves phase SPP near the metal-oxide interface and in the metal over the range containing oxygen-K and Fe-L signal, (d) comparison of EELS spectra of Laves phase SPP near the metal-oxide interface and in the metal over the range containing the Zr-L and Nb-L signals, (e) concentration profile of Nb and Zr in Laves phase SPP.

This suggests that although the SPP is in crystalline state, Fe in this SPP may have begun to oxidise. The core loss spectrum of the SPP in (d) shows the Zr-L and Nb-L peaks. The Zr-L peak shift is clear and the expanded Nb-L3 spectrum suggests that the Nb peak has shifted from 2376.56 eV to 2378.31 eV, which corresponds well with our earlier calibration of the Nb²⁺ peak at 2378 eV. The Zr-L peak is at 2232.6 eV. The concentration profile in (e) shows a Zr/Nb concentration ratio of 2:3, which is similar to the earlier measurement of crystalline Laves phase SPP in the metal from Figure 3-28.

- *SPPs in the middle of the oxide*

In the middle of the oxide, more SPPs are starting to oxidise, and some of them have become amorphous, while other still remains crystalline/partially crystalline while they oxidise.

Figure 3-34 shows an example of a β -Nb SPP (SPP8) in the middle of the oxide, 1.47 μm away from the metal-oxide interface. The STEM HAADF image in Figure 3-34 (a) shows the SPP has a slightly lighter contrast than the oxide, but appears darker comparing with the crystalline SPPs near the metal-oxide interface, which suggests that it may be partially oxidised. The TEM BF image in (b) shows it is in amorphous state and around 50 nm in diameter. By comparing the core loss spectrum from line profiles across this SPP with the reference spectrum from a β -Nb SPP in the metal in Figure 3-28 (d), it is possible to measure the Nb and Zr oxidation states. Figure 3-34 (c) shows the line profile overview of Zr-L and Nb-L peaks. The peak shift in the Nb-L lines across the top, middle and bottom part of the SPP are easy to see. (d) shows the detailed comparison; the Zr-L peaks of different parts of the SPP lie at 2230.7 eV while in the metal it is at 2228.4 eV. It is interesting to see that Nb L3 and L2 peaks show bigger shift in different parts of the SPP. In the expanded spectra comparison on the right, it is found that the top and middle part of the SPP have the Nb-L3 peak at 2378.7 eV, which is different from the metallic Nb peak at 2376.7 eV, but the bottom part of the SPP has the Nb-L3 peak at 2380.2 eV, which indicates that it has been oxidised to

a higher state, possibly Nb^{4+} or Nb^{5+} . This suggests that the Nb in this β -Nb SPP in the middle part of the oxide is oxidised to a higher state at the bottom part of the SPP. The oxygen signal area density in (f) confirms that the bottom part of the SPP shows higher oxygen signal. Concentration profile of Nb and Zr in (e) shows a 40% Zr and 60%Nb in most part of the SPP, while the edges show a higher Zr concentration.

The STEM HAADF and TEM BF images in Figure 3-35 show three Laves phase SPPs in the middle of the oxide. SPP9 is a crystalline SPP 220 nm in width and 160 nm in length. It is 1.16 μm above the metal-oxide interface. There is one amorphous Laves phase, SPP10, around 80 nm in diameter, 1.27 μm above the metal-oxide interface. There is a partially amorphous and partially crystalline SPP11, 160 nm in width and 110 nm in length, 0.8 μm above the metal-oxide interface.

Three SPPs are analysed in detail by EELS. Here I use the amorphous SPP10 as an example to show the peak shift. By comparing the core loss spectrum from line profiles across the SPP with the reference spectrum from a Laves phase SPP in the metal in Figure 3-28 (c) and (d), the results are shown in Figure 3-35 (c) and (d). The oxygen peak in the 532 eV range again suggests that there is oxygen in the SPP. The core loss spectrum of the SPP in (c) shows the Fe-L3 and Fe-L2 peaks. Comparing with Fe in Laves phase SPP in the metal, the Fe L3 peak in this SPP has shifted about 1.25 eV, from 709.4 eV to 710.5 eV, similar to the shift in the crystalline Laves phase SPP near the metal-oxide interface as shown in Figure 3-33. This suggests that when the SPP is amorphous, the Fe is not necessarily oxidised to a higher state than the crystalline Laves phase SPPs in the oxide.

The core loss spectrum of the SPP in Figure 3-35 (d) shows the Zr-L and Nb-L peaks. The Zr-L peak shift is clear and the expanded Nb-L3 spectrum suggests that Nb peak has shifted from 2376.9 eV to 2380.1 eV, which corresponds well with our earlier calibration of Nb^{4+} peak at

2380 eV. The Zr-L peak is at 2231.4 eV. The concentration profile in (e) shows a concentration of 50% Zr and 50% Nb, a higher concentration of Zr compared to the earlier calculation of crystalline Laves phase SPP in the metal in Figure 3-28, and it is interesting to see the bottom 30 nm of the SPP has 60% Zr and 40% Nb which suggest that Nb seems to leak out of the SPP as the SPP is oxidising.

- *SPPs at the top surface of the oxide*

Several SPPs at the top surface of the oxide were chosen for analysis by EELS. Both STEM HAADF and TEM BF have proven difficult to be used to find these SPPs; the only way to find them reliably is by EELS low loss spectrum imaging.

Figure 3-36 (a) shows the location of four β -Nb SPPs at the top surface of the oxide. Line profiles were drawn across the SPP, and the EELS signal from 500 eV- 950 eV identifies the O-K signal from both the SPP and oxide, indicating that these SPP have fully oxidised. By comparing the core loss spectrum from line profiles across the SPP with the reference spectrum from a β -Nb SPP in the metal in Figure 3-28 (d), it is possible to analyse the Nb and Zr oxidation states. Again, the Zr-L peak from the SPP and oxide lies at 2230.1eV while in the metal at 2227.9 eV. It is interesting to see that Nb L3 and L2 peaks also show a slight shift. In the expanded spectra comparison on the right, it is found that the SPP has the Nb-L peak at 2380.2 eV which is significantly different from the metallic Nb peak at 2376.4 eV. In the other oxidised β -Nb SPPs, the Nb peaks all lie around 2379.5 to 2380.2eV, indicating the Nb⁵⁺ oxidation stage in fully oxidised SPPs.

- *SPP oxidation state vs distance to metal-oxide interface*

Figure 3-37 summarises the peak position of the Nb-L3 edge of some of the β -Nb SPPs analysed as a function of their distance from the metal-oxide interface. This data suggests that the oxidation of β -Nb SPPs is a dynamic process during the corrosion of Zr-alloys, with parts

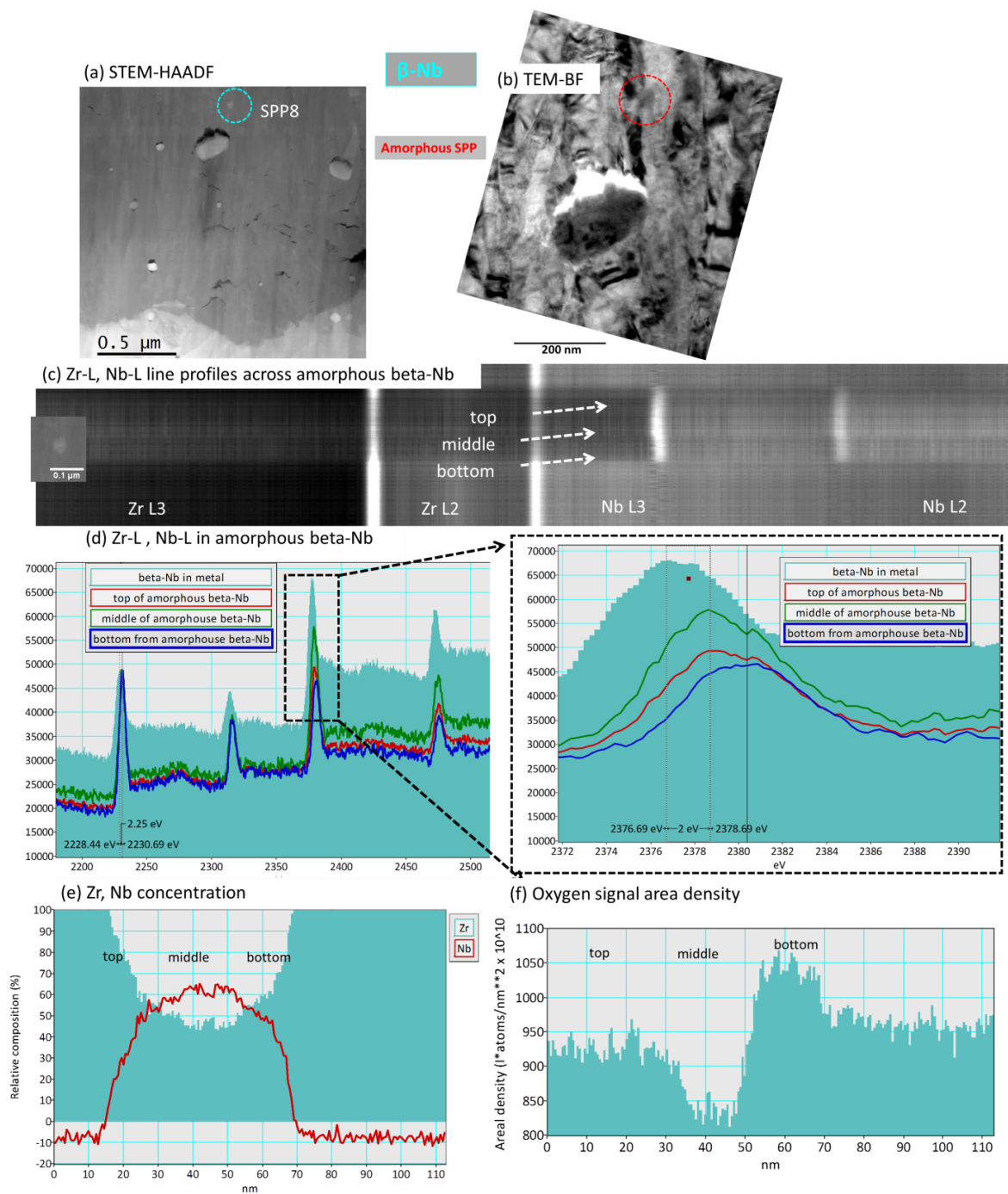


Figure 3-34: Example of EELS analysis of a β -Nb SPP in the middle of the oxide in the 360-day Zr-1.0Nb sample: (a) STEM HAADF image and (b) TEM BF image showing the location of the amorphous β -Nb SPP, (c) EELS line profiles of this β -Nb SPP over the range of Zr-L and Nb-L signal, with the shift in the top, middle and bottom of SPP identified with arrows. (d) comparison of EELS spectrum of β -Nb SPP in the middle of the oxide (top, middle and bottom part) and in the metal over the range containing Zr-L and Nb-L signal, (e) concentration profile of Nb and Zr in β -Nb SPP; (f) oxygen signal area density from β -Nb.

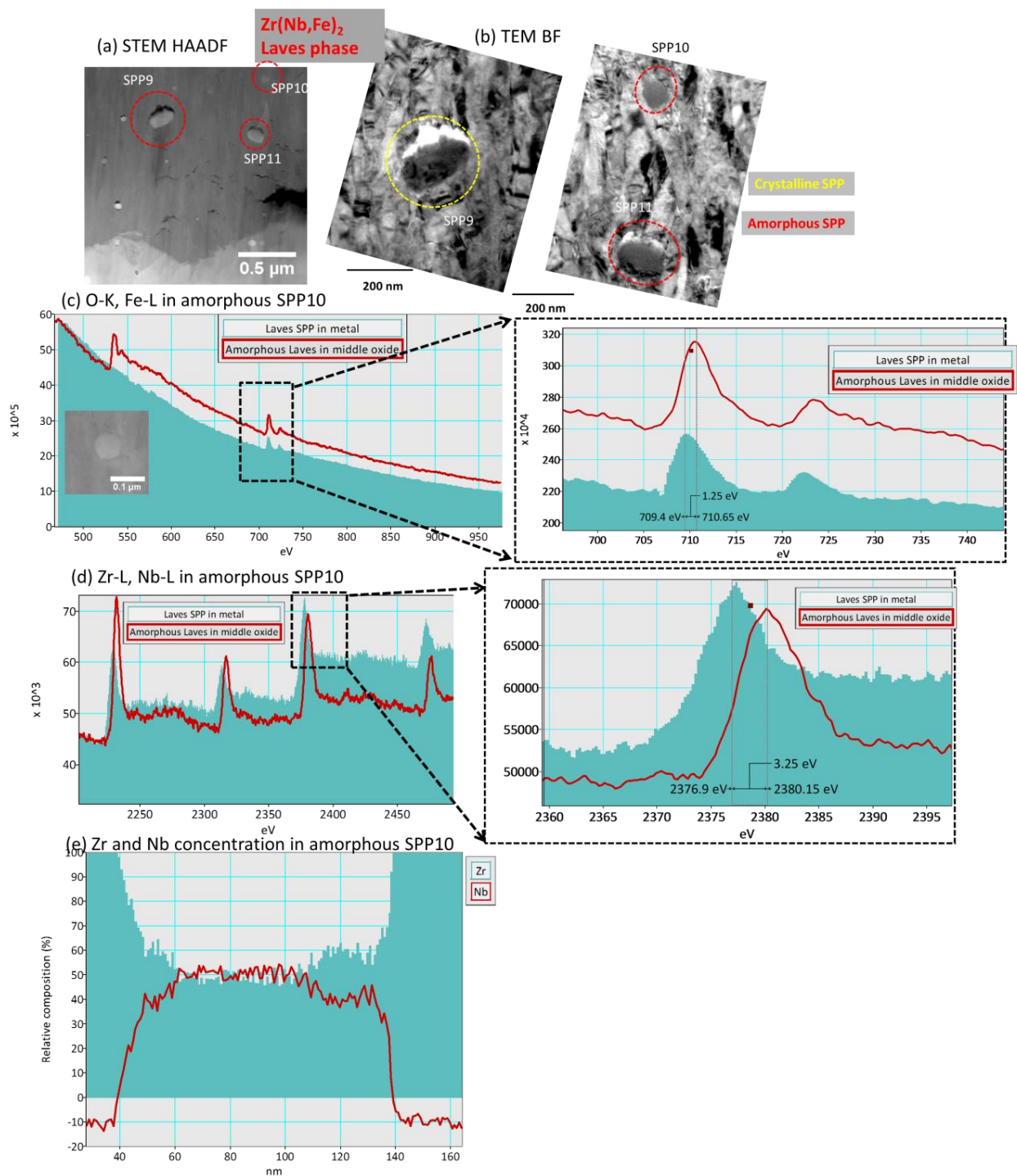


Figure 3-35: Example of EELS analysis of Laves phase SPPs in the middle of the oxide in the 360-day Zr-1.0Nb sample: (a) STEM HAADF image and (b) TEM BF image showing the location of the Laves phase SPPs, (c) comparison of EELS spectrum of amorphous Laves phase SPP in the middle of the oxide and in the metal over the range containing Oxygen-K and Fe-L signal, (d) comparison of EELS spectrum of amorphous Laves phase SPP in the middle of the oxide and in the metal over the range containing the Zr-L and Nb-L signals, (e) concentration profile of Nb and Zr in Laves phase SPP

of the same SPP being at different stages of oxidation and releasing aliovalent Nb-ions to the surrounding oxide. Near the metal-oxide interface, the β -Nb SPPs remain crystalline, however, the Zr in these crystalline SPPs are oxidised, and Nb is oxidised to Nb^{2+} state. The cracks on top of these SPPs may also be influential in controlling the rate of local oxidation, some of the SPPs are oxidising from the bottom or from the outside surface of SPP. In the middle part of the oxide, the SPP starts to become amorphous, both Zr and Nb in the particles are oxidised, with Nb possibly to an intermediate stage of Nb^{4+} . At the top surface of the oxide, the SPPs are fully oxidised, with Nb possibly to a final stage of Nb^{5+} .

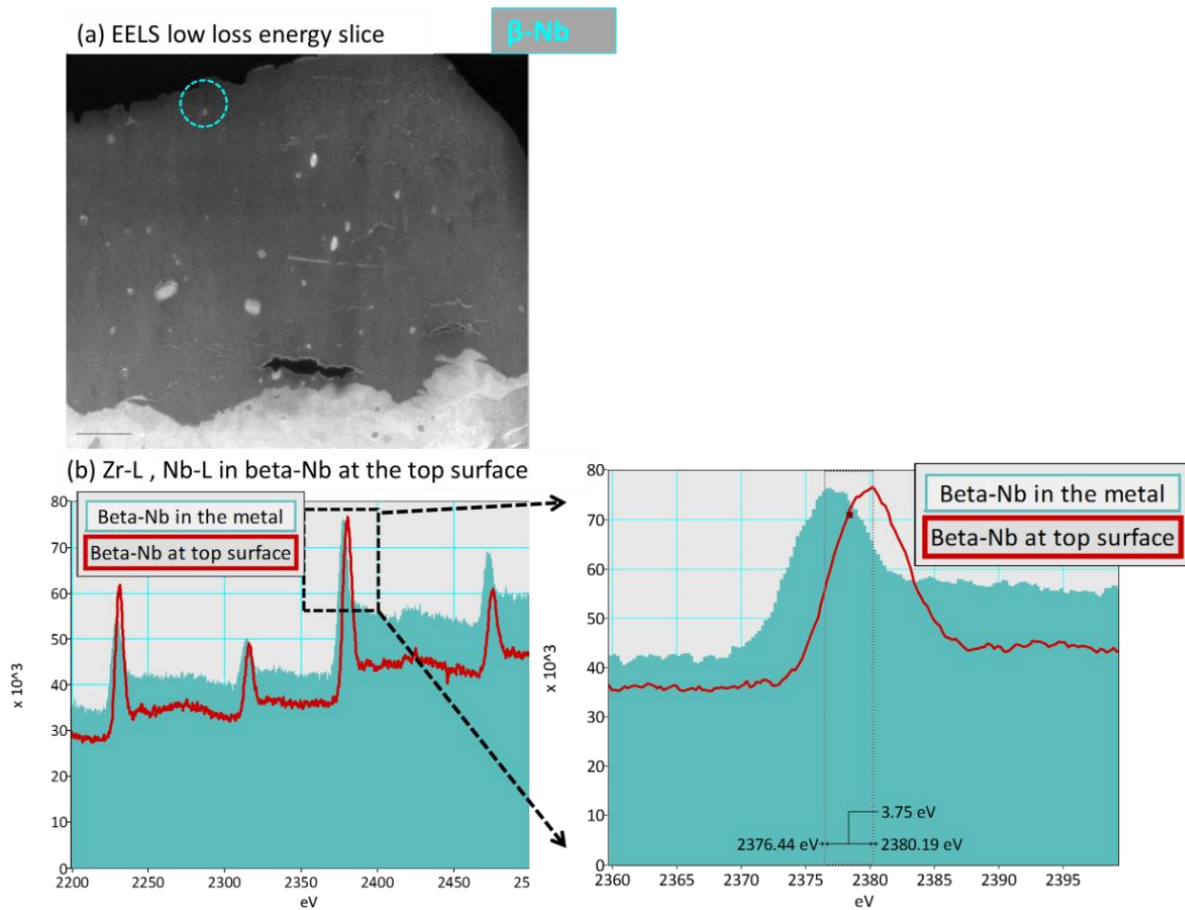


Figure 3-36: Example of EELS analysis of fully oxidised β -Nb SPPs at the top surface of the oxide in the 360-day Zr-1.0Nb sample: (a) EELS low loss spectrum imaging energy slice showing the position of fully oxidised SPPs and (b) comparison of EELS spectrum of fully oxidised β -Nb and β -Nb in the metal over the range containing the Zr-L and Nb-L signal.

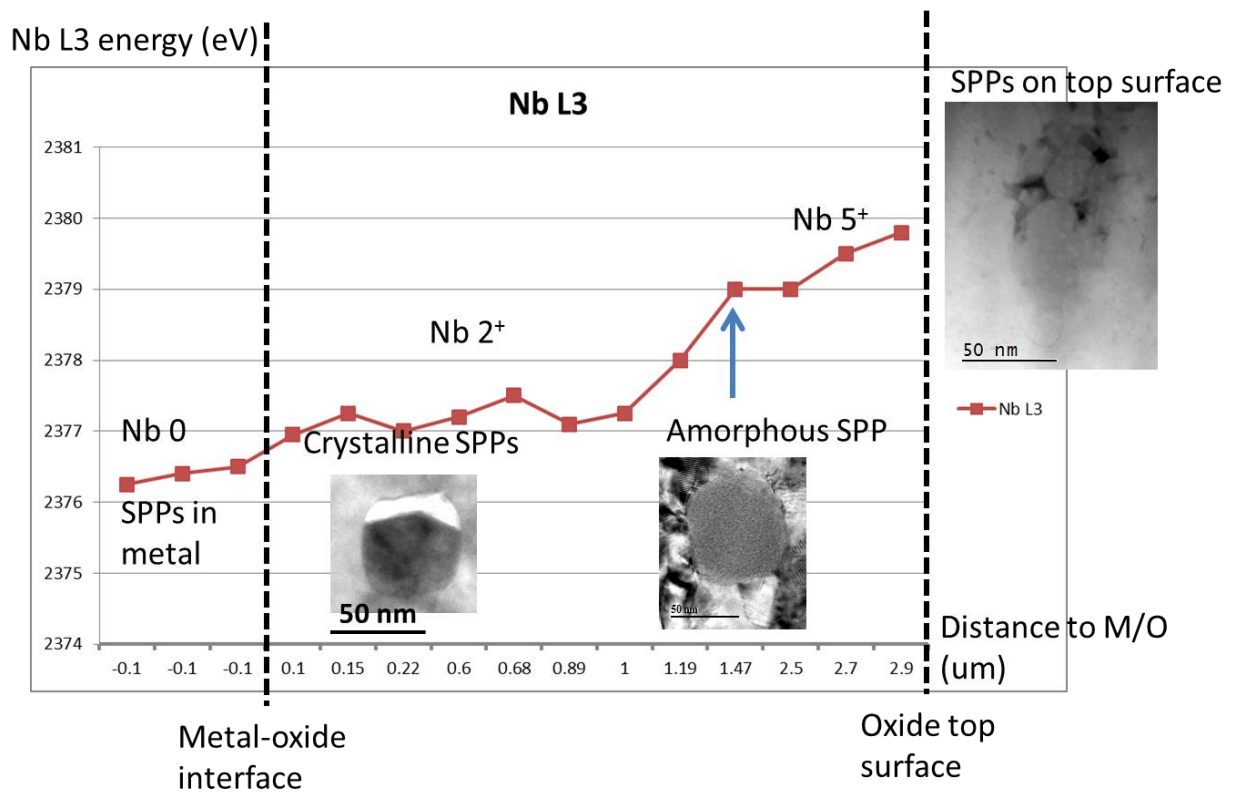


Figure 3-37: Nb-L3 edge position in SPPs with their distance to the metal-oxide interface.

3.3.SUBOXIDE

In this thesis, different state-of-the-art techniques have been used to study suboxide. By using TEM, STEM, Convergent Beam Diffraction (CBD), Transmission Kikuchi Diffraction (TKD), automated crystal orientation mapping with TEM (ASTAR) and EELS, the structural and chemical properties of the metal–oxide interface of corroded Zr alloys has been analysed in unprecedented detail. Some of the results have been published^{128,150}. TEM, STEM and diffraction results revealed the complexity of the distribution of suboxide grains at the metal–oxide interface. EELS provides accurate quantitative analysis of the oxygen concentration across the interface, identifying the existence of local regions of stoichiometric ZrO₂, also oxygen saturated Zr layer with varying thickness. TKD and ASTAR mapping confirmed that the suboxide grains can be indexed with the hexagonal ZrO structure as described below. The TKD and ASTAR analysis has also allowed for the mapping of a relatively large region of the metal–oxide interface, revealing the location and size distribution of the suboxide grains. The

relationship between suboxide and oxygen saturated Zr thickness and the stage of oxide growth has also been investigated by looking at samples after different oxidation durations. It was not possible to use TKD and ASTAR mapping on all the samples, as access to these equipments was kindly provided by our colleagues in University of Manchester.

3.5.1. 3-day Zr-1.0Nb sample

A combination of low-loss EELS spectrum imaging mapping and core loss spectrum line profiles were carried out for the 3-day Zr-1.0Nb sample.

Low-loss EELS mapping was done with a step size of 4 nm and acquisition time is 10^{-5} s/pixel. Several reference spectra for different parts of the complex microstructure were acquired as shown in Figure 3-38. (a) shows the unique spectra from the possible Zr-O combinations in the system: ZrO_2 has three peaks at 15 eV, 26.7 eV and 43 eV. ZrO suboxide has two peaks, the first one is a delayed peak at 15.2 eV and the second peak is at 42.2 eV. Zr(Osat) has two peaks at 17.8 eV and 41.2 eV. Zr metal has two peaks at 16.9 eV and 40.8 eV. Figure 3-38 (b) shows the spectra from a typical β -Nb SPP and a hydride in the sample.

After MLLS fitting over the energy range of 10-60 eV, the separation of phases by their characteristic low loss spectra are shown in Figure 3-39. As seen in the STEM HAADF image in (a), most of the fitting works very well, (b), such that the bulk oxide, metal, SPPs and hydrides are clearly distinguished. However, it is interesting to see that although the reference spectra of ZrO and Zr(Osat) have different peak shapes and positions, the fitting was not able to separate them. Instead, the suboxide and oxygen saturated metal area are combined together to form an almost uniform layer with average thickness of 65 nm.

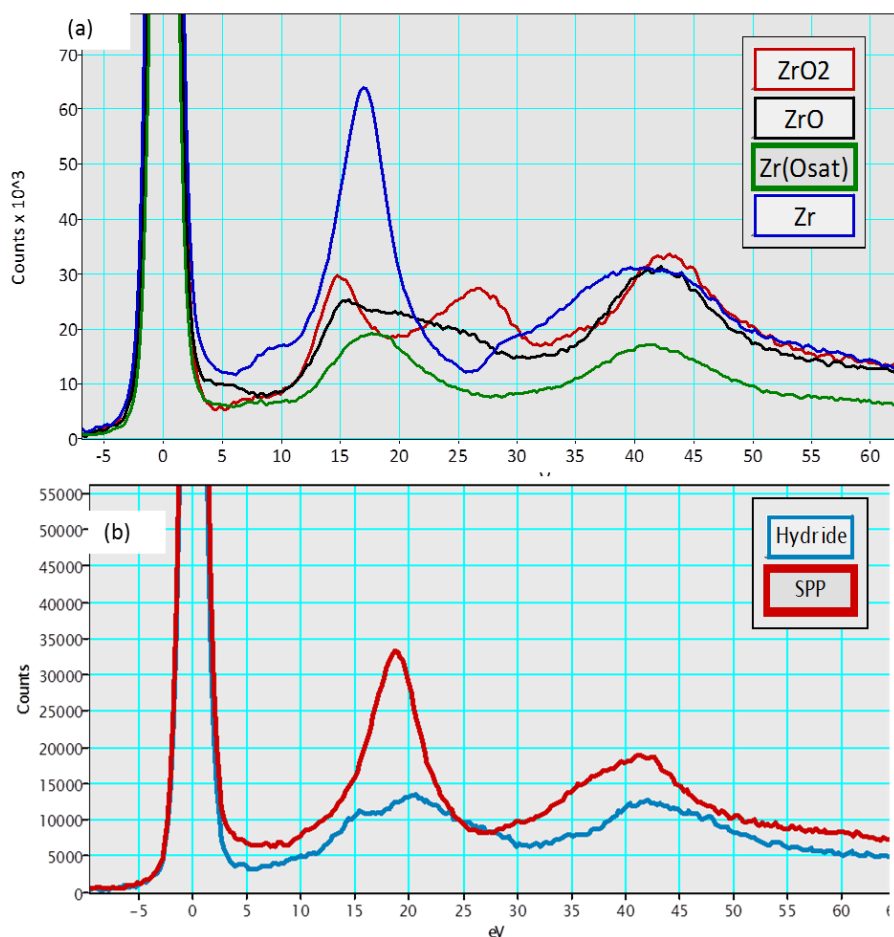


Figure 3-38: Reference spectra from low loss EELS mapping, (a) spectra of ZrO₂, ZrO, Zr(Osat) and metal, (b) spectra of hydride and β -Nb SPP.

3.5.2. 120-day Zr-1.0Nb sample

Figure 3-40(a) shows the HAADF STEM image of the 120-day Zr-1.0Nb sample. The oxide thickness is around 2 μm , there are some lateral cracks at the metal-oxide interface, and one part has an undulation underneath the crack which suggests delayed oxidation. The sample was further thinned down to around 50 nm in order to do accurate ASTAR and EELS mapping. ASTAR phase mapping is shown in Figure 3-40 (b) of this TEM lamella. Columnar oxides with monoclinic-ZrO₂ (m-ZrO₂) structure are clearly seen, and scattered equiaxed tetragonal-ZrO₂ (t-ZrO₂) grains mostly at the metal-oxide interface. The top layer of t-ZrO₂ is considered to be a result of FIB damage. At the metal-oxide interface, there are smaller grains with width around 100-150 nm and length of 100-150 nm, some of these smaller grains are

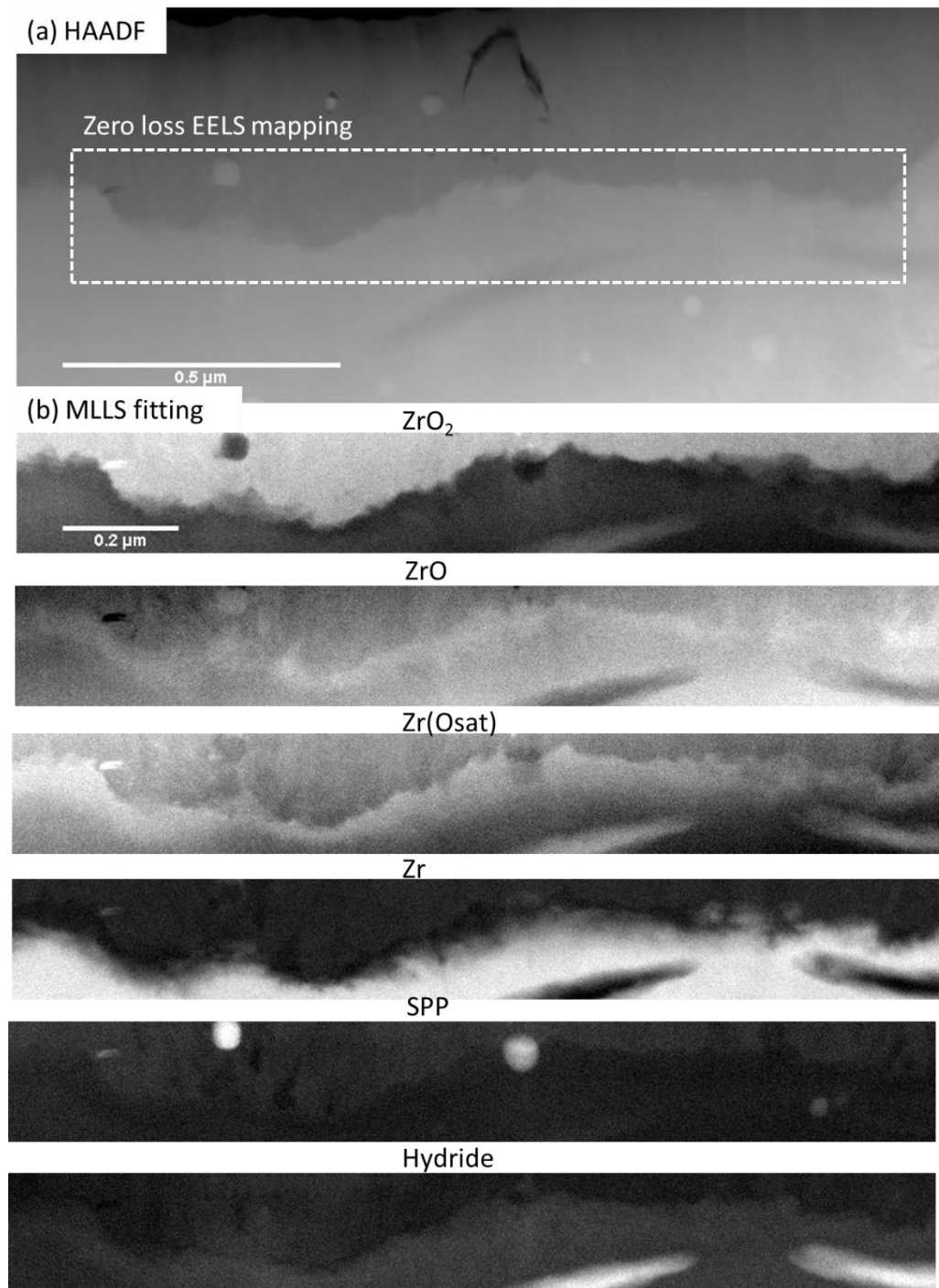


Figure 3-39: (a) STEM HAADF image of an area from 3-day Zr-1.0Nb TEM sample (b) MLLS fitting of the reference spectra from low loss EELS mapping for the ZrO_2 , ZrO , $\text{Zr}(\text{Osat})$, metal, hydride and β -Nb SPP phases, respectively.

identified as a continuous layer of suboxide with the hexagonal ZrO structure predicted with *ab initio* modelling⁶⁸, with P-62m symmetry and lattice parameters $a=5.31 \text{ \AA}$ and $c=3.20 \text{ \AA}$. Other grains at the interface match Zr metal with P 63/m symmetry and lattice parameters

$a=3.23 \text{ \AA}$ and $c=5.14 \text{ \AA}$. However, the undulating area under the parallel crack shows a more uniform saw-tooth shaped suboxide region with metal underneath intact.

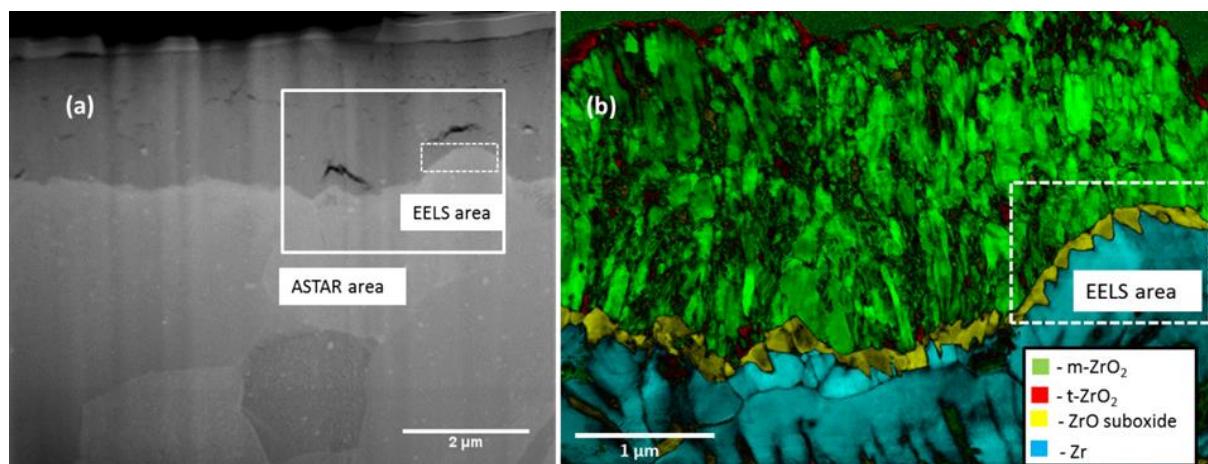


Figure 3-40: (a) HAADF STEM image of the 120-day Zr-1.0Nb sample. The areas for automated crystal orientation (ASTAR) and EELS mapping are highlighted. (b) Phase map in ASTAR mapping with the area for EELS mapping highlighted.

A higher magnification HAADF STEM image of the highlighted area in Figure 3-40 is shown in Figure 3-41(a). The z-contrast in the image shows the saw-tooth shaped suboxide as seen in the ASTAR map in (c), and the oxygen and Zr concentration maps in (b1, b2) also confirm the saw-tooth shaped suboxide. Line profiles across the suboxide region confirms again that there is a region of $\sim 86 \text{ nm}$ thickness with Zr:O ratio close to 1:1, followed by oxygen saturated metal containing $\sim 25 \text{ at\%}$ oxygen. Combining these advanced microscopy techniques on the same area of the material, and achieving confident results on the microchemistry and crystallography of this complex interface, quite confidence that we have a reliable set of technique to apply to other samples.

Low loss mapping provides a quicker and easier way to identify suboxide and oxygen saturated Zr regions, and several regions were chosen to be representative of different locations of the sample. Figure 3-42(a) shows the chosen four regions for zero loss mapping and their MLLS mapping results are shown in (b). In area 1, where there is a slight undulation

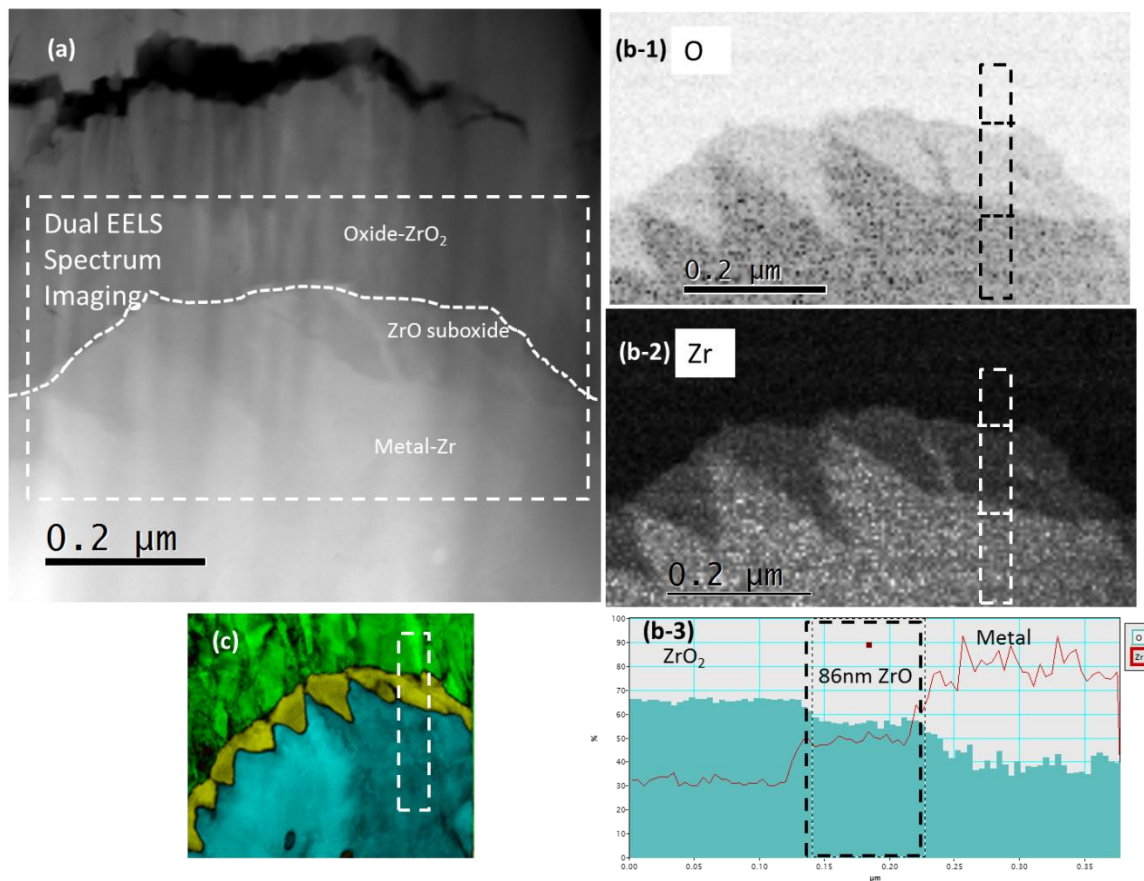


Figure 3-41: (a) HAADF STEM image of the area for EELS core loss mapping of the 120-day Zr-1.0Nb sample, (b-1) Oxygen concentration map, (b-2) Zr concentration map, (b-3) Line profiles across suboxide region, (c) same region from ASTAR mapping.

at the metal-oxide interface, there is suboxide only at the undulation area, the thickest part being around 130 nm with an average thickness around 60 nm. At the region next to the undulation, there is uniform layer of oxygen saturated Zr 180 nm thickness. The ZrO suboxide and oxygen saturated Zr form a combined Zr-O region of around 215 nm thick. In area 2, there is a suboxide layer at the almost uniform part of the metal-oxide interface, some of these suboxide grains are saw tooth shape while most are flat suboxide grains, with average thickness of 105 nm. Again, the oxygen saturated metal is an almost uniform layer of 160 nm thickness and the combined Zr-O layer is 200 nm thick. In area 3, which has a crack on the top, the saw tooth suboxide is around 100 nm thick and the oxygen saturated area is slightly thicker, 210 nm. The combined Zr-O region is thicker as well, 250 nm. In area 4 the MLLS

fitting results agree with ASTAR mapping and core loss mapping, with the saw tooth shaped suboxide most obvious, with the thickest part penetrating into the metal by 200 nm. The average suboxide thickness is 130 nm. The oxygen saturated region is uniform, 290 nm and the Zr-O combined region is the thickest among all these location, 270 nm.

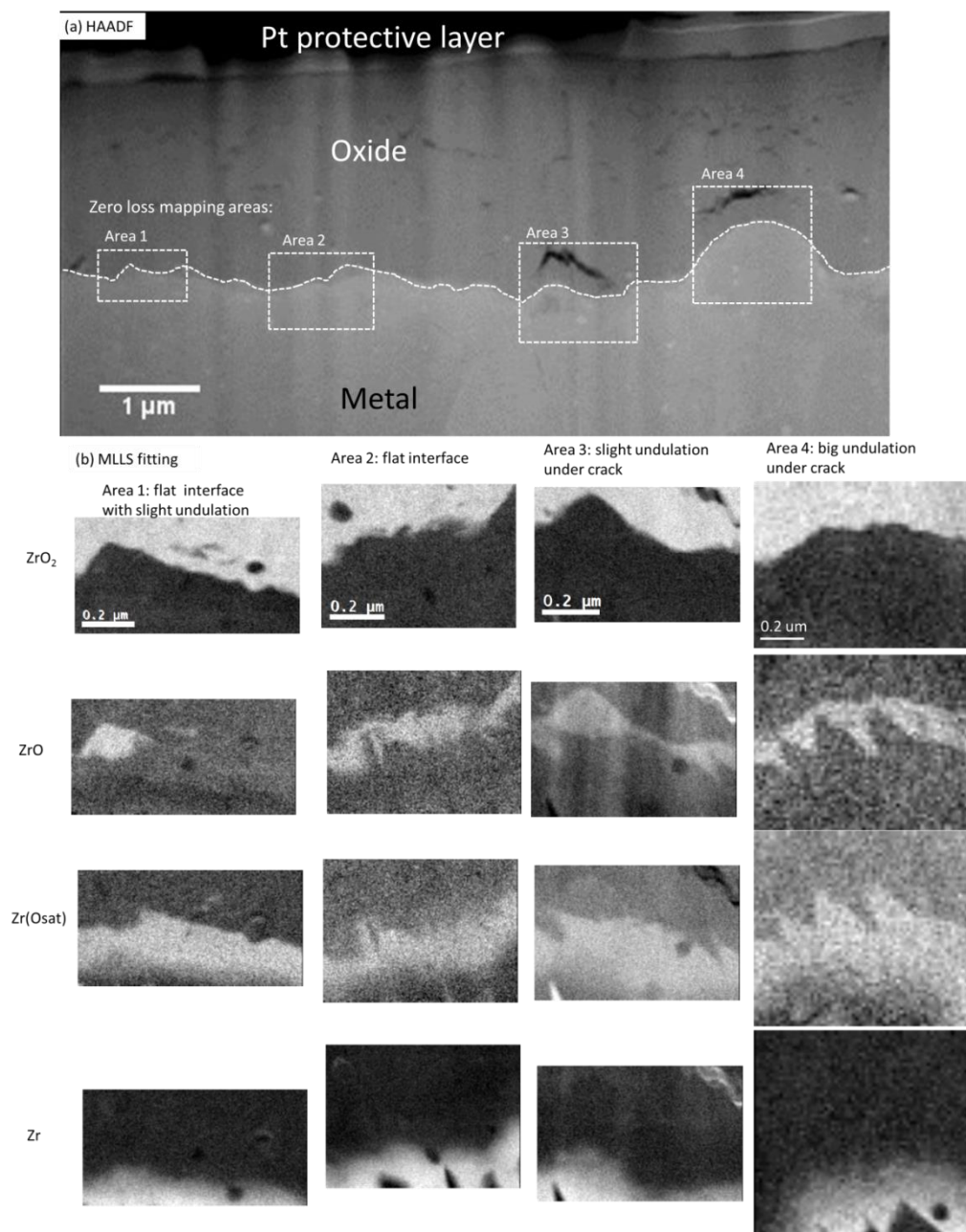


Figure 3-42: Low loss mapping of 120-day Zr-1.0Nb. (a) STEM HAADF image identifying the chosen four locations for zero loss mapping, (b) MLLS fitting results for oxide, suboxide, oxygen saturated metal and metal in four different locations.

This suggests that the undulation area is associated with a more well-defined saw tooth suboxide shape and with a thicker Zr-O region of around 250 nm. At the flatter metal-oxide interface region, the suboxide can be discontinuous and have different shapes, but, this does not affect the uniform but slightly thinner total of the combined Zr-O region of around 200 nm.

3.5.3. 225-day Zr-1.0Nb sample

Core loss EELS spectrum imaging was carried out on the 225-day Zr-1.0Nb sample. Figure 3-43 shows the saw-tooth shape suboxide in a region where the metal-oxide interface has an undulation. While it is very hard to see the suboxide from diffraction contrast in the TEM BF image, the suboxide region shows medium contrast between dark oxide and white metal matrix in the STEM HAADF image in (a). (c) shows the concentration map of Zr and O, and we can clearly see three saw tooth shaped suboxide grains in this region, the thickest part around 360 nm with an average suboxide thickness around 205 nm. The oxygen saturated area is around 160 nm in thickness, and the combined Zr-O region is 396 nm thick. The line profiles in (d) show the suboxide contains around 45at% Zr and the oxygen saturated area contains around 40 at% O.

At a flat metal-oxide interface region shown in Figure 3-44, EELS core loss mapping shows that the suboxide grains form a uniform layer of around 130 nm thickness, followed by an uniform oxygen saturated layer of 180 nm. The combined Zr-O layer is around 260 nm, thinner than the saw tooth suboxide region in Figure 3-43. The line profiles in (c) show the suboxide has around 45at% Zr and the oxygen saturated area contains around 40 at% O.

3.5.4. 360-day Zr-1.0Nb sample

Figure 3-45(a) shows a TEM BF image of the TEM sample of the 360-day Zr-1.0Nb sample. Below the Pt layer used to protect the sample during FIB milling, a ZrO₂ layer can clearly be

seen. Below the metal-oxide interface, large Zr metal grains are visible in both images, with embedded metallic second phase particles. The inset in (a) is the higher magnification TEM bright field image of the region chosen for convergent beam electron diffraction (CBED) and EELS analysis.

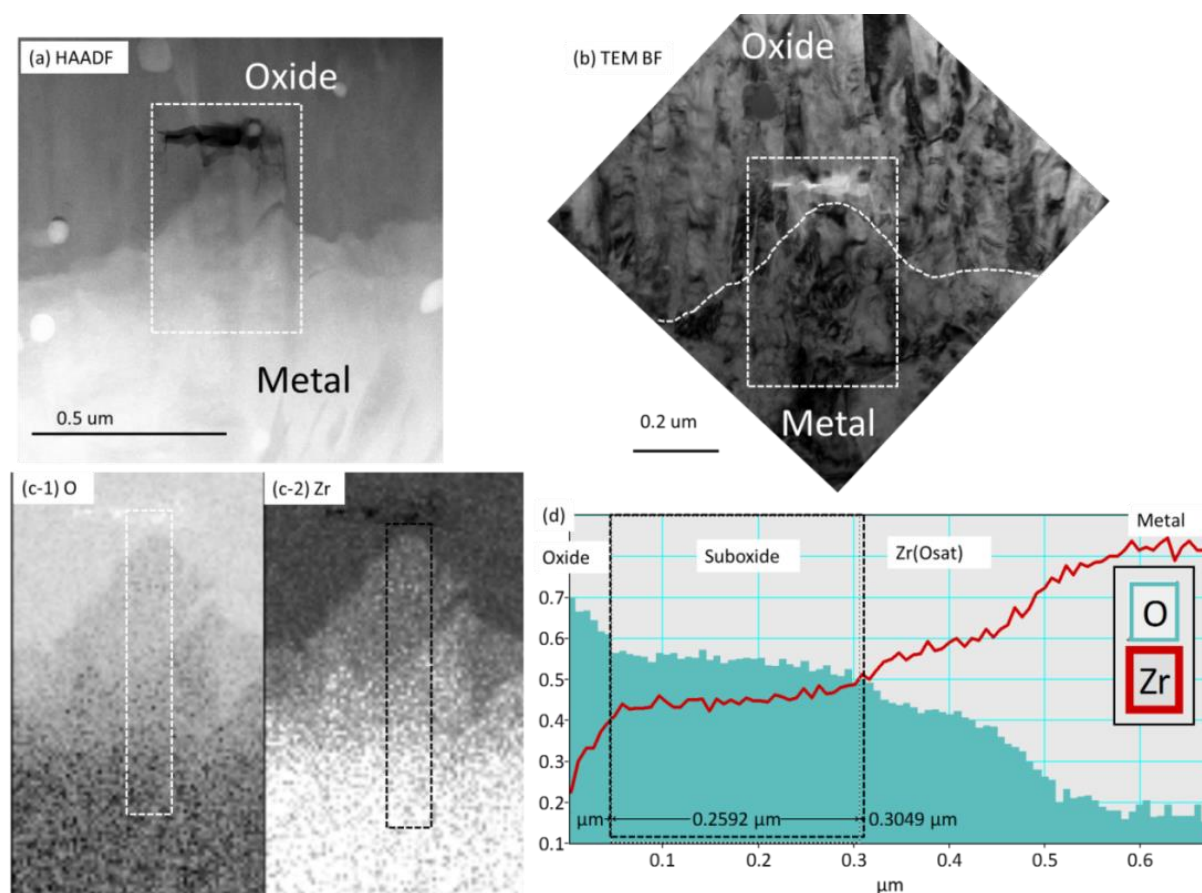


Figure 3-43: EELS core loss analysis of the 225-day Zr-1.0Nb sample. (a) STEM HAADF image of chosen area, (b) TEM BF image of chosen area, (c-1,2) concentration maps of oxygen and Zr, (d) line profiles of oxygen and Zr across the suboxide region.

CBED patterns were acquired from a region as shown in (b), and the suboxide grain which is strongly diffracting is highlighted by the arrows. A STEM dark field image of the suboxide grain area is shown in (c); the z-contrast helps to identify the suboxide as a region of intermediate contrast between the brighter metal substrate and the darker stoichiometric ZrO_2 and the suboxide is highlighted by arrows in the figure. The area where the CBED pattern was taken is also highlighted. A typical diffraction pattern is shown in (d) and can be indexed as

matching with the $[32\bar{4}]$ zone axis of the hexagonal ZrO phase with P-62m symmetry and lattice parameters $a=5.31 \text{ \AA}$ and $c=3.20 \text{ \AA}$ predicted by Nicholls et al⁶⁸.

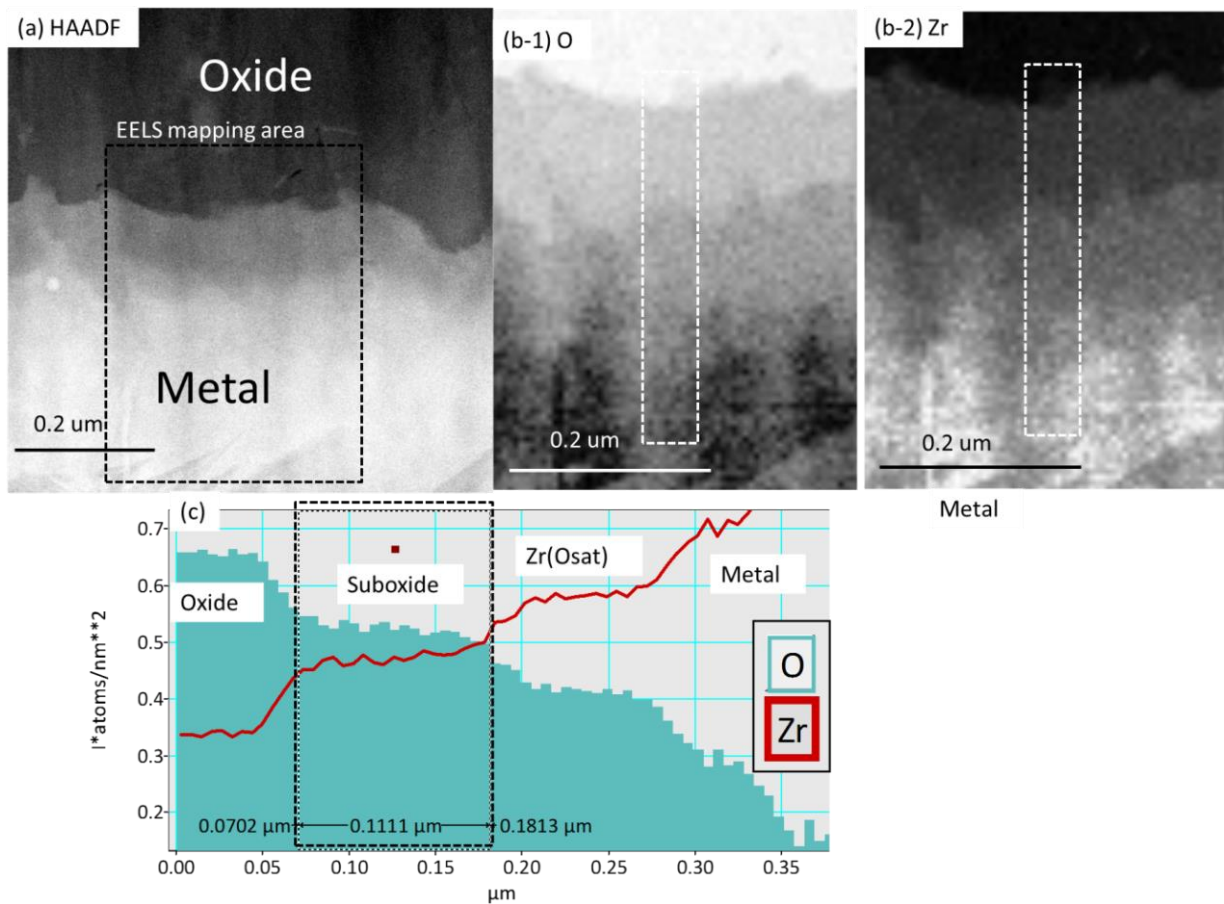


Figure 3-44: EELS core loss analysis of the 225-day Zr-1.0Nb sample. (a) STEM HAADF image of chosen area, (b-1,2) concentration maps of oxygen and Zr, (c) line profiles of oxygen and Zr across the suboxide region.

Core loss EELS mapping was performed in the region highlighted in previous images using the step size of 8.5 nm. In this region, both TKD as seen in Figure 3-7(a) and CBED analysis have confirmed the existence of hexagonal ZrO. The HAADF image in (b) also shows grain structures with different contrasts at the interface, and several second phase particles. The oxygen and Zr concentration maps in (c) confirm the shape of one big rectangular suboxide grain. It is interesting to see there is one small part on the top of grains that has oxide intruding into suboxide grain as highlighted by circles. Four EELS profiles were taken in total from this region, with all four detecting some regions with ZrO

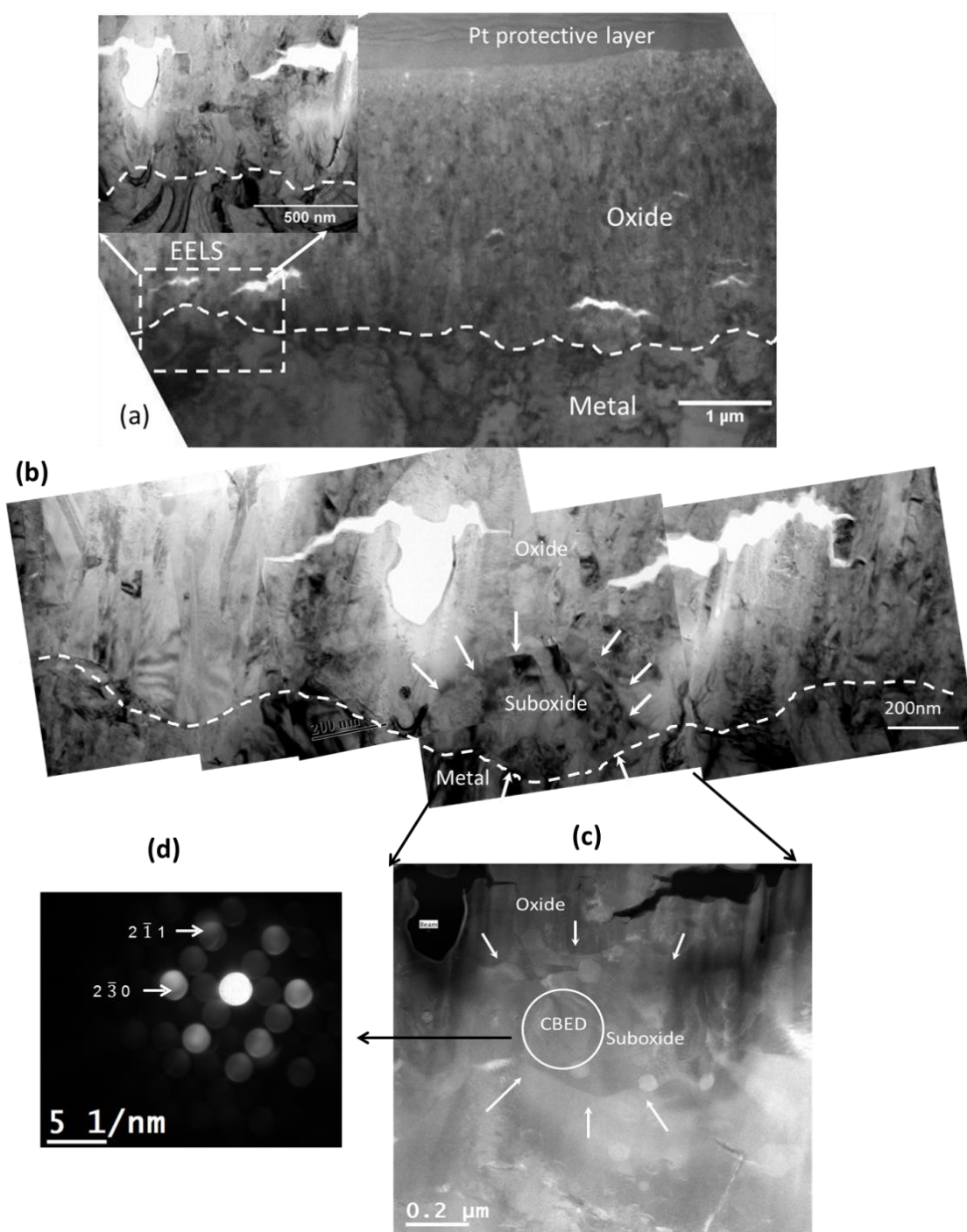


Figure 3-45: (a) TEM Bright field image of 360-day Zr-1.0Nb sample. The area used for EELS analysis is highlighted. The inset shows higher magnification images of this same area after further FIB thinning (which has created the hole under the left hand crack) (b) High magnification TEM bright field image of the area near the metal-oxide interface, which was chosen for CBED and EELS analysis. The suboxide grain, which was in a strongly diffracting condition, is highlighted using arrows. (c) STEM dark field image of the suboxide grain area, with the area where CBED pattern was taken highlighted. (d) CBED pattern of the suboxide grain which matched with the predicted hexagonal ZrO phase with P-62m symmetry and lattice parameters $a=5.31 \text{ \AA}$ and $c=3.20 \text{ \AA}$.

We can be confident of the accuracy of these compositional measurements because we measure the ZrO_2 stoichiometry on the oxide side of all the scans. On the metal side of the interface there is a gradient of oxygen into the metal which also seems to vary over the small area analysed here, also in agreement with previous observations⁶¹. On line profiles 2 and 3, there seems to be another plateau region around 100 nm thickness after the suboxide region with an oxygen content of 25 at% (Zr_3O), which suggests that the Zr metal here is saturated with oxygen. In all four line scans, the oxygen content drops to a value close to zero deeper into the metal, indicating that the final sample cleaning has successfully removed most of the surface oxide.

Low loss spectrum imaging provides a quicker and easier way to identify oxide, suboxide, oxygen saturated metal and metal across a significant width of the metal-oxide interface. Figure 3-47(a) shows a HAADF image of the TEM sample of the Zr-1.0Nb 360-day sample. Due to z-contrast, it is possible to see there are grey contrast saw tooth shaped grains at the metal-oxide interface. MLLS fitting results for oxide, suboxide, oxygen saturated metal and metal are shown in (b).

Area one and area two have a relatively flat metal-oxide interface and it is interesting to see the differences in suboxide distribution between these two areas. Area one has a very thin suboxide around 60-100 nm, but the oxygen saturated area is thick, around 250 nm. The combined Zr-O region is around 310 nm thick. In area two, there are several very well defined saw-tooth shape suboxide grains. Saw tooth suboxide is around 80-105 nm in width and the thickest tip is around 130-250 nm in length, with average of around 160 nm. Although the suboxide is not continuous, the oxygen saturated area fills the gap between the suboxide grains with average thickness of 225 nm, and the combined region of Zr-O region is 350 nm thick.

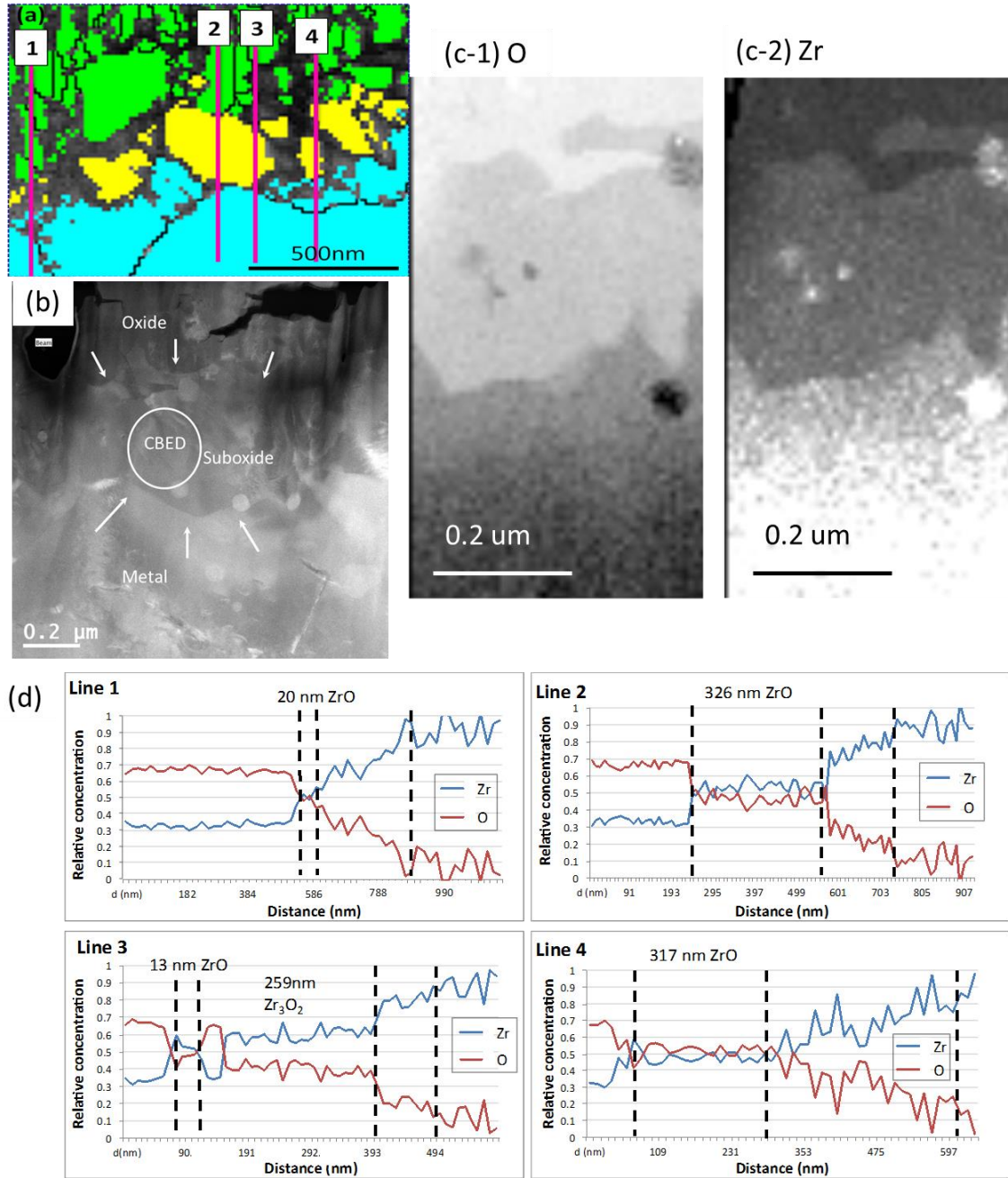


Figure 3-46: CBED patterns were acquired from a region as shown in (b), and the suboxide grain which is strongly diffracting is highlighted by the arrows. A STEM dark field image of the suboxide grain area is shown in (c); the z-contrast helps to identify the suboxide. Positions of EELS line scans from the suboxide region in the 360-day Zr-1.0Nb sample relative to (a) the TKD map, (b) the HAADF image, (c) EELS core loss concentration maps of oxygen and Zr, (d) line profiles of oxygen and Zr across the suboxide region. All profiles started from the oxide towards metal. (1)20 nm ZrO, (2)326 nm ZrO, (3)13 nm ZrO+259 nm Zr₃O₂, (4)317 nm ZrO.

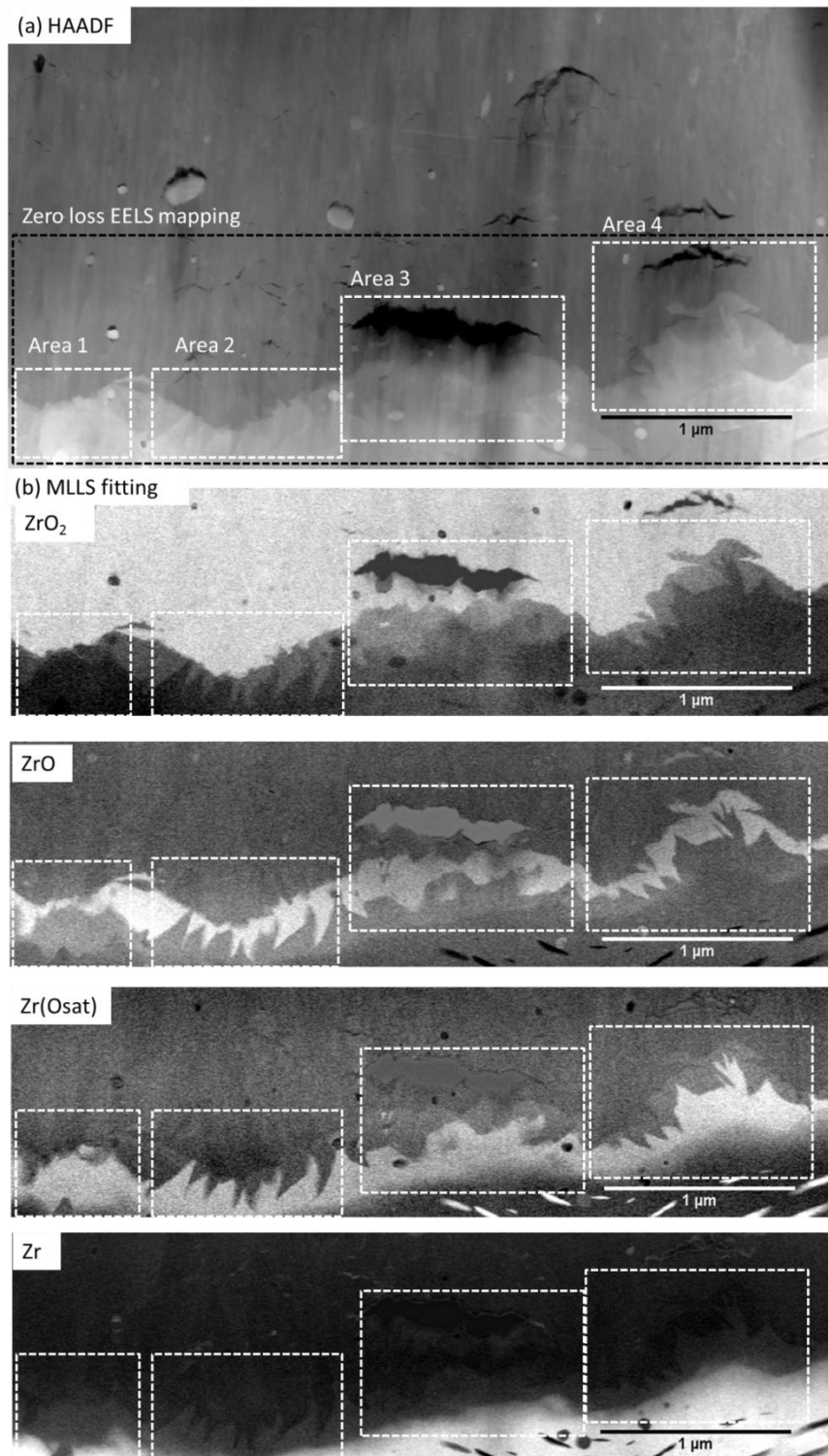


Figure 3-47: Low loss EELS +MLLS mapping of 360-day Zr-1.0Nb. (a) STEM HAADF image for the chosen four locations of zero loss mapping, (b) MLLS fitting results for oxide, suboxide, oxygen saturated metal and metal. Four different areas are circled.

Area three is under a parallel crack near the metal-oxide interface, and is still relatively flat. In this region the suboxide becomes blocky and with a less defined saw tooth shape. The

average suboxide thickness is around 195 nm and 265 nm oxygen saturated region, growing a combined Zr-O region thicker than in area one 400 nm.

Area four is a slightly undulated area under a parallel crack. In this region most of the suboxide grains are saw tooth shaped, with an average thickness of 135 nm, and with 265 nm of oxygen saturated area, so that the combined Zr-O region is thicker than area one, 385 nm in length. This suggests that in general under the parallel crack regions, the combined Zr-O region is slightly thicker than where there is no crack on top. This observation suggests that the parallel cracks on the metal-oxide interface can prevent oxygen getting into the metal easily, thus creating thicker suboxide.

3.5.5. 540-day Zr-1.0Nb sample

Low loss EELS spectrum mapping was carried out on the 540-day Zr-1.0Nb sample. Figure 3-38 (a) shows a HAADF image of the TEM sample. Just above the metal-oxide interface there is a layer of cracks, suggesting the sample has just gone through second transition. MLLS fitting results for oxide, suboxide, oxygen saturated metal and metal are shown in (b). Area one has a relatively flat metal-oxide interface with one slight undulation under a parallel crack. The undulation area is full of suboxide grains, and in other regions along the interface suboxide grains are blocky and with less defined saw tooth shape. The average suboxide thickness is around 145 nm, with a 200 nm oxygen saturated area, so that the combined Zr-O region is 353 nm in thickness.

Area two is a slight undulation area under a parallel crack. In this region, most of the suboxide grains are saw tooth shaped and the average thickness of 122 nm, with a 165 nm oxygen saturated area, so that the combined Zr-O region is 255 nm in thickness. Although the sample has gone through transitions, this shows that across a very large area at the interface $\sim 3\mu\text{m}$, the suboxide and oxygen saturated Zr still exist at the metal-oxide interface.

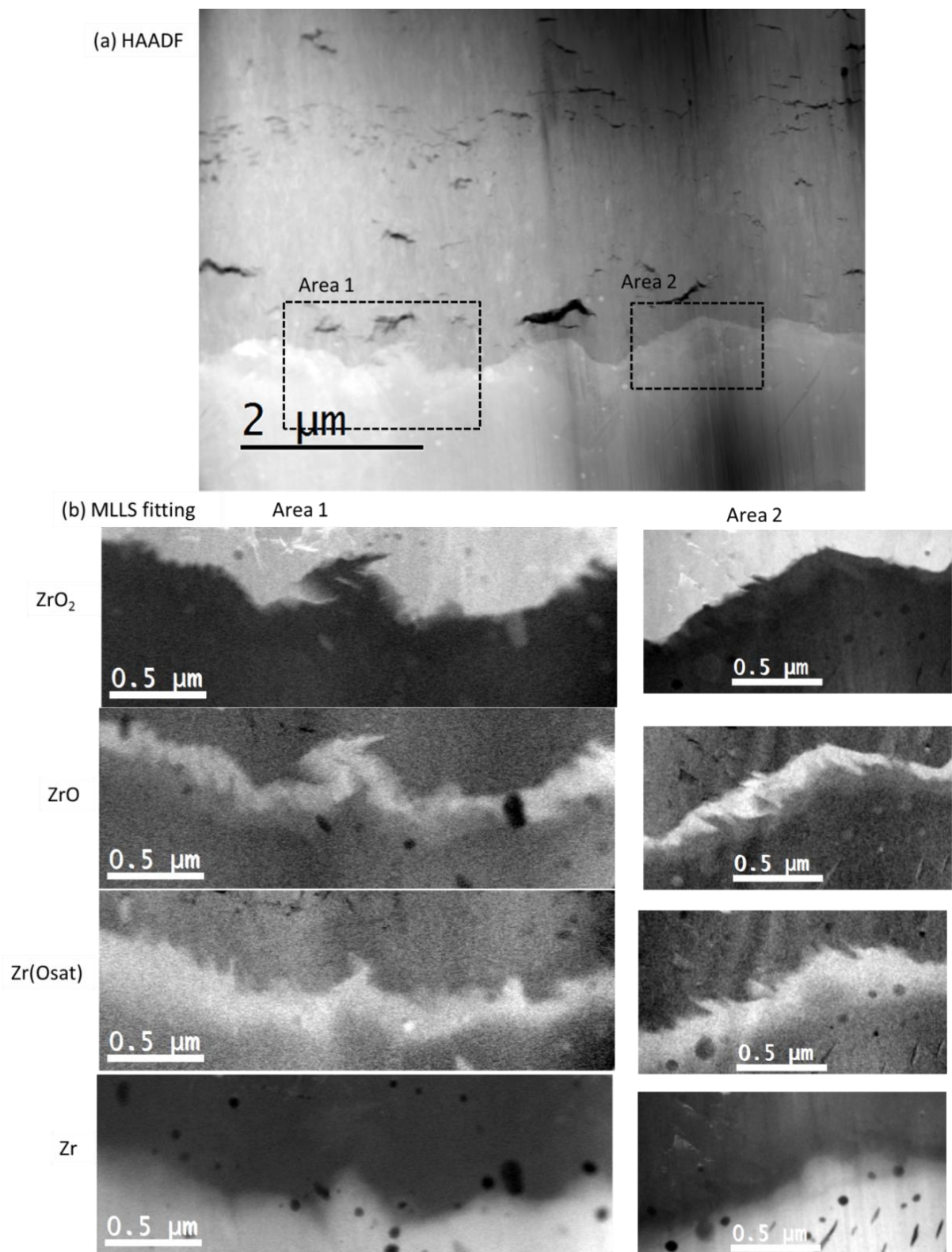


Figure 3-48: Low loss EELS +MLLS mapping of 540-day Zr-1.0Nb. (a) STEM HAADF image of the chosen four locations for low loss mapping, (b) MLLS fitting results for oxide, suboxide, oxygen saturated metal and metal.

3.5.6. 585-day Zr-1.0Nb sample

The 585-day sample is post-second transition as shown from the HAADF image in Figure 3-49(a) where after the second layer of cracks, another 1.65 μm oxide has grown during the 45 days after the 540 days sample just described, we believe 540-day sample is just around second transition, while 585-day sample has passed second transition.

The core loss EELS line profiles in Figure 3-49 show that there is hardly any suboxide at this stage as oxygen saturated area. ASTAR mapping at the metal oxide region suggests that there is a discontinuous layer of blocky suboxide grains about 50 nm in thickness. Although ASTAR mapping does not show oxygen saturated area directly, from previous images such as Figure 3-49, I have observed that hydrides do not grow in the oxygen saturated region. In this ASTAR map, hydride is mistakenly mapped as tetragonal oxide as we didn't put hydride as a separate phase to match, so hydride-free metal region can be roughly considered as defining the oxygen saturated region. In this sample it is around 100 nm thick which is possibly slight over estimate. From the EELS core loss line profile, the combined Zr-O region is 137 nm. This suggests that post-transition sample has a much thinner suboxide and oxygen saturated region than pre- and at-transition samples.

3.5.7. Correlating Zr-O with oxidation stage

By combining this kind of low loss EELS mapping and TKD, ASTAR analysis of the metal-oxide interfaces, I have been able to correlate the total thickness of the suboxide and Zr(Osat) regions in a large number of different samples at different stages of oxidation, as shown in Figure 3-50. The error bars show the standard error for the measurements on each sample. Looking at all the alloys as one, the data suggests that during stages of rapid oxidation there is a thinner layer of suboxide and Zr(Osat). This suggests that the accumulated suboxide during the slow oxidation process is fastly consumed during the faster oxidation process, there is enough oxygen to develop zirconium oxide directly without going through suboxide stage.

Considering that recrystallised Zr-1.0Nb has a better corrosion resistance than ZIRLO[®], this implies that alloys with better corrosion resistance form more suboxide and the combined Zr-O region (suboxide + Zr(Osat)) is thicker.

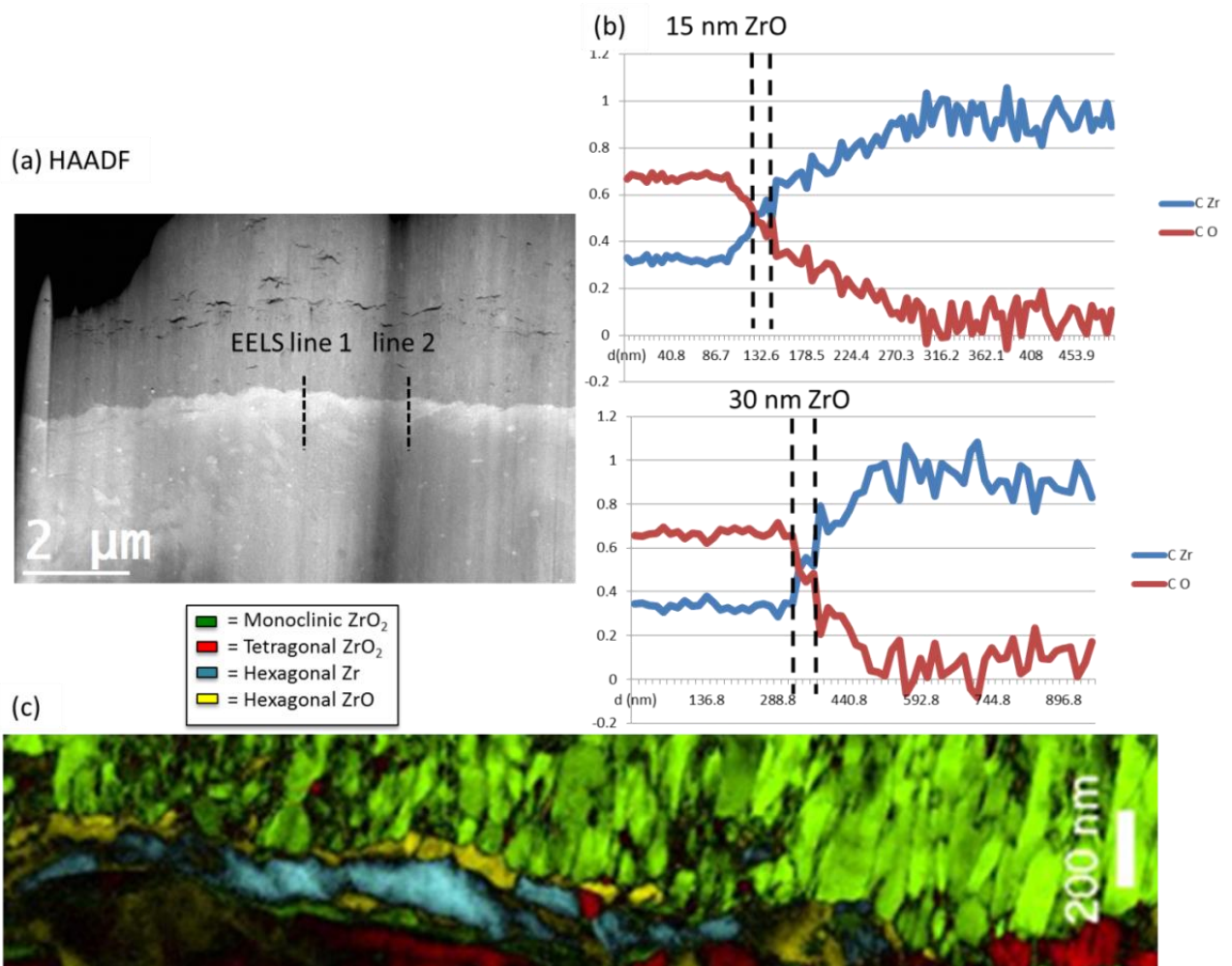


Figure 3-49: (a) STEM HAADF image of the 585-day Zr-1.0Nb sample with two EELS line profile positions, (b) concentration of Zr and oxygen in two EELS line profiles, (c) ASTAR mapping of metal-oxide region of this sample.

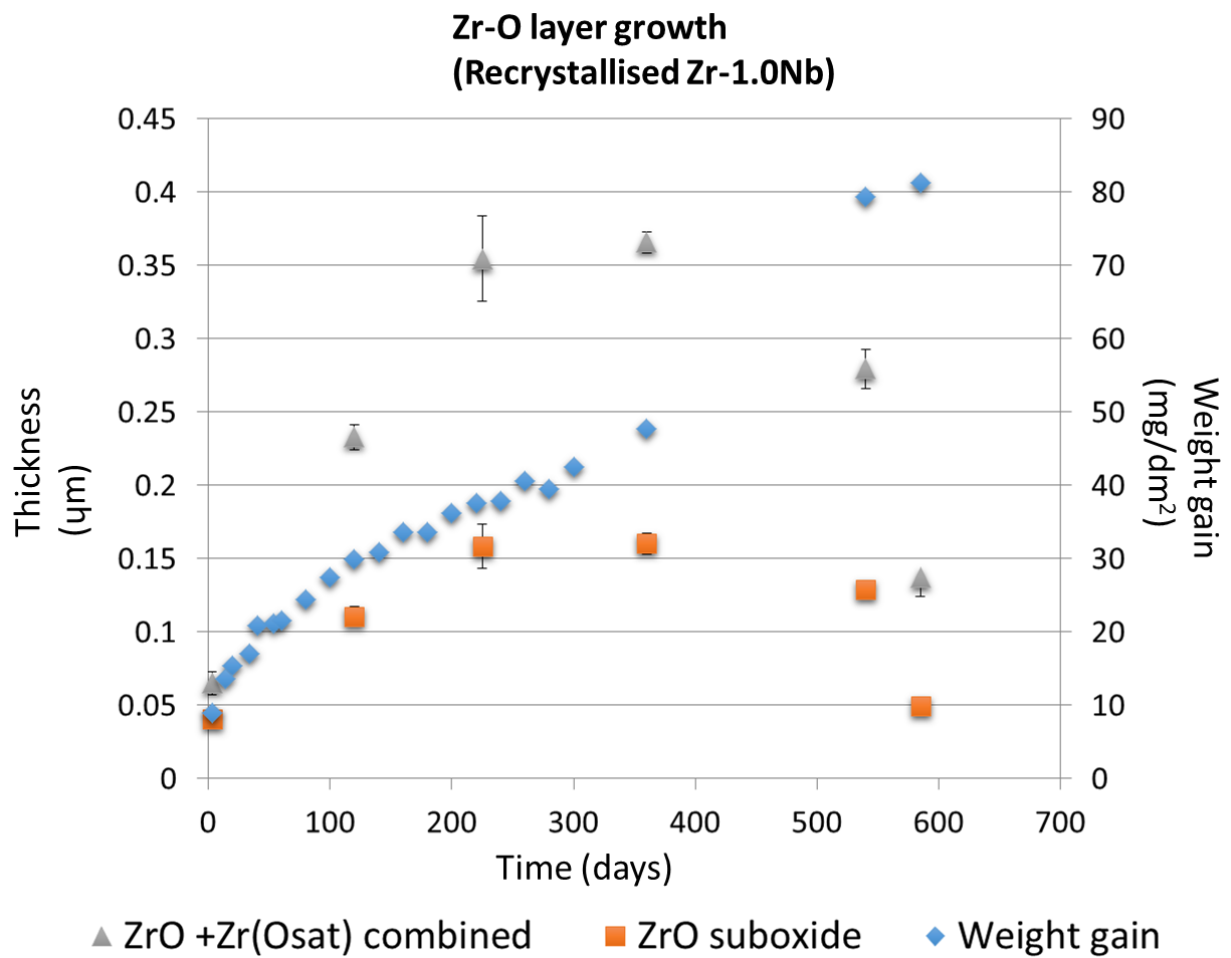


Figure 3-50: Suboxide and combined region growth with oxidation days.

4 CHAPTER 4 Zr-1.0Nb IN THE ANNEALED STATE

4.1.OXIDATION AND HPU DATA

To complete the study of the autoclave oxidised samples discussed in Chapter 3, a set of the same Zr-1.0Nb sheet samples were given an additional anneal at 720°C for 24 hours in order to study the effect of SPPs on oxidation and hydrogen pickup.

These annealed Zr-1.0Nb samples were put into a static stainless steel autoclave at Westinghouse™ in pure water at 360°C. The oxidation data was measured every 15 days until 225 days, and the hydrogen content was measured as before by inert gas diffusion. Autoclave and hydrogen pickup data is given in Figure 4-1, and more comparison of this sample with other Zr samples used in the MUZIC-2 project is given in Topfuel 2015 paper¹⁵¹.

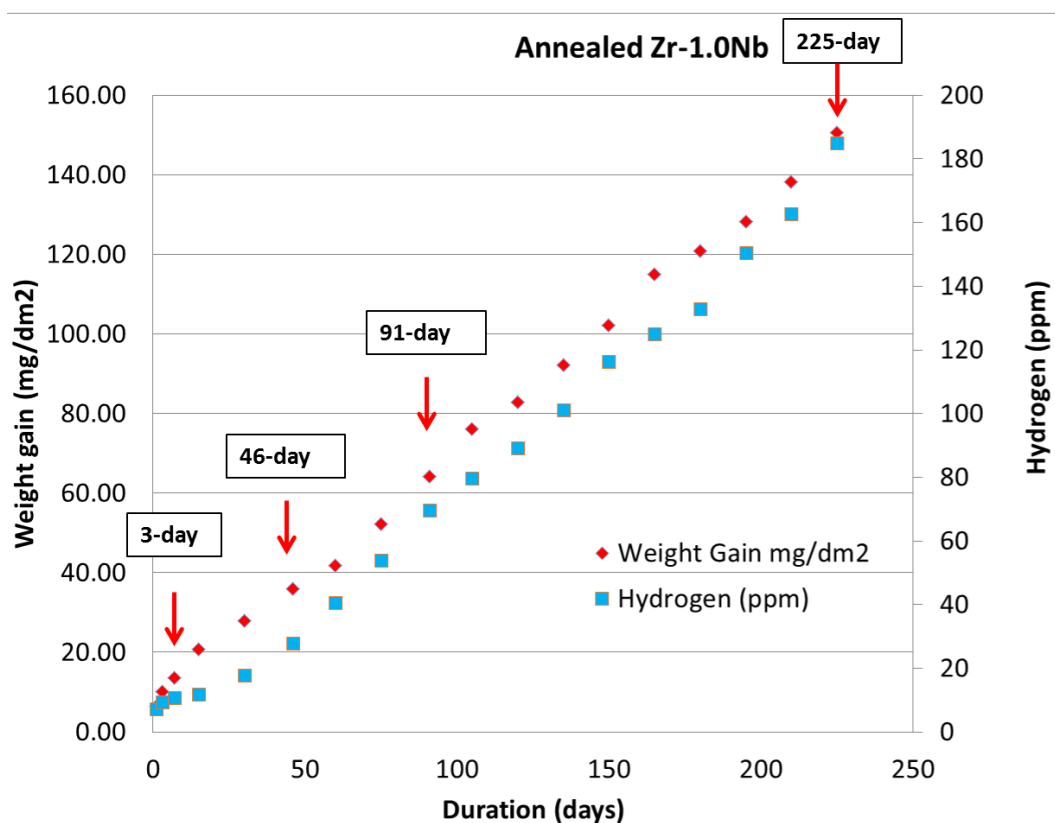


Figure 4-1: Weight gain and hydrogen content data of the annealed Zr-1.0Nb samples, with four samples chosen for this study identified with arrows.

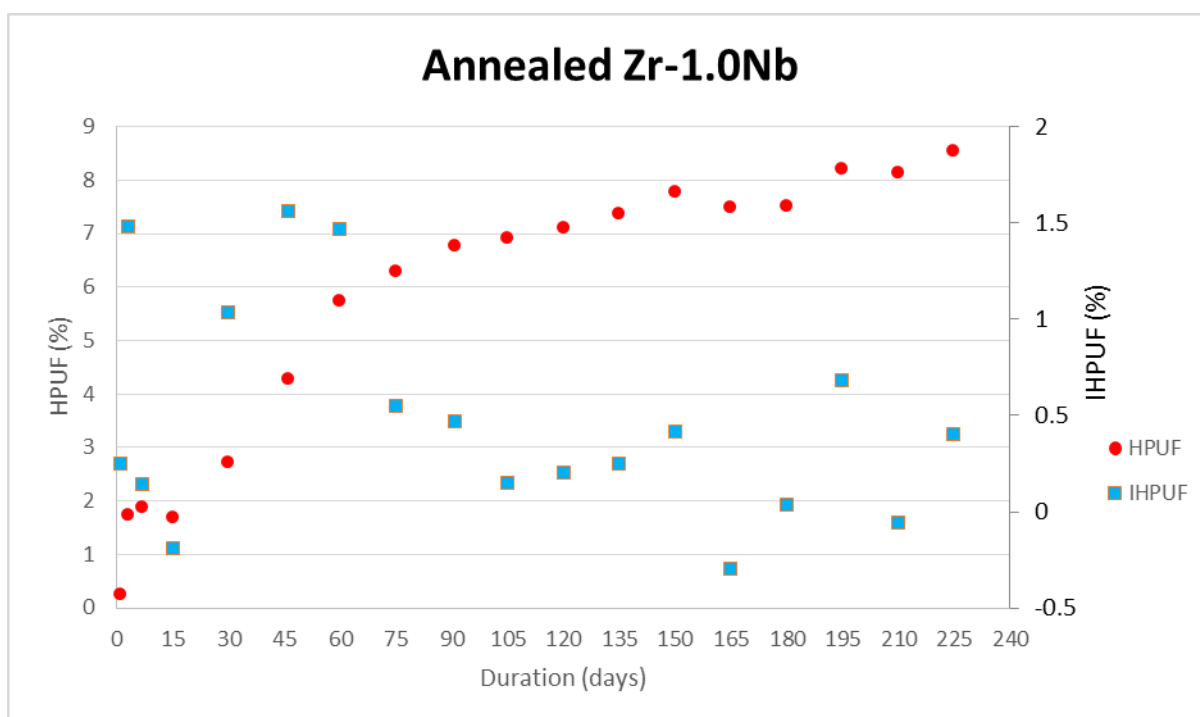


Figure 4-2: Hydrogen pickup fraction and instantaneous hydrogen pickup fraction data of the annealed Zr-1.0Nb samples.

Compared with the as received Zr-1.0Nb samples which have an increasing HPUF after the first transition, with final pickup fraction of 12%, these annealed Zr-1.0Nb samples have a much faster (3-4 times) oxidation rate and also have an almost constant HPUF after the first transition at around 9%. This means that the hydrogen content is linear with the time until 225 days of oxidation, as seen in Figure 4-1.

Four samples were chosen out of this oxidation profile, the first one is after 3 days which represents an early oxidation state. The second one has had 15 days in the autoclave plus another 31 days in a deuterated autoclave to make 46-days of oxidation in total, just before the first-transition which appears from Figure 4-1 to be at approximately 60 days. Compared with as received Zr-1.0Nb samples that have first-transition after 360 days, the transition in the annealed samples is much earlier, and the oxidation rate faster. The third sample has 60 days in the autoclave plus another 31 days in a deuterated autoclave to make 91-days of oxidation in total, which represents a post first-transition stage. The fourth sample has gone through 225

days oxidation in the autoclave, representing a late stage of oxidation. Table 4-1 shows the individual weight gain data, total hydrogen content, hydrogen pickup fraction (HPUF) and instant hydrogen pickup fraction of the selected samples.

Table 4-1: Weight gain and hydrogen pickup data of four samples chosen for this study.

Sample (oxidation days)	Point of oxidation	Weight gain (mg/dm ²)	Hydrogen content (ppm)	HPUF(%)	Instantaneous HPUF (%)
3-day (H ₂ O)	Early oxidation	10.21	9.51	1.73	1.48
46-day (31 day H ₂ O +15 day D ₂ O)	Before 1 st transition	34.29	27.8	4.29	1.56
91-day (60day H ₂ O +15 day D ₂ O)	After 1 st transition	66.39	69.74	6.77	0.47
225-day (H ₂ O)	Post transition	150.61	184.74	8.55	0.40

4.2.MICROSTRUCTURAL ANALYSIS

4.2.1. 3D FIB-SEM

It was noticed during the sample making procedure in the FIB that this set of samples has very uneven metal-oxide interfaces, especially the 3-day, 46-day and 91-day samples. The metal-oxide interface of 225-day sample is relatively flat, presumably because the sample is at a very post-transition stage when the oxidation has breakaway, so that the oxide growth is uniformly fast. Several FIB-SEM images were taken during the 3D FIB process in order to illustrate the unevenness of the interface in Figure 4-3. (a) and (b) from 46-day first transition sample. In (a) it is interesting to see under a huge parallel crack, there is an apparent local acceleration in oxidation rate. It is more common to observe delayed oxidation under parallel cracks. In (b), at both left and right side of the image region have cracks running from the surface vertically towards the metal-oxide interface, penetrating deeper on the right hand side than the left hand side. (c) and (d) are both from the 91-day sample. (c) shows that under an

oxide protrusion, there is a metal grain boundary right in the middle, there are many examples showing that the metal grain boundary does not necessarily relate with advanced or delayed oxide growth, which suggests that matrix orientation and texture do not influence oxide growth. This idea is supported by earlier observation using XRD. Another example is shown in Figure 4-3 that the metal grain boundaries don't influence the oxide thickness above. (d) shows that at some locations there are two layers of cracks while some positions have only one.

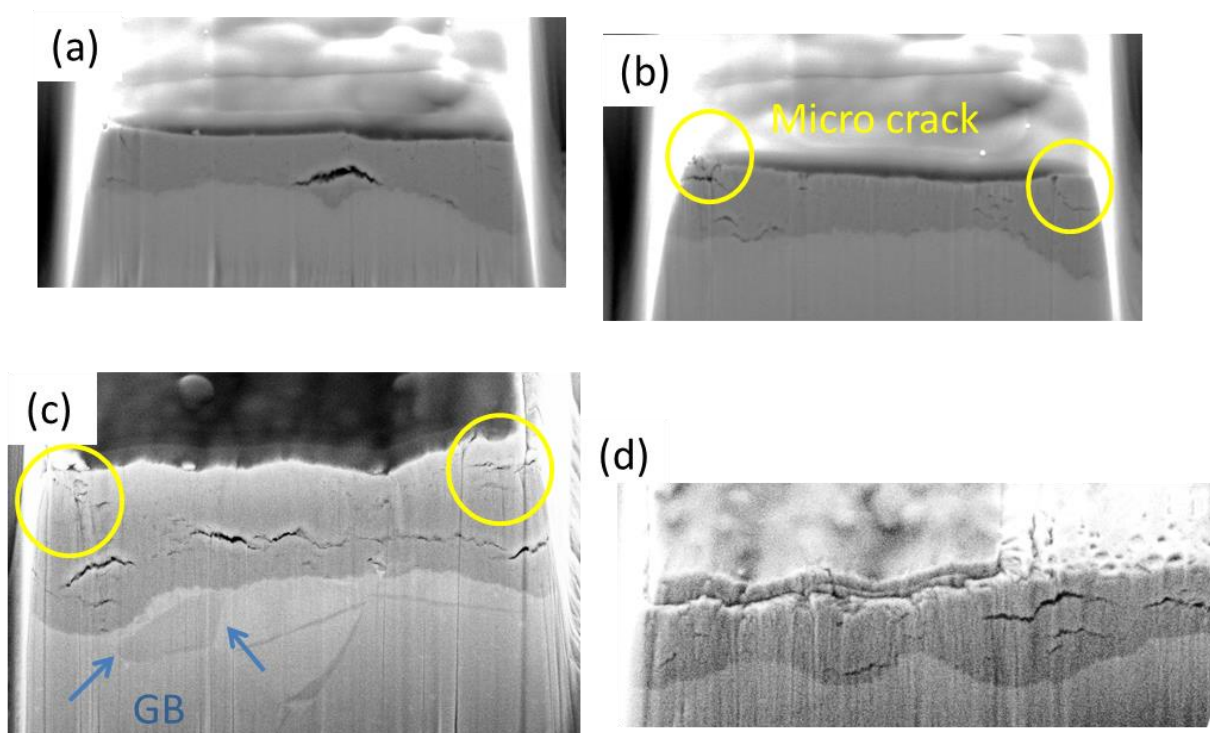


Figure 4-3: Examples of SEM images which was taken during FIB milling process. (a) and (b):46-day first-transition sample. (c) and (d) 91-day post transition sample.

Figure 4-4 (a)-(d) are a series of FIB-SEM slices during the 3D FIB process of the 91-day sample. It is clear to see metal-grain boundaries, β -Zr SPPs and hydrides in the SEM images. (a) shows an SPP right at the metal-oxide interface, while in (b), a few slices further, there is protrusion of oxide near the SPP. However, it is noticeable that this protrusion does not create a huge mismatch between the SPP and oxide, as shown in (c) that the metal-oxide interface is

uniform again. (d) shows that when the FIB slices have passed through the SPP, the oxide-metal interface is uniform, also noted that the metal grain boundary underneath doesn't have an influence either.

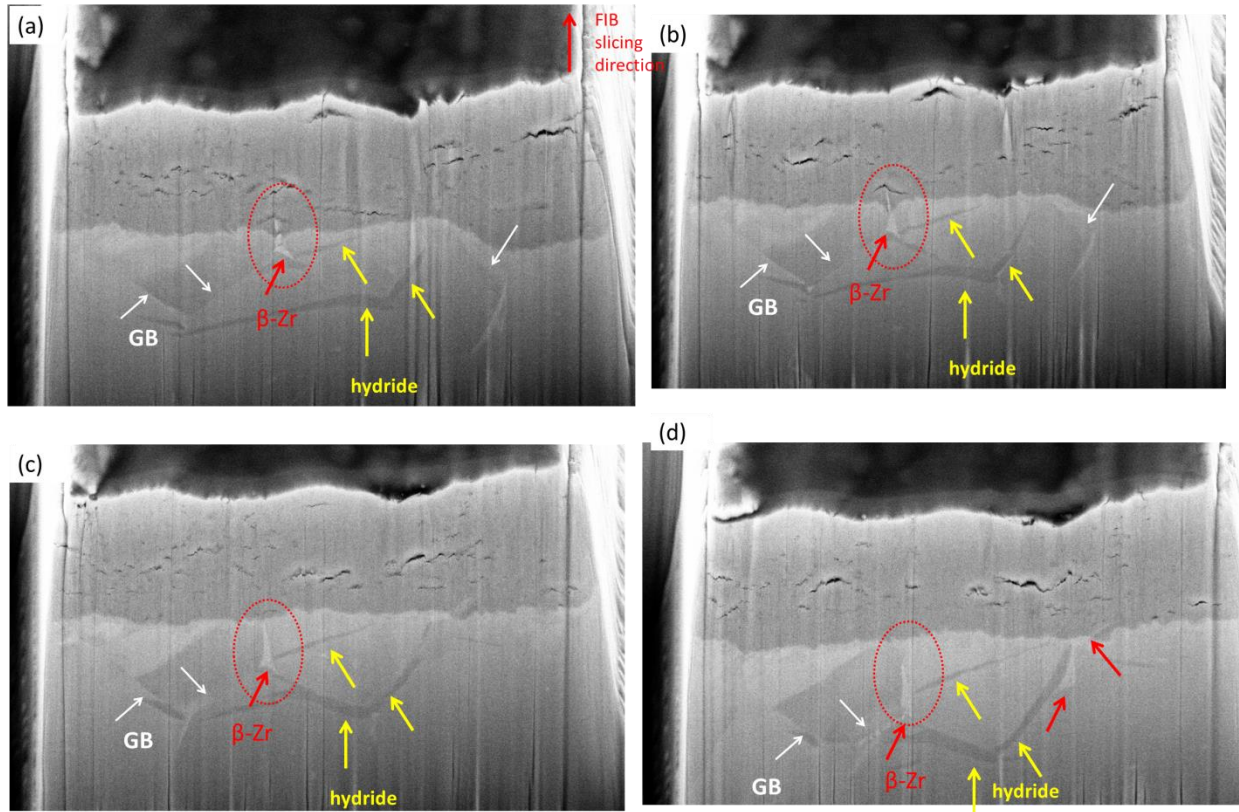
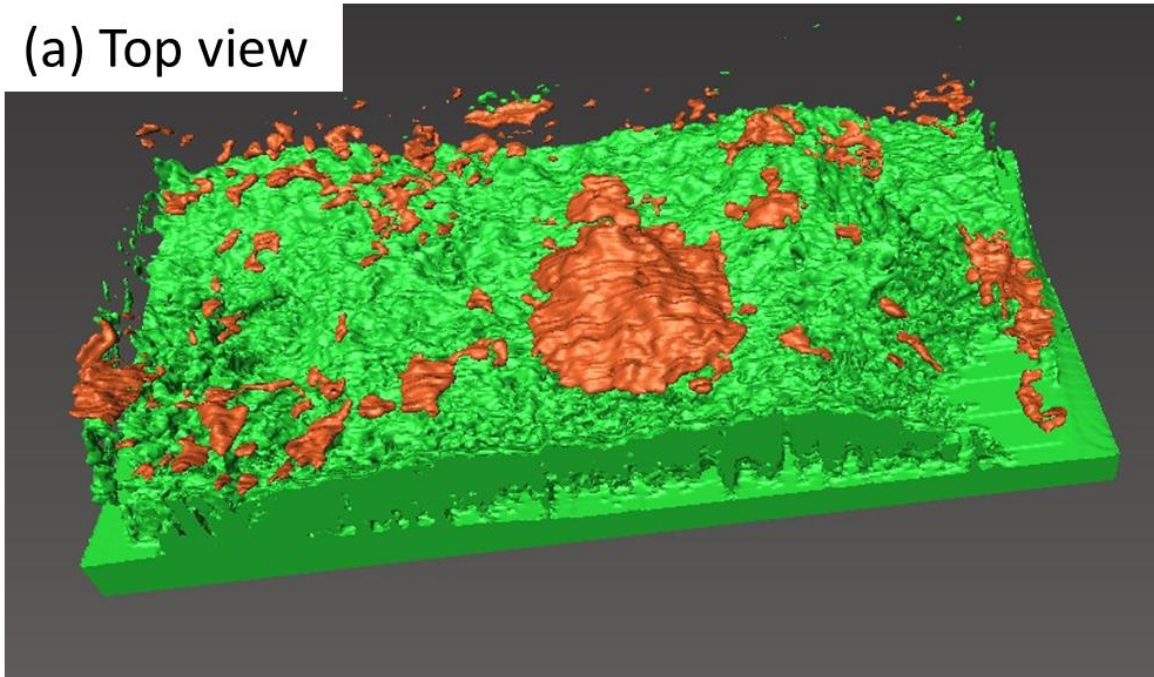


Figure 4-4: 3d-FIB slicing SEM images across a β -Zr SPP at the metal-oxide interface in the 91-day post transition sample. (a)-(d).

As seen from previous observation, the metal-oxide interface of annealed Zr-1.0Nb is often very uneven, often accompanied with layers of cracks at different location. By doing 3D FIB reconstruction, it is possible to have a more comprehensive view of the metal-oxide interface and crack distribution. Figure 4-5 shows the top and side view of 91-day sample. The top view (a) shows a large patch of cracks on the top of the metal-oxide interface, suggesting all the big cracks are interconnected. The side view (b), on the other hand, shows the uneven distribution of cracks and their relationship with metal-oxide interface. Particularly on the left side of (b), there is a protrusion of oxide where some cracks near the metal-oxide interface

have shown, suggesting a local transition has happened while the rest of the oxide is still growing.

(a) Top view



(b) Side view

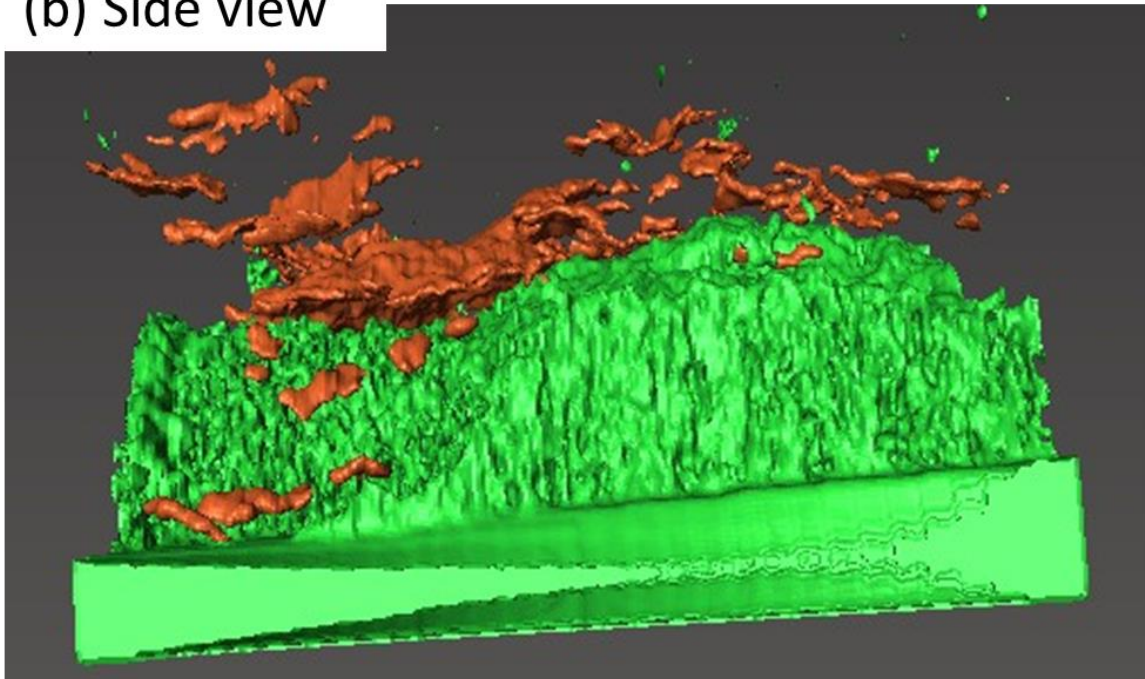


Figure 4-5: 3D-FIB reconstruction results of 91-day annealed Zr-1.0Nb sample, top view (a) and side view (b).

4.2.1. (S)TEM

Except for the 225 days sample which takes a very long time to make because the oxide is 13 μm thick, from all the other samples two TEM samples were made from each in order to make sure the selected area is representative. Figure 4-6 shows typical STEM HAADF overview pictures of the four samples chosen in this study. The left column of images shows regions where the metal-oxide interface is relatively flat, while the right column of images shows very uneven metal-oxide interfaces. This indicates that oxidation rate varies a lot at different locations in the samples.

The 3-day sample represents the early stage of oxidation. The even part of the oxide (a-1) has an average thickness of 0.8 μm . The oxide is very dense at most positions, with only some micro cracks 100-150 nm in length parallel to the even metal-oxide interface. At the uneven interface region as seen in (a-2), the oxide thickness ranges from 0.5 μm to 0.9 μm . There is one big crack 600 nm in length, about 50 nm from the metal-oxide interface.

The 46-day sample is just before the first transition. The even part of the oxide (b-1) has an average thickness of 2.6 μm . The middle part of the oxide contains micro cracks around 200-300 nm in length. In a region about 700 nm above the metal-oxide interface, there are several parallel cracks around 500nm in length. In the uneven interface part (b-2), the oxide thickness ranges from 3.4 μm to 4.2 μm . The top part of the oxide has big cracks around 800 nm in length, followed by a 2.5 μm region with only 300 nm micro cracks, until at the metal-oxide interface there is the first layer crack of 500 nm suggesting another transition is about to happen. Detailed ASTAR analysis of this region is discussed later.

The 91-day sample is post first transition. The even part of the oxide (c-1) has an average thickness of 5.2 μm . At around 2.2 μm from the metal-oxide interface, there is one layer of cracks of around 1.4 μm in length, which are likely to come from the first transition. (c-2) is

from a FIB-SEM image, showing that some parts of the sample have two layers of cracks, while some parts have one. Figure 4-6 (c) gives more examples of uneven metal-oxide interfaces in a larger area in FIB-SEM images.

The 225- day sample represents a stage for post transition. It has an average oxide thickness of 13.7 μm . It shows four layers of cracks, suggesting it has gone through four transitions, each layer of cracks has around 3.2-3.5 μm in between.

It is worth mentioning that the high temperature annealing process not only makes the sample oxidise much faster, but also changes the metal microstructure. As seen in (d-2), the metal grains are around 12-14 μm in diameter. Detailed SPP analysis is in chapter 4.4.

4.2.1. ASTAR analysis

Due to time constraints, ASTAR TEM precession diffraction was used to study the microstructure and micro texture only of the 46-day sample, as shown in Figure 4-7. The area chosen is shown in the STEM HAADF image in (a). It is easy to see the oxide has a very uneven interface in a lower magnification SEM image of this area taken during FIB lift out in (b), with the chosen area highlighted. From the STEM HAADF image, the left part of the oxide has an oxide thickness of 2.6 μm and we can guess that locally it has just gone through first transition with all the cracks about 1 μm above the metal-oxide interface. The right part of the oxide has a much faster oxidation rate with a 4.2 μm oxide thickness. The cracks associated with the first transition are seen at the very top surface, followed by about 2.5 μm of dense oxide without cracks, and the first micro-cracks for the second transition appear right at the metal-oxide interface which may indicate the beginning of a local second transition.

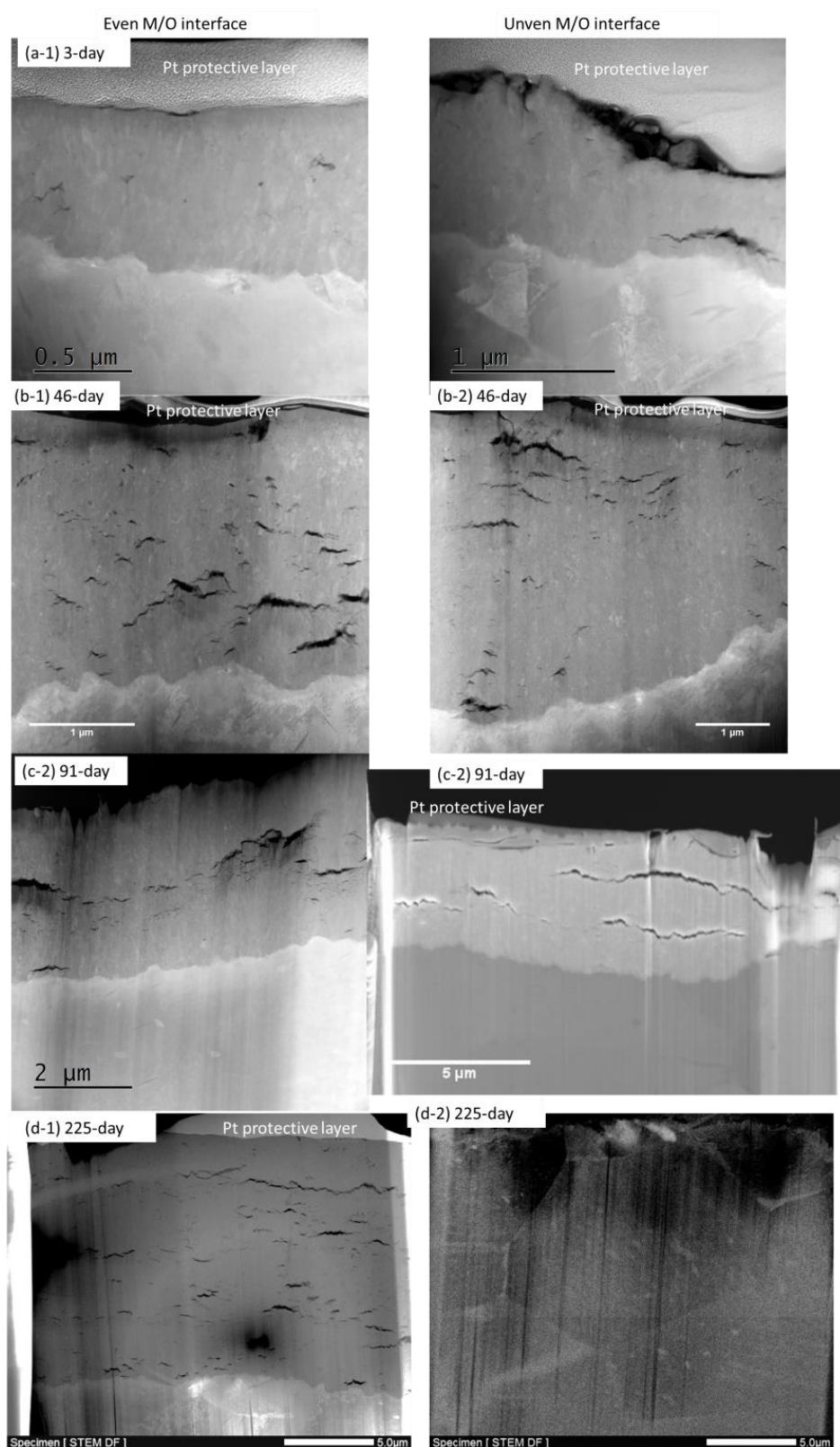


Figure 4-6: STEM HAADF overview pictures of the four samples: (a) 3-day: early oxidation; (b) 46-day: first transition; (c) 91-day: post transition; (d) 225-day: late transition. The left column of images show the even part of metal-oxide interface, while the right column of images show the uneven metal-oxide interface. (c-2 is a FIB-SEM image).

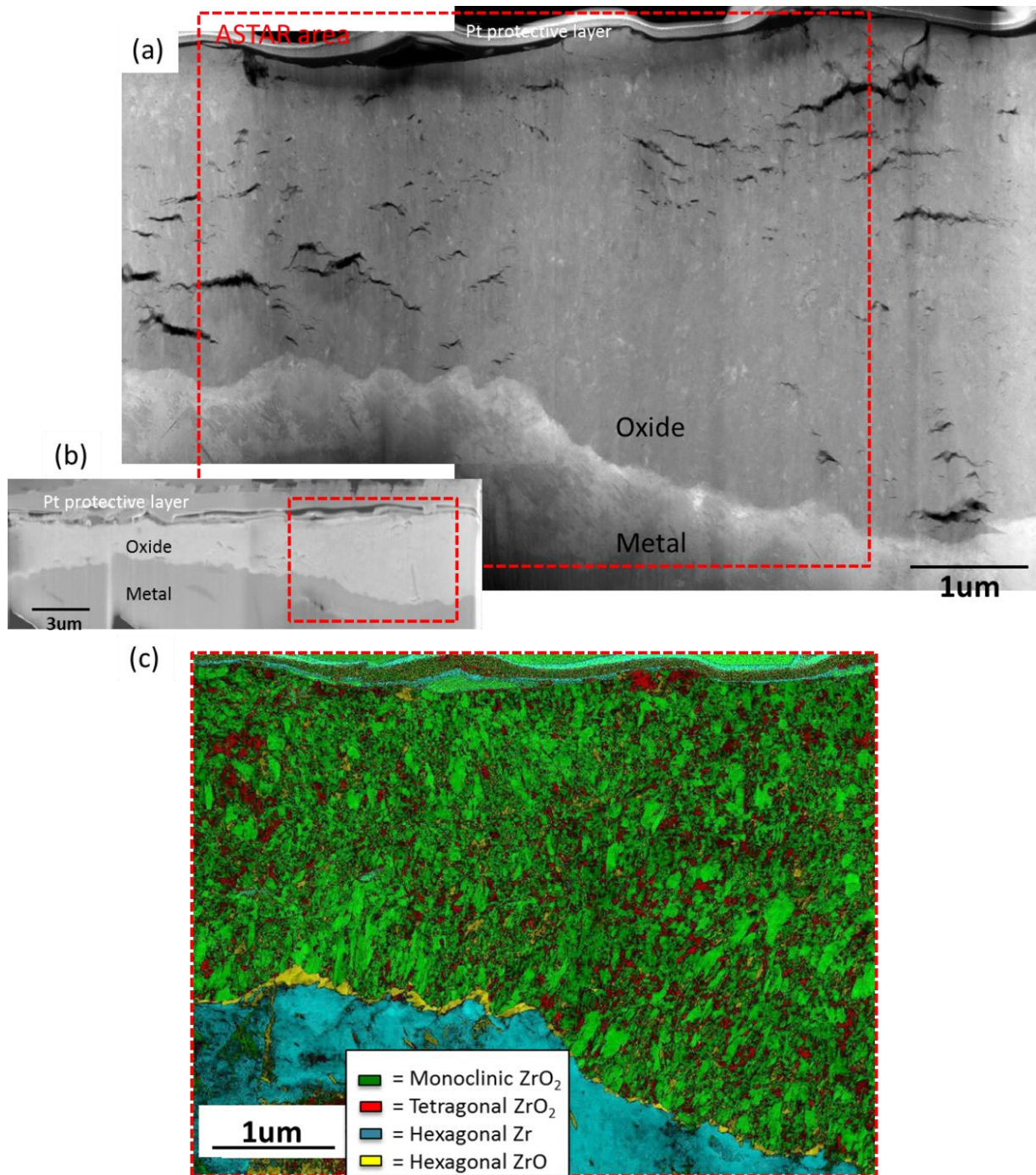


Figure 4-7: (a) STEM HAADF overview of the TEM lamella of the 46-day annealed Zr-1.0Nb sample with the position of the ASTAR mapping indicated. (b) lower magnification FIB-SEM image showing the unevenness of the metal-oxide interface in this area; (c,d,e) ASTAR mapping: the pattern quality map, phase map and texture map of the region indicated.

Comparing with RXA Zr-1.0Nb, it shows a more complicated oxide grain structure. It is hard to see any clear identification of the oxide microstructure at the top surface, possibly due to

the smaller grain size and complicated diffraction patterns. In the middle part towards the metal-oxide interface, the oxide grains become more organised and some suggestion of columnar grain growth.

It is interesting to see that at the curved metal-oxide interface, the columnar oxide all grows perpendicular to the metal-oxide interface, not parallel to the macroscopic oxidation direction. This also suggests that the oxide growth happens locally rather than macroscopically.

Figure 4-7 also shows the distribution of monoclinic and tetragonal oxide phases. Most of the columnar oxides are identified with the monoclinic-ZrO₂ (m-ZrO₂) structure. However, compared with RXA Zr-1.0Nb samples, this annealed sample has more tetragonal-ZrO₂ (t-ZrO₂) grains, some of them around 40-50 nm in diameter and scattered in the equiaxed oxide from the top surface throughout the oxide thickness. It is interesting to see that more tetragonal oxide exists where there are no cracks, and this might be associated with stress stabilisation of tetragonal oxide, while at some locations there are tetragonal oxide grains around the cracks as well. This indicates that at the crack region, there may use to be more tetragonal grains, but they are destabilised by cracking of the oxide, which relates with tetragonal and monoclinic oxide grain transformation. At the metal-oxide interface, there are smaller grains identified as a discontinuous layer of Widmanstatten-type suboxide with the hexagonal ZrO structure predicted with ab initio modelling, with P-62m symmetry and lattice parameters $a=5.31 \text{ \AA}$ and $c=3.20 \text{ \AA}$, while other grains match Zr metal with P 63/m symmetry and lattice parameters $a=3.23 \text{ \AA}$ and $c=5.14 \text{ \AA}$. The same area will be analysed in the EELS mapping in Chapter 4.5.

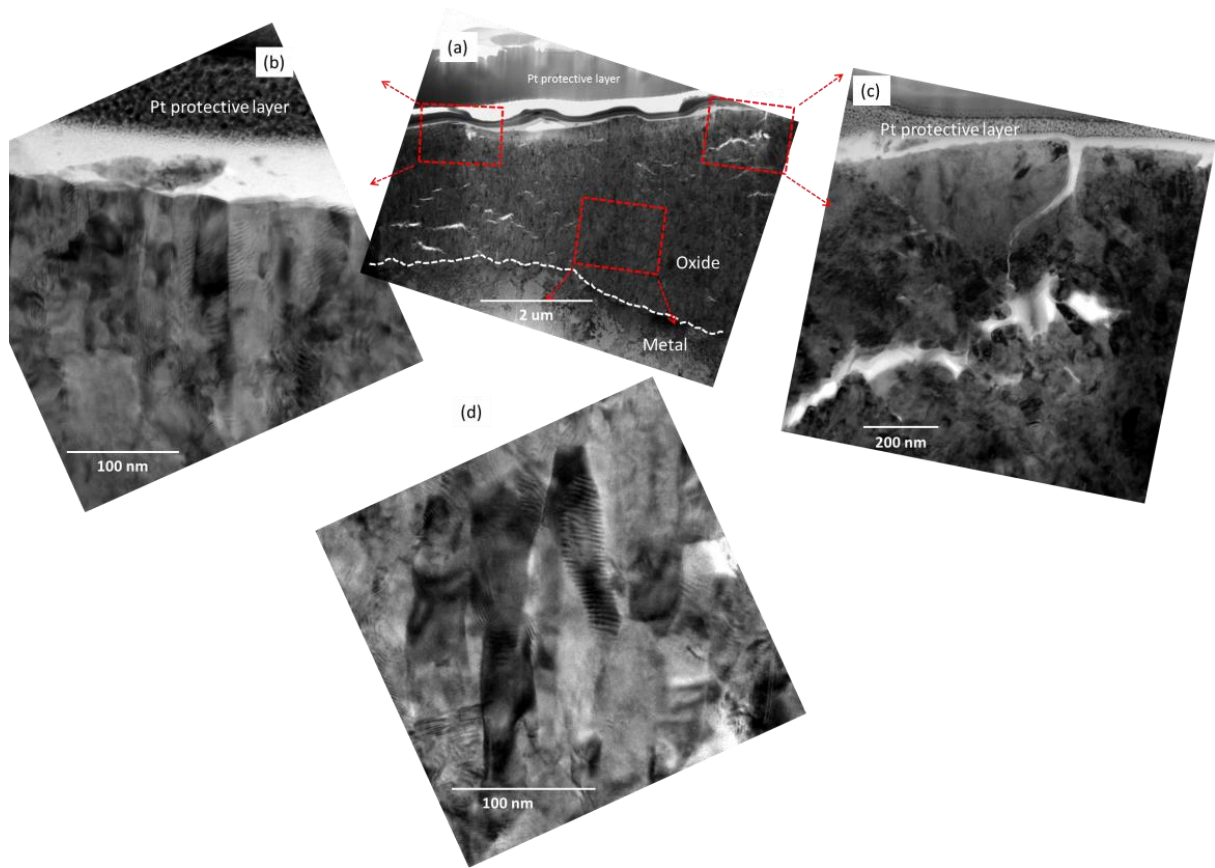


Figure 4-8: TEM BF images of oxide grain structures in the 46-day annealed Zr-1.0Nb sample: (a) overview of oxide microstructure with positions of the high magnification imaging (b) (c) (d) highlighted. (b) top surface of the left part of the oxide where one transition has happened, (c) right side of the oxide which has begun the second transition. (d) higher magnification image of columnar oxide grain structure in the middle of the oxide.

Further TEM BF imaging was carried in the same region as shown in the ASTAR map.

Figure 4-8 illustrates the complexity of oxide grain structures in this annealed Zr-1.0Nb sample. (a) shows the position where the higher magnification images were taken. On the left hand side of the oxide as shown in (b), the top of the oxide has columnar grains around 20-25 nm in width. It is very unusual to see oxide have a columnar structure right up to the oxide-water interface. In this material, this feature is not uncommon in four different TEM samples with Pt protective layer intact, so I can be confident that this is not just a TEM sample that has broken in the middle of the oxide. On the right hand side of the imaged region where the rate of oxidation has been locally much faster, a vertical crack runs from the surface 400 nm into the oxide and then develops into a bigger crack parallel to the metal-oxide interface. The

oxide grain structure is quite disorganised in this area, but around the parallel crack there are equiaxed oxide grains. (c) represents the middle part of the oxide which consists of normal columnar oxide grains, but with an average size of 35 nm which is smaller than I usually observed in RXA Zr-1.0Nb (50 nm), see Figure 3-4

4.3.POROSITY IN THE OXIDE

By using Fresnel imaging, different types of porosity can be seen in TEM imaging. Generally speaking, these annealed samples have more porosity compared with the RXA Zr-1.0Nb samples studied previously.

Figure 4-9 shows several examples of different types of porosity in the 91-day Zr-1.0Nb sample. In (a), which is around 1 μm away from the metal-oxide interface, there is a lot of continuous porosity along the columnar grain boundaries, although there are also some isolated pores around 2-4 nm in diameter inside the columnar grains. 200 nm away from the metal-oxide interface as seen in (b), there are some small flake-like pores around 10-20 nm in length parallel to the metal-oxide interface. The vertically interconnected porosity gradually becomes disconnected around 50 nm from the metal-oxide interface. Also, lying at the metal-oxide interface, another type of flake-like porosity is seen under the columnar grains.

In general, comparing with the RXA Zr-1.0Nb in Chapter 4, the annealed Zr-1.0Nb has much more porosity in the oxide. Figure 4-10 (a) and (b) are the lower magnification over focus images showing examples of the huge amount of individual pores scattered throughout the oxide, many of the columnar grains are also decorated with vertically continuous porosity as well. My observations in over 10 TEM samples all confirm that the oxide in the annealed samples is very porous.

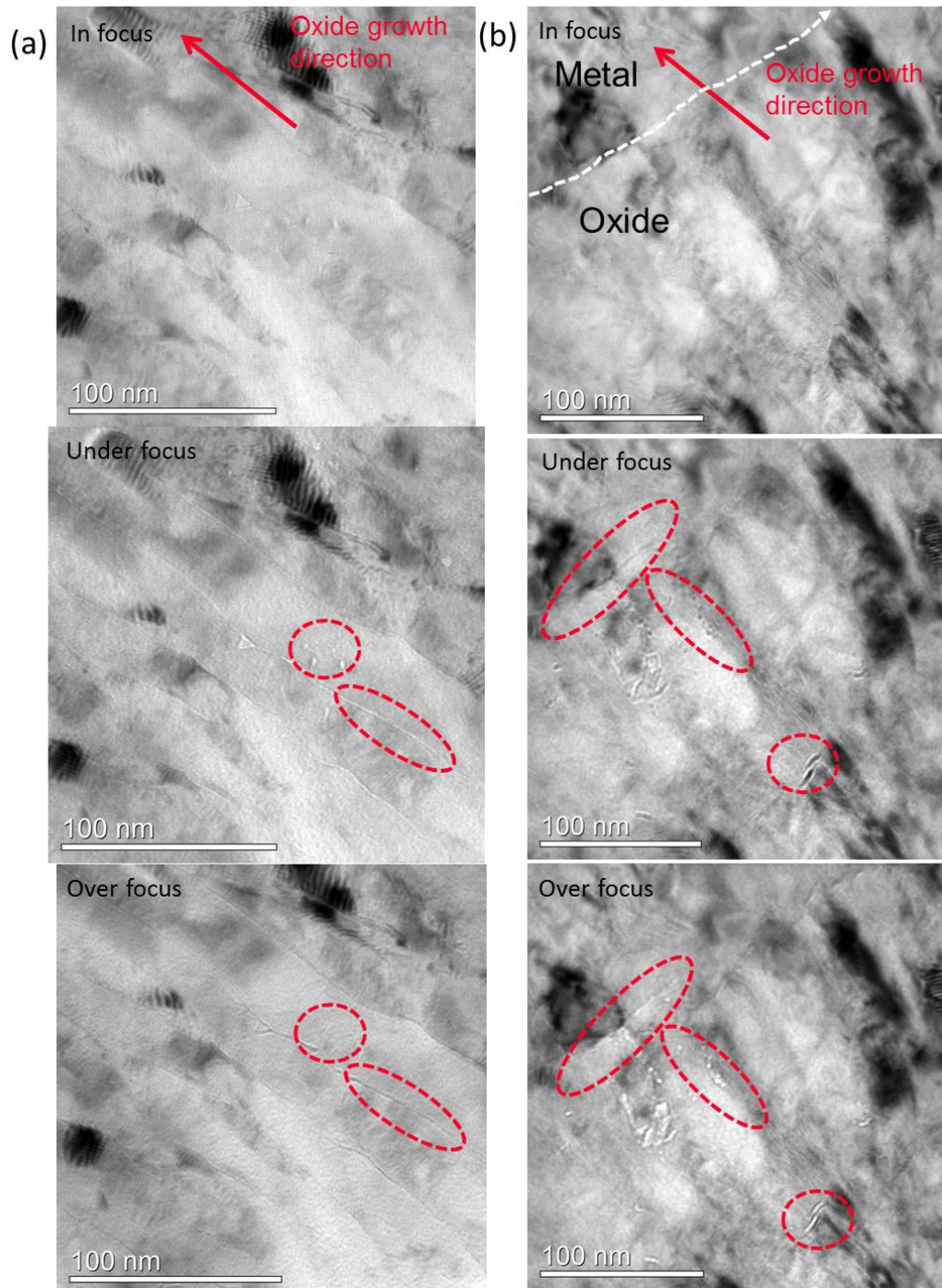


Figure 4-9: (a) and (b): Through-focal imaging of fine pores (circled) in the oxide on the 91-day Zr-1.0Nb sample. The pores are invisible in top in-focus images ($\Delta f = 0$ nm), but show Fresnel contrast in the middle under-focussed images ($\Delta f = -980$ nm) and in the lower layer over-focussed images ($\Delta f = +980$ nm). Different types of porosity are revealed at different locations: (a) in the middle of the oxide: vertically interconnected pores along the columnar oxide grain boundary and individual pores; (b) near the metal-oxide interface: disconnected pores towards metal-oxide interface for around 50nm, 20nm flake-like parallel interconnected pores at the interface, connected porosity under the columnar grains which is parallel to the metal-oxide interface.

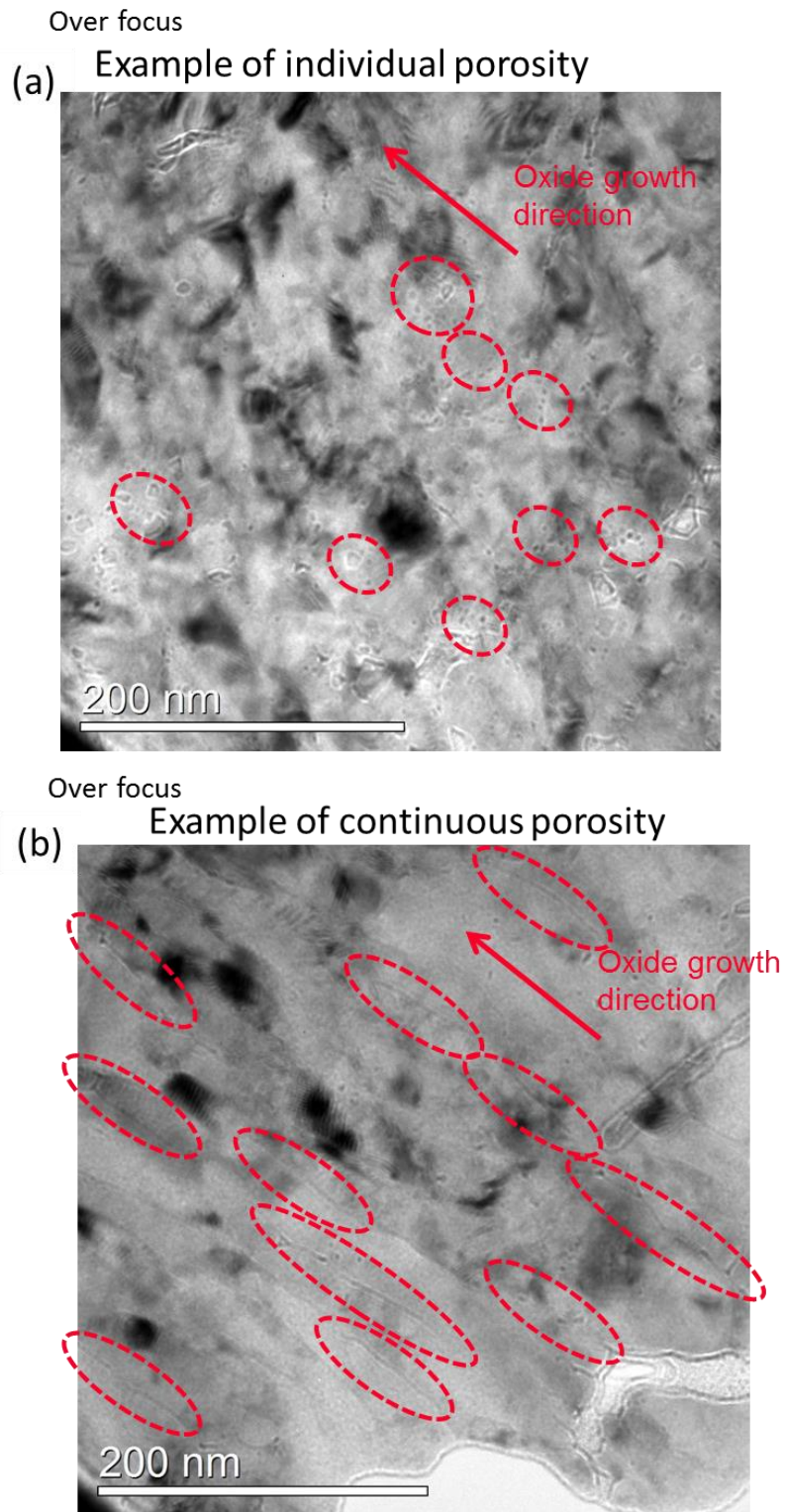


Figure 4-10: (a) and (b) Over focus images showing examples of the huge amount of individual pores and vertically interconnected porosity in annealed Zr-1.0Nb sample.

4.4.SPP

4.4.1 SPP distribution in (S)TEM

Based on the Zr-Nb phase diagram, after an anneal at 720°C for 24 hours the alloy should be in the β -Zr region and so should have β -Zr as the second phase particles (Figure 1-5 and Figure 2-3). Alloys containing β -Zr have a very different microstructure to the materials described above, especially in the size, shape and distribution of the second phase particles as discussed in the literature review.

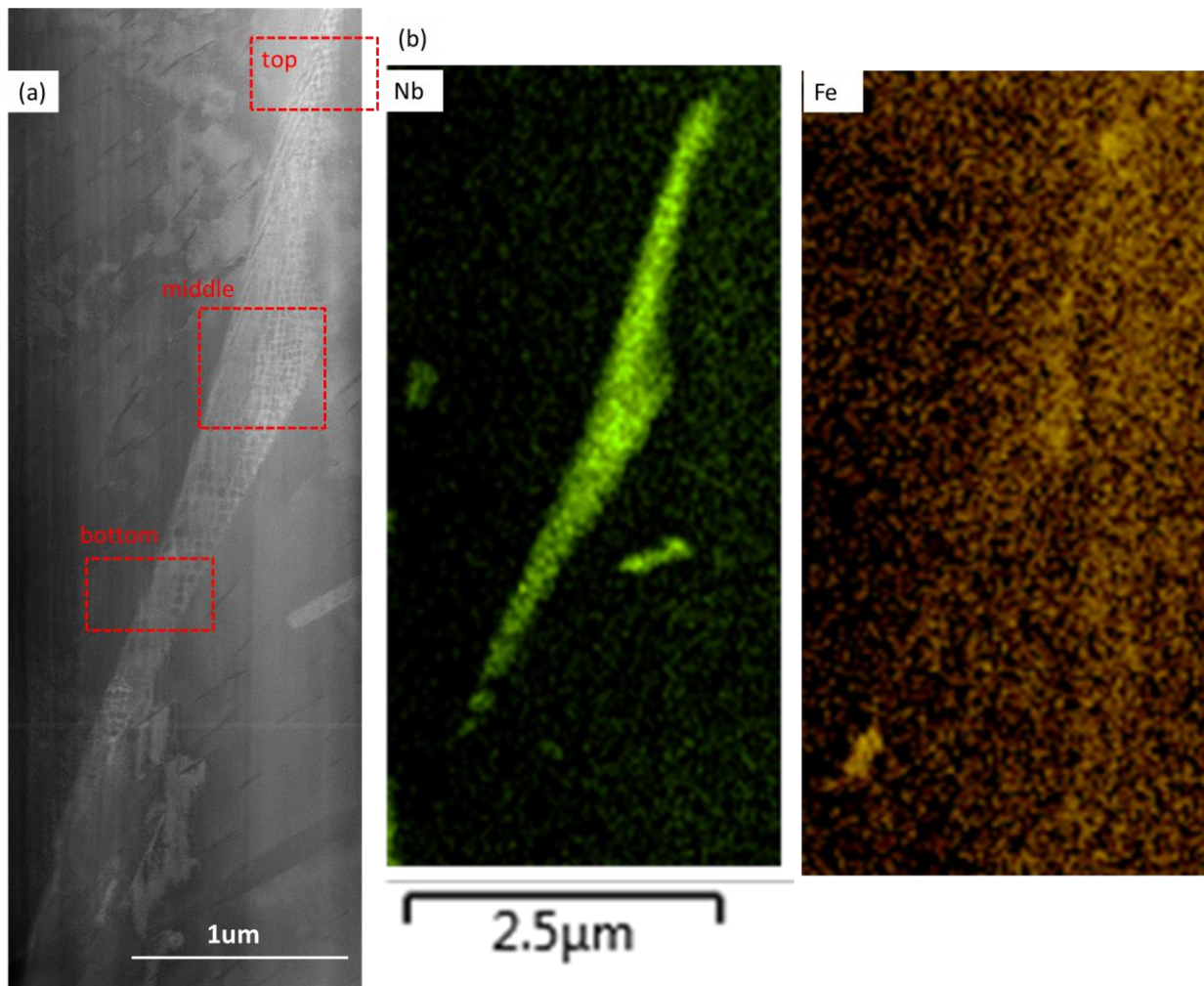


Figure 4-11: β -Zr phase at a metal grain boundary: (a) STEM HAADF overview image of the SPP (b) EDX mapping of Nb and Fe. Three positions are highlighted with higher magnification STEM HAADF and TEM BF image in Figure 4-12.

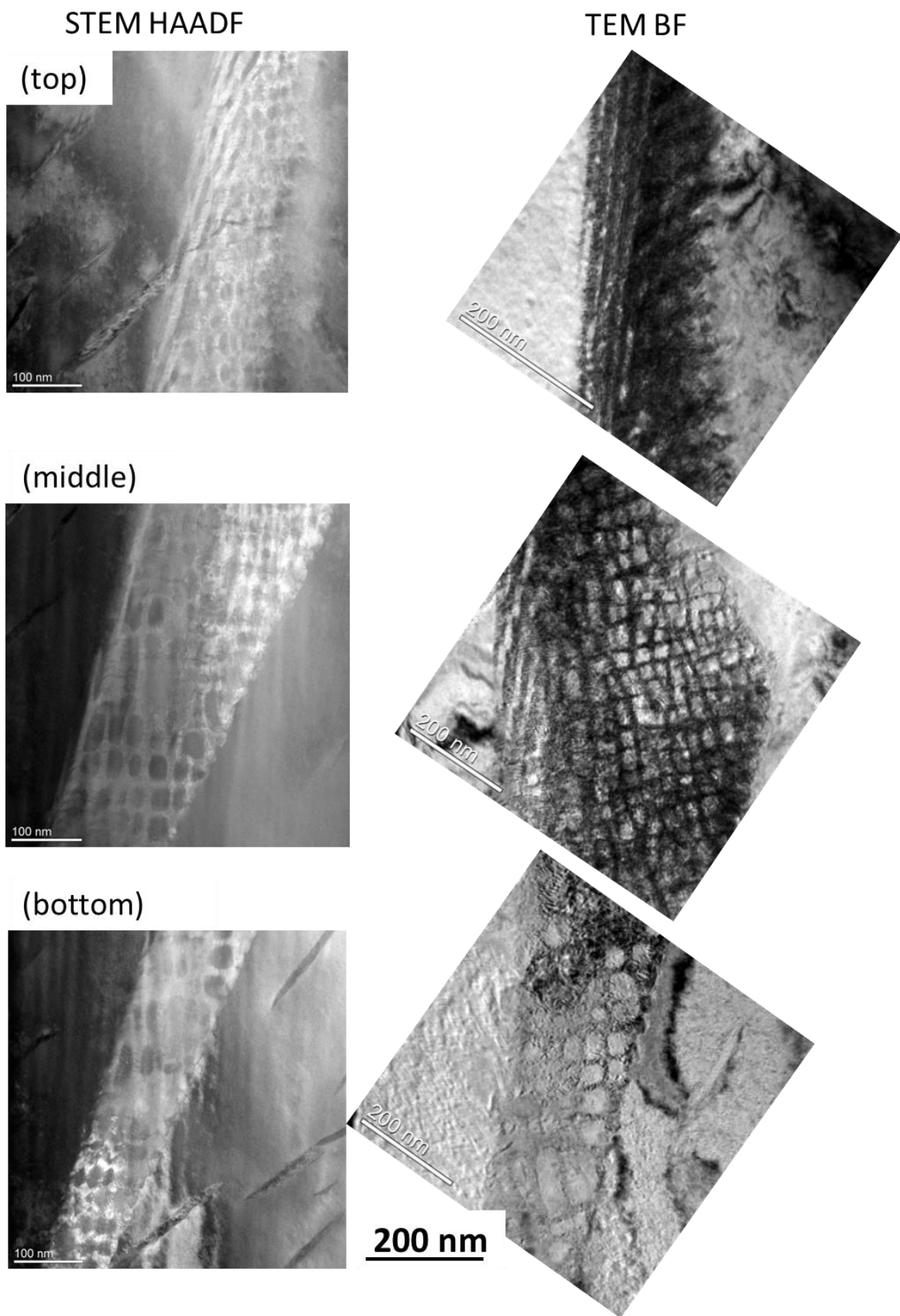


Figure 4-12: STEM HAADF and TEM BF images of the top, middle and bottom part of the β -Zr particle.

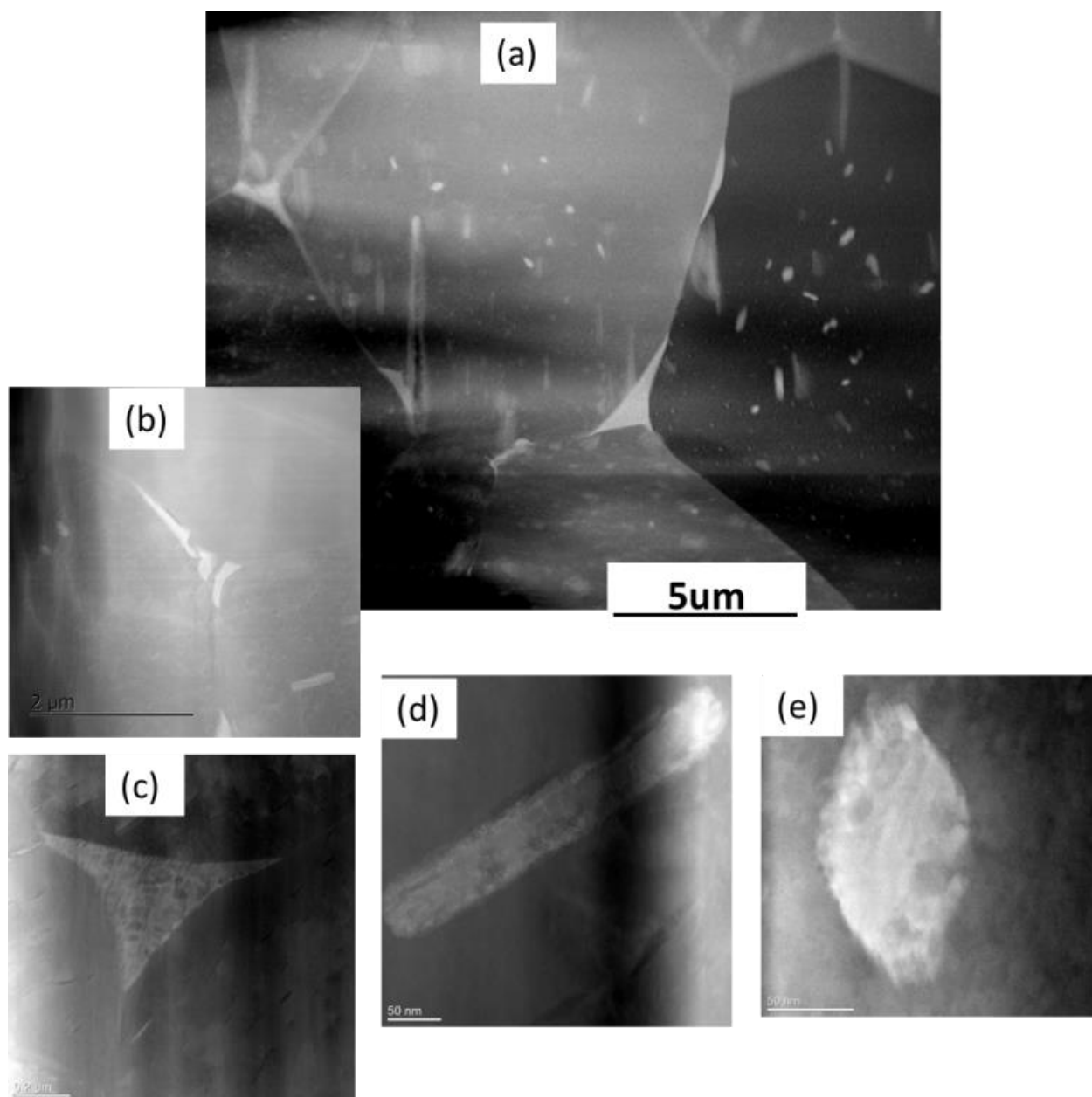


Figure 4-13: STEM HAADF images of different types of SPPs in annealed Zr-1.0Nb metal. (a) Overview of metal grains and SPPs, (b) and (c) SPPs at metal grain boundary triple point, (d) and (e) SPPs inside the metal grains.

Figure 4-11 shows one example of a large β -Zr SPP at a metal grain boundary. (a) shows the overview of this SPP, which has a roughly triangular shape, with three sides of 3.9 μm , 1.5 μm and 2.5 μm . The EDX maps show that this SPP is Nb-rich, but also contains some Fe. Figure 4-12 shows that the SPP is nano crystalline with very complicated microstructure, the top part of the SPP, with thin strips of black and white contrast of 15 nm thick and 890 nm long. On the right hand side are smaller equiaxed dark grains 15 nm in diameter in a lighter

matrix. Noting that in STEM HAADF images, the contrast comes primarily from average atomic mass, this suggests that the light part is heavier than the dark part. At the middle part of the SPP where it has a width of 634 nm, it consists of mostly equiaxed grains around 30 nm in diameter. This area has also been studied by EELS analysis as shown in Figure 4-18 and Figure 4-19. Similar observations can be seen in the (d-1) and (d-2) at the bottom part of this SPP.

Figure 4-13 shows other types of SPPs in annealed Zr-1.0Nb metal. At the metal grain boundary triple point, there are normally triangular shaped SPPs with different sizes up to 1-2 μm or even larger, while inside the metal grains there are smaller SPPs like the rectangular one in (c), 77 nm width and 500 nm in length, and the diamond-shaped with 120 nm diameter. The distribution of SPPs agree with previous work on β -Zr second phase in the high temperature annealed alloys.

4.4.2 EDX mapping of SPPs

Figure 4-14 shows examples of β -Zr SPPs in an oxidised and metallic state in the 46-day sample. There are two big β -Zr SPPs in this area, both triangular in shape. The first one (SPP 1) lies at the metal-oxide interface, the geometry is $1.2 \mu\text{m} * 0.65 \mu\text{m}$. EDX mapping in (b) and elemental concentration analysis in (c) suggest it contains mainly Zr and Nb, with a tiny amount of Fe concentration inside. The top part of SPP1 is oxidised as seen from the oxygen concentration increase, while the bottom part of SPP1 is still in the metal matrix and remains unoxidised. By comparing the Zr/Nb ratio from these two parts, it seems that while the metallic β -Zr oxidises, the Zr/Nb ratio increases from 3.45 to 4.80, suggesting that Nb might leak out during oxidation.

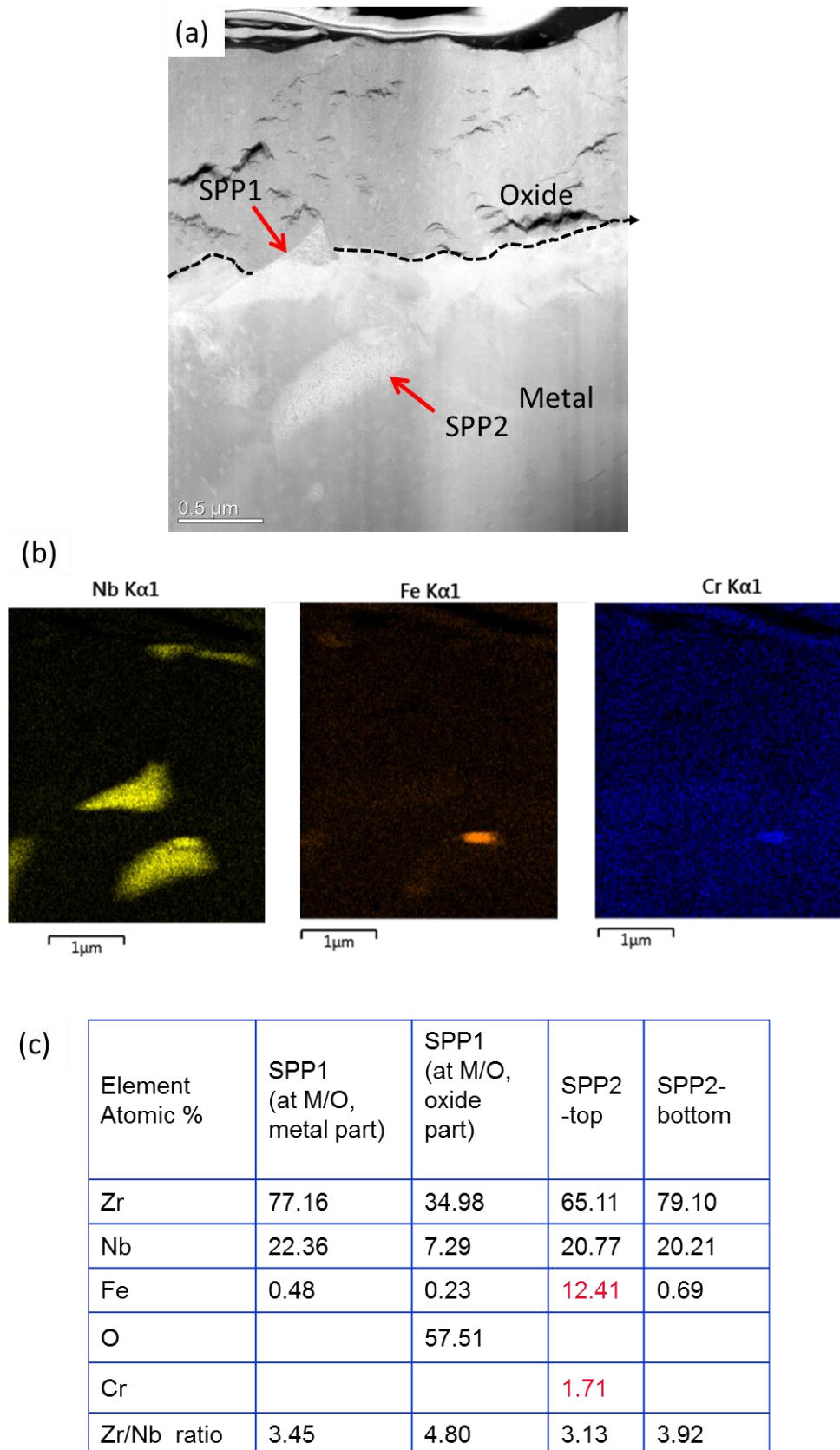
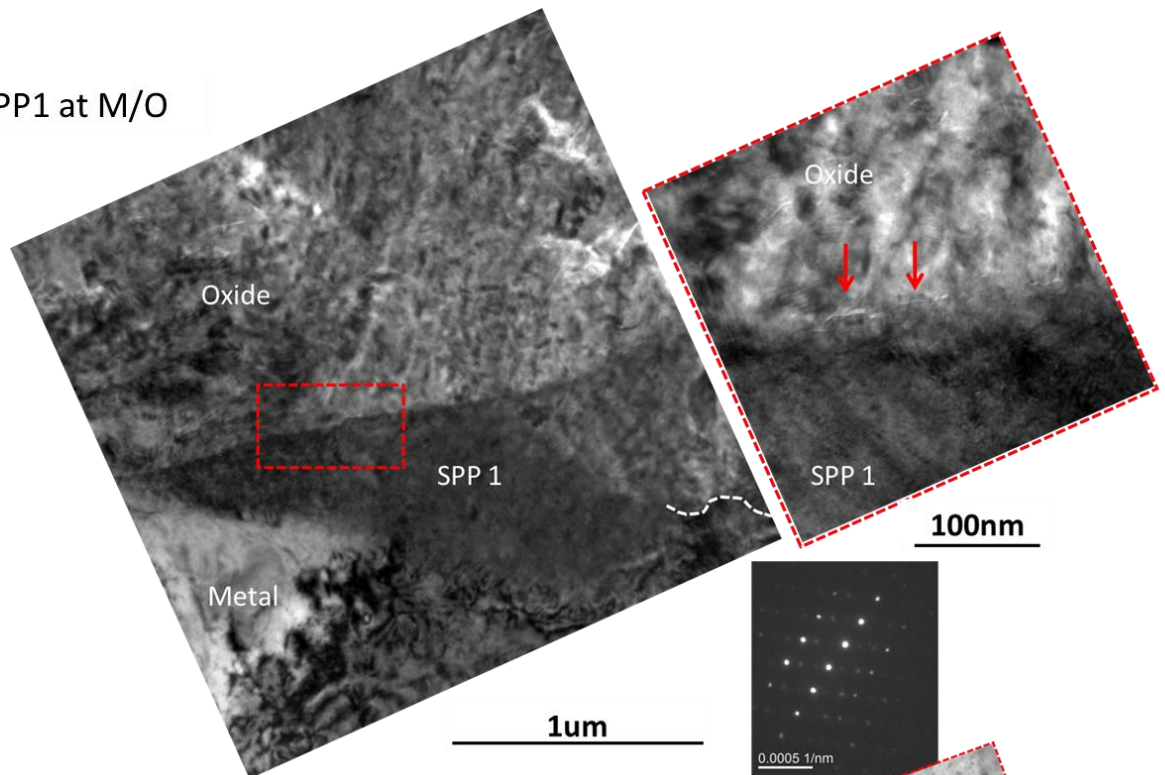


Figure 4-14: (a) STEM HAADF image of two β -Zr SPPs with EDX maps in (b) showing Nb, Fe and Cr.(c) Concentration of different part of these two SPPs in terms of Zr, Nb, Zr/Nb ratio, Fe, Cr and oxygen content.

(a) SPP1 at M/O



(b) SPP2 in metal

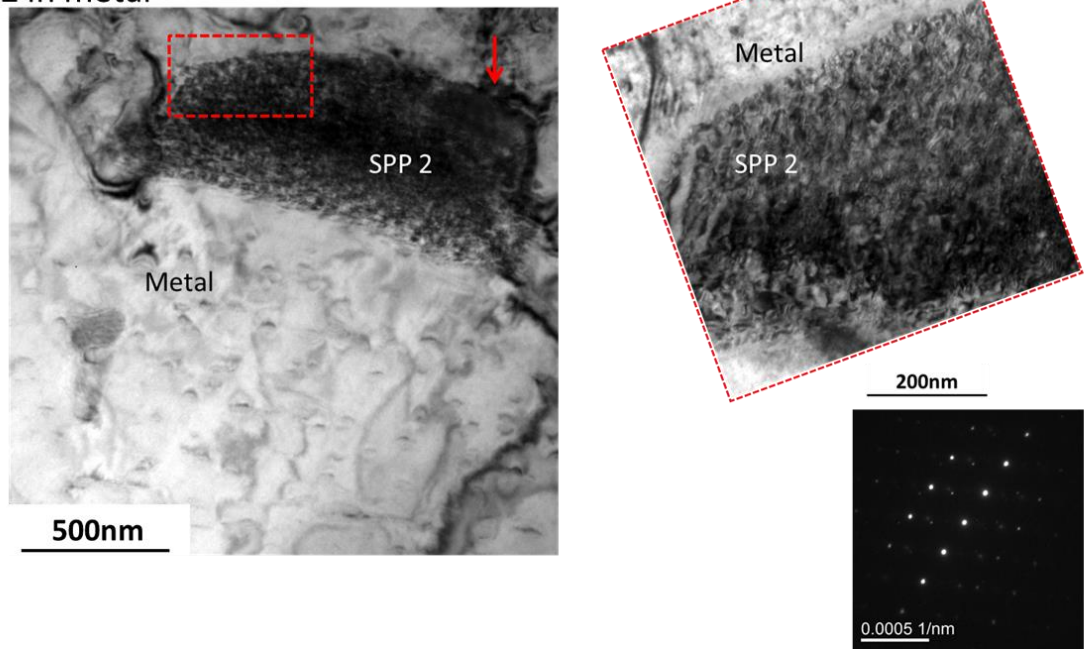


Figure 4-15: Further analysis of Figure 4-14: (a) TEM BF images of SPP 1, with a high magnification image of the oxide-SPP interface containing micro cracks. The inset diffraction pattern from the oxidised part of the SPP suggests it is crystalline. (d) TEM BF images of SPP 2 and diffraction pattern from SPP2.

In the TEM BF image of SPP1 in Figure 4-15(a), there are some micro cracks along the oxide-SPP interface due to the volume expansion after oxidation, and the diffraction pattern suggest that it still remains crystalline after oxidation.

The other β -Zr SPP (SPP 2) in the metal contains 12.41 at% Fe and 1.71 at% Cr at the top part of the SPP. The whole SPP 2 is 1.3 μm by 0.55 μm , with the Fe/Cr enriched part around 100 nm by 300 nm.

Another example of β -Zr been oxidised at metal-oxide interface is given in Figure 4-16. There are also three SPPs in the 225-day annealed Zr-1.0Nb sample. Since the oxide is more than 10 μm thickness, it is very difficult to make a FIB liftout sample, so that there is a crack in the middle of the oxide. It is clear to see that the β -Zr SPP that is partially in the oxide and contains Nb. In the metal, there is one β -Zr SPP that contains both Fe and Nb. A similar SPP is seen in the EDX map in the oxide however the contrast of the SPP is not visible in the STEM HAADF image due to the crack.

Figure 4-17 shows an example of an oxidised β -Zr SPP in the 225-day sample. EDX mapping shows that after oxidation, there is still Nb in the SPP, as well as Cr and Fe, together with traces of Ni. STEM HAADF image also confirms with the shape of SPP. It worth noting that although there is volume increase of SPP when oxidised, the SPP does not seem to associate with the horizontal cracks, however, it does connect the horizontal cracks vertically due to its large size.

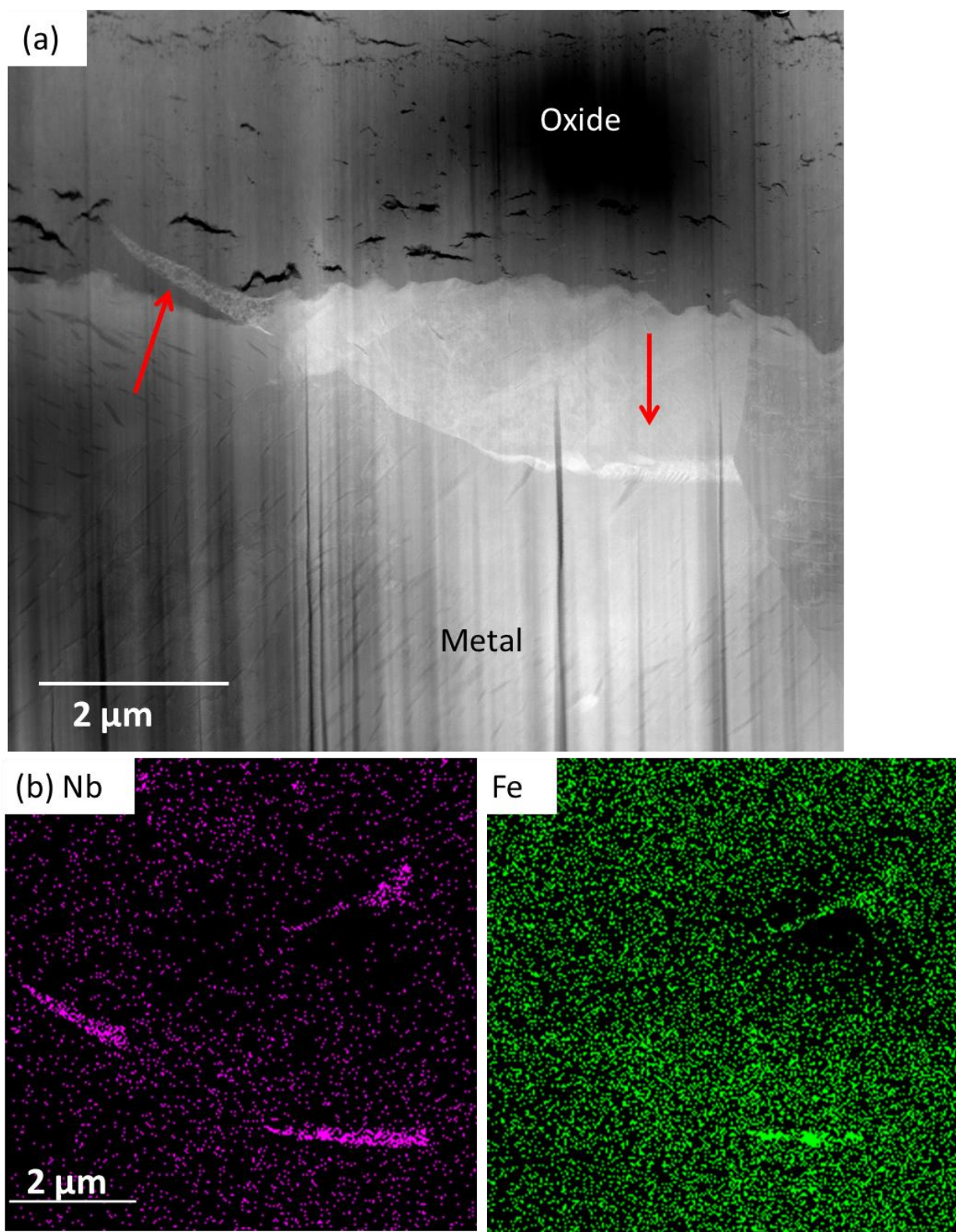


Figure 4-16: (a) STEM HAADF image of three β -Zr SPPs with EDX maps in (b) showing Nb and Fe.

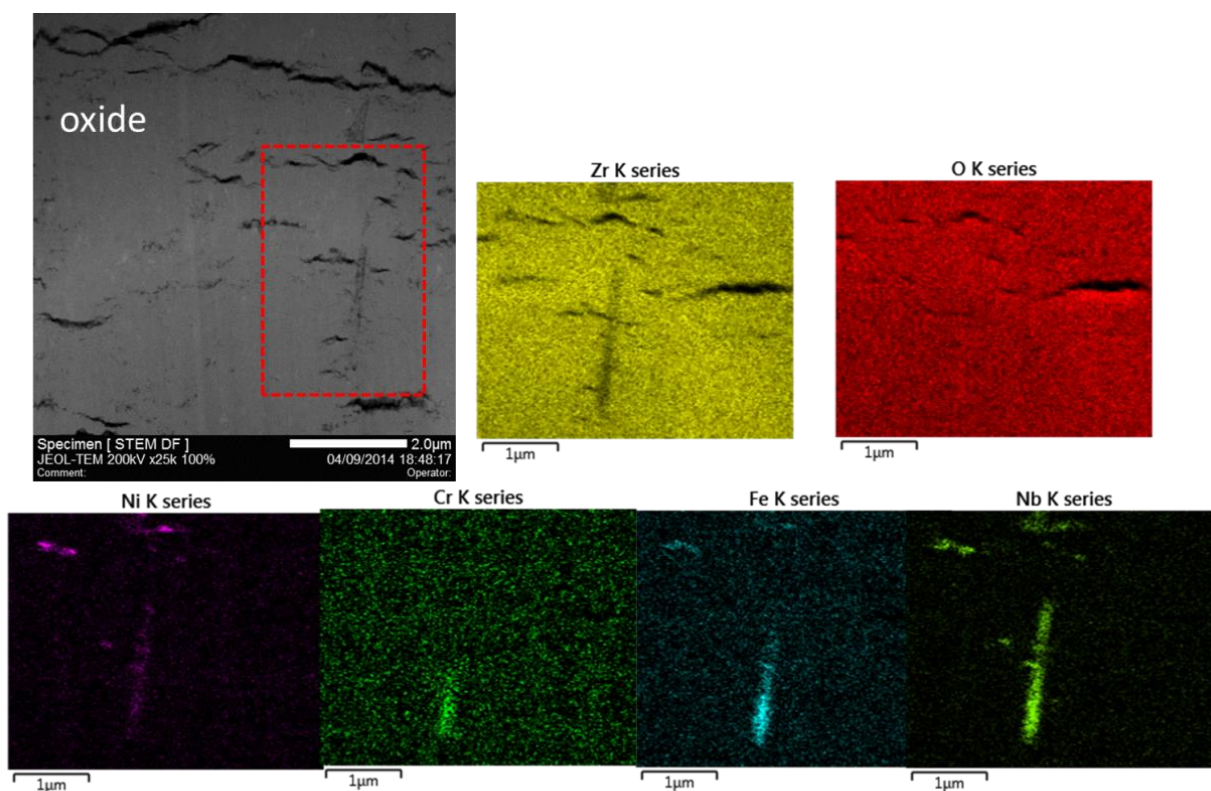


Figure 4-17: STEM HAADF image of an oxidised β -Zr SPP with EDX maps showing Zr, O, Ni, Nb, Fe and Cr.

4.4.3 EELS analysis

As illustrated in Figure 4-18, the big β -Zr SPP which lies at a metal grain boundary shows a complex contrast in STEM HAADF imaging. In order to study the composition of this region of material, in the area shown in Figure 4-18 (c), low loss mapping was done with step size of 2.3 nm, 0.25 eV per channel and an acquisition time of 10^{-5} s per pixel. Several core loss line profiles across the SPP were done with 2.3 nm step size, 0.25 eV per channel and 0.1s per pixel as acquisition time.

Figure 4-18 shows the low-loss spectrum imaging of this SPP. (a) shows the locations for zero loss mapping and the positions where reference spectra were taken: in the metal matrix, 1-in the darker region of the SPP, 2-in the lighter region of the SPP, 3-in the right part of the SPP, in the hydride. (b) shows the low-loss spectra taken from these different positions across the SPP and matrix. Three reference spectra were taken, and each of them has different plasmon

peak positions. In the darker region of the SPP, the first peak lies at 17.3 eV which is very close to that in the metal (17.0 eV) and the second peak is at 42.6 eV. In the darker region of the SPP, the first peak lies at 18.9 eV and the second peak is at 43.6 eV. In area 3, the first peak is at 18.3 eV, which is similar to the position of the hydride peak, and the second peak is at 41.9 eV. MLLS fitting results using spectra from 1-darker region, 2-lighter region and 3 are shown in (c-1,2,3) respectively. It seems that the nano crystalline β -Zr particle contains smaller grains with a similar composition to the Zr matrix, and an average grain size around 30-40 nm. It is unclear what is in region 3 that gives a unique low loss spectrum.

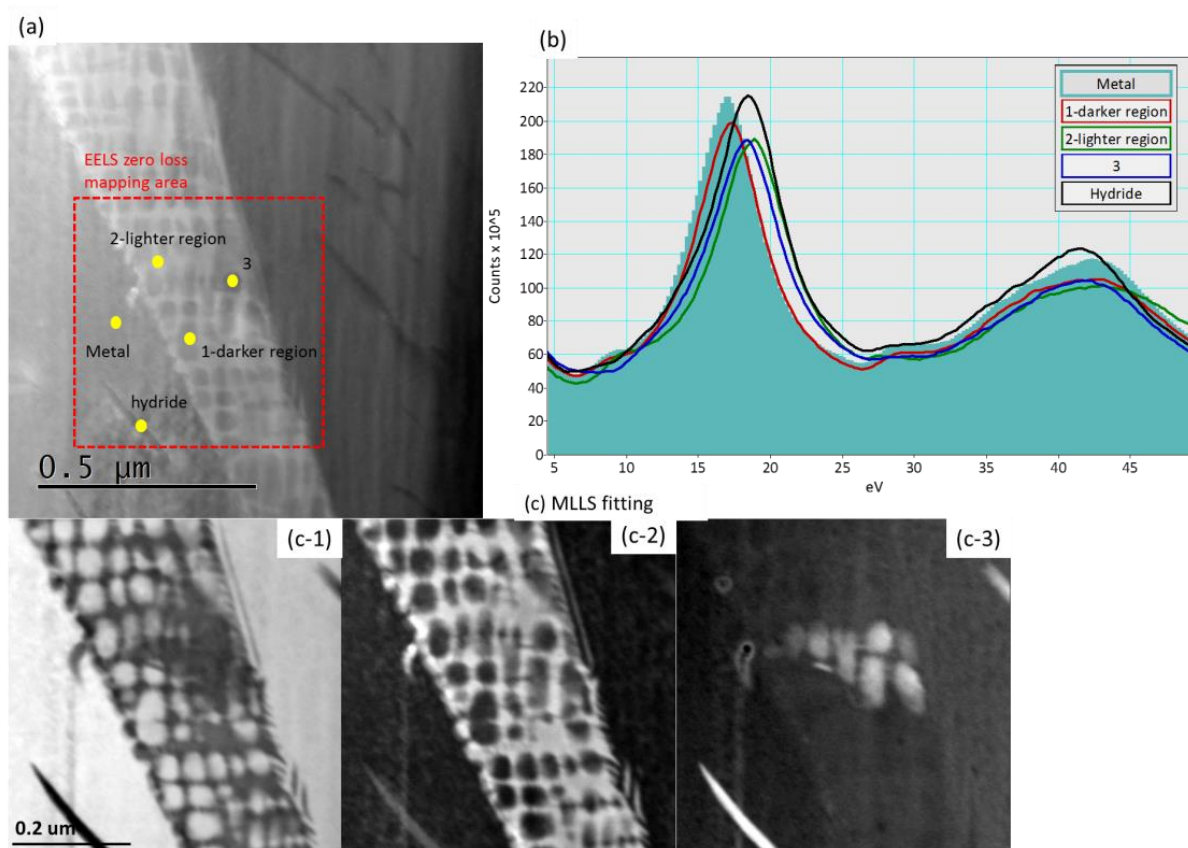


Figure 4-18: EELS low loss spectrum imaging of β -Zr SPP. (a) STEM-HAADF image of the SPP, highlighting locations of zero loss mapping and the position where the reference spectra were taken. (b) comparison the zero loss spectra of 1-darker region of SPP, 2- lighter region of SPP, region 3, metal and hydride. (c-1,2,3) MLLS fitting results using spectra from 1, 2 and 3, respectively.

Core loss line profiles have been used to study the concentration of Zr and Nb in different parts of the β -Zr SPP, as seen in Figure 4-19. Examples of typical core loss spectra are shown

in (b), and the lighter part of the SPP contains Nb inside while the darker part does not. I also notice that the positions of the first peaks are slightly different, varying from 2306.3 eV in the lighter region of SPP to 2371.3 eV in the darker region to 2381.1 eV in metal matrix. (c) shows the concentration of Zr and Nb across the line profiles. The dark area contains around 75% Zr and 25% Nb, while the light area contains 50% Zr and Nb.

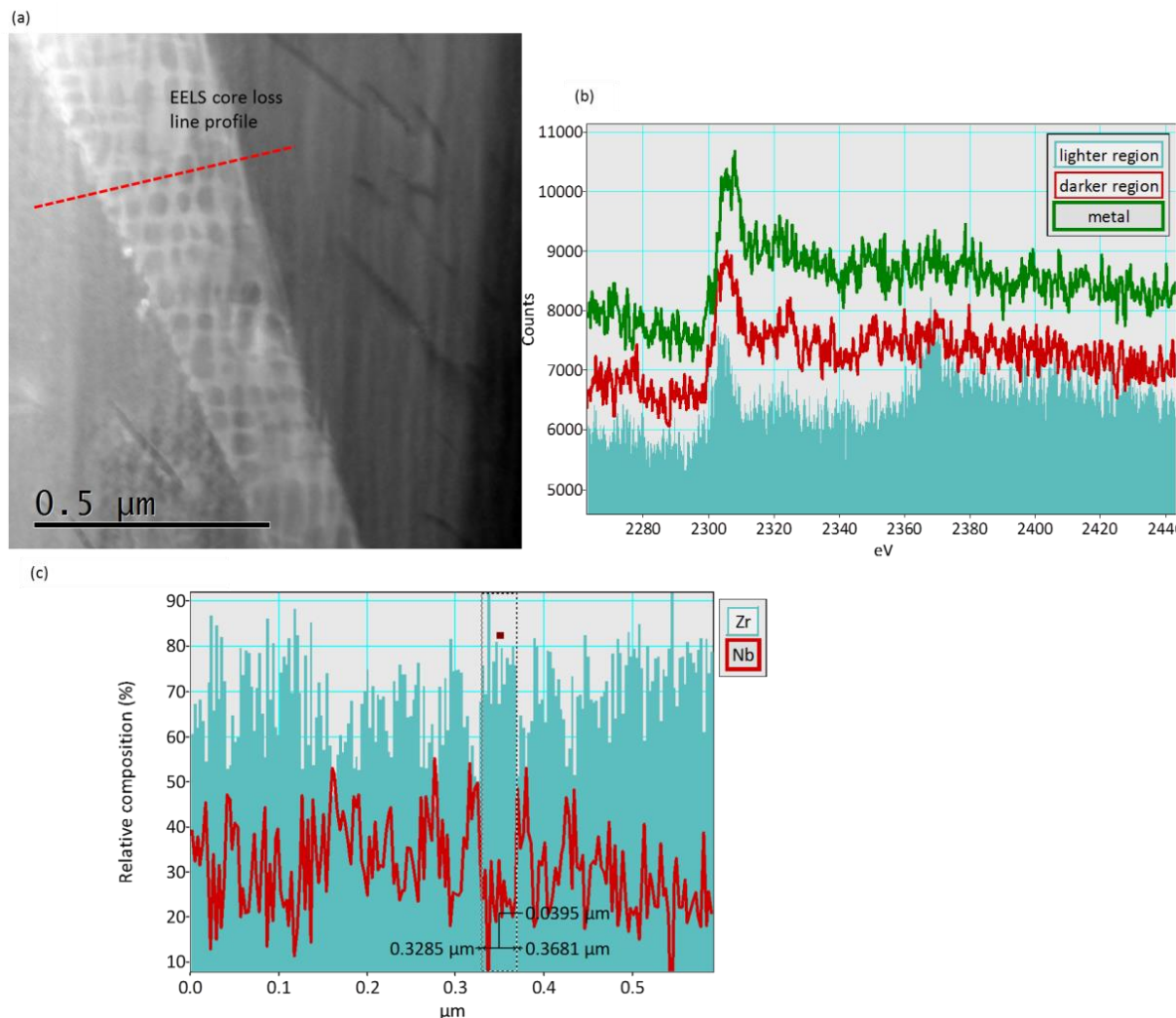


Figure 4-19: EELS core loss line profile of the β -Zr SPP. (a) STEM-HAADF image of the SPP, highlighting locations of EELS core loss line profile; (b) comparison of the core loss spectra of a darker region, a lighter region of SPP and the metal; (c) concentration of Zr and Nb across the SPP

4.5.SUBOXIDE ANALYSIS

4.5.1 EELS and ASTAR analysis of uneven metal-oxide interface

The same area as the ASTAR mapping in Figure 4-7 was analysed using EELS low loss mapping. By carrying out MLLS fitting over an energy range of 10-60 eV, the results are shown in Figure 4-20. As seen by comparing the HAADF image in (a) and the detail of the ASTAR map in (b), most of the MLLS fitting works very well in (c), identifying clearly oxide, metal, suboxide, oxygen saturated metal, SPP and hydride regions. It is interesting to see that the thickness of both the suboxide and oxygen saturated are different in the left and right part of the image, which also show very different oxide thickness. On the left hand side with a thinner oxide length of 2.6 μm , the oxide has just gone through first transition, the

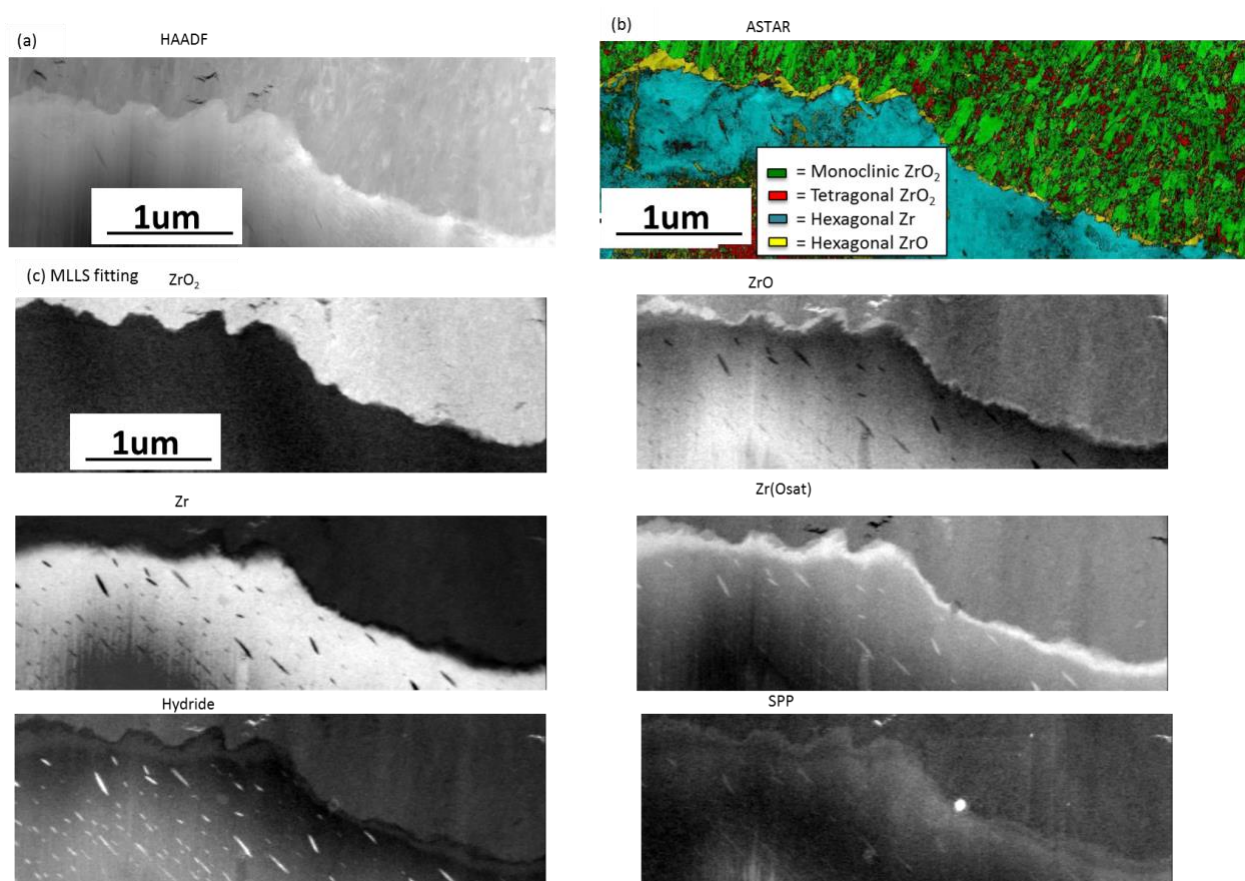


Figure 4-20: EELS and ASTAR analysis of 46-day annealed sample (a) STEM HAADF image of the area (b) ASTAR map of the area (c) MLLS fitting of the reference spectra from low loss EELS mapping, ZrO_2 , ZrO , $\text{Zr}(\text{Osat})$, metal, hydride and SPP, respectively.

suboxide length is around 100-130 nm and the oxygen saturated area is thicker as well, around 130-150 nm. The combined thickness of Zr-O region (suboxide + oxygen saturated Zr) is around 220 nm, with the thickest part around 300 nm. On the other hand, on the right side of the oxide, where the oxidation thickness is around 4.2 μm and second transition cracks have just occurred at the metal oxide interface, I observed a much thinner total Zr-O layer of around 100 nm, with around 50 nm of each of the suboxide and oxygen saturated layer.

4.5.2 EELS analysis on the metal-oxide interface with a β -Zr SPP

EELS analysis was done in the area where there is one β -Zr particle lying at the metal-oxide interface as highlighted in the EDX map in Figure 4-14.

Low-loss mapping was done with a step size of 4 nm, 0.05 eV per channel and acquisition time of 10e^{-5} s per pixel. Core loss line profile across the SPP was done with a 4 nm step size, 0.25 eV per channel and 0.1s per pixel as acquisition time. Figure 4-21(a) shows the locations of low-loss mapping, the core loss line profile and the position where the reference spectra were taken.

Figure 4-21 (b-1) shows the zero loss spectra at three different positions across the SPP. The top part of the SPP which is in the oxide has a delayed peak at 14.4 eV and another peak at 42.5eV. From the SPP in the metal to the area at the metal-oxide interface, the first peak has shifted from 17.9 eV to 18.6 eV, while the second peak remains at 41.4 eV.

The core loss spectrum for the SPP in (b-2) shows Zr-L and Nb-L edges. Across the SPP from the part in the oxide towards metal, the Nb-L peak seems to remain unchanged at 2375.8 eV, which is close with our earlier calibration of Nb metallic peak at 2378.5 eV, which suggests the Nb in the β -Zr particle has not been oxidised. However, the Zr-L peak shifted from 2228.0 eV to 2227.8 eV, which suggests that Zr in the β -Zr particle has started to oxidise.

I used several reference spectra from oxide, suboxide, oxygen saturated Zr, Zr, hydride and also SPP region in the metal and oxide for MLLS fitting. The results are shown in (c). The saw tooth shaped suboxide is around 90-110 nm in length and the undulation region has a thicker suboxide around 140 nm. Inside the SPP, there seems to be no suboxide but the outside surface of the SPP seems to have a very thin (10 nm) layer of suboxide. The oxygen saturated area is around 120-140 nm thick, with the thickest part around 240 nm. Around the bottom part of SPP, there is a layer of 80-100 nm oxygen saturated metal as well. The combined layer of Zr-O region (suboxide+ oxygen saturated Zr) is around 180-200 nm thick, with the thickest part next to the SPP around 350 nm.

4.5.3 Evolution of suboxide and oxygen saturated region

In order to see how the suboxide and oxygen saturated region develop during oxide growth and hydrogen pickup, detailed EELS analysis has been carried out for 3-day, 46-day, 91-day and 225-day samples in a similar way as discussed in previous chapter, as seen in Figure 4-22.

The 3-day sample is still in an early oxidation stage, with very dense oxide as seen in (a). MLLS mappings for oxide, suboxide, oxygen saturated Zr and metal are shown on the right hand side. It is hard to see any suboxide in this sample, and the suboxide region in the detected area is not continuous, with an average suboxide thickness of only 12 nm. The oxygen saturated area shows a relatively uniform layer with average length of 41 nm. The average thickness of suboxide plus oxygen saturated Zr area (Zr-O) is around 53 nm.

The 46-day sample is around the first transition, and as shown earlier this sample has a very uneven metal-oxide interface with different suboxide thickness. Here to represent first-transition, we chose the thinner oxide area where one layer of cracks can be seen in (b). MLLS mapping of oxide, suboxide, oxygen saturated Zr and metal are shown on the right

hand side. There is a layer of continuous saw tooth shaped suboxide in this sample, with an average suboxide thickness around 75 nm. The oxygen saturated area shows a relatively uniform layer with average thickness of 118 nm. The average length of suboxide plus oxygen saturated Zr region (Zr-O) is around 193 nm.

The 91-day sample is between the first and second transitions. Again, we chose the area as seen in (c) that has a relatively even oxide thickness to represent this sample. MLLS mapping of oxide, suboxide, oxygen saturated Zr and metal are shown on the right hand side. There is a layer of continuous suboxide with the average suboxide thickness around 92 nm. The oxygen saturated area shows a relatively uniform layer with average length of 92.5nm. The average thickness of suboxide plus oxygen saturated Zr area (Zr-O) is around 113 nm.

The 225-day sample is at a late oxidation stage, with layers of cracks in the oxide. (d) shows the core loss spectrum imaging of an area with oxygen and Zr concentration maps. Similar to the early oxidation sample, it is hard to see any suboxide in this sample, and the suboxide grains are not continuous. The average suboxide thickness is around 28 nm. The oxygen saturated area shows a relatively uniform layer with average thickness of 111 nm. The average thickness of suboxide plus oxygen saturated Zr area (Zr-O) is around 136 nm.

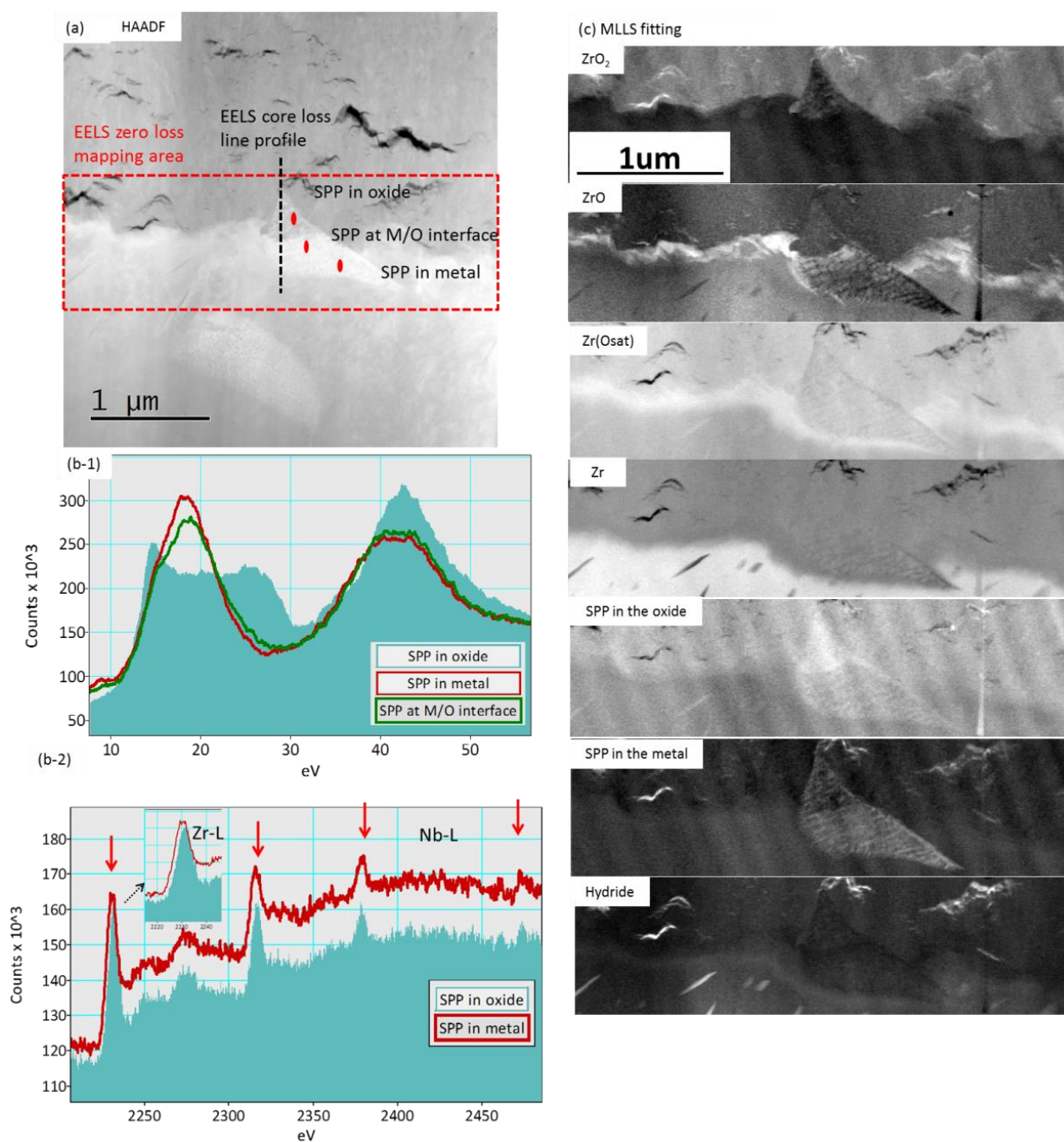


Figure 4-21: EELS analysis of 46-day annealed sample (a) STEM HAADF image of the area; (b-1) zero loss spectra of SPP in the oxide, at the metal-oxide interface and in the metal, (b-2) core loss spectra of SPP in the oxide and metal, inserts showing the peak shift of the Zr-L first peak; (c) MLLS fitting of the reference spectra from low loss EELS mapping for ZrO₂, ZrO, Zr(Osat), SPP in the oxide, SPP in the metal and hydride, respectively.

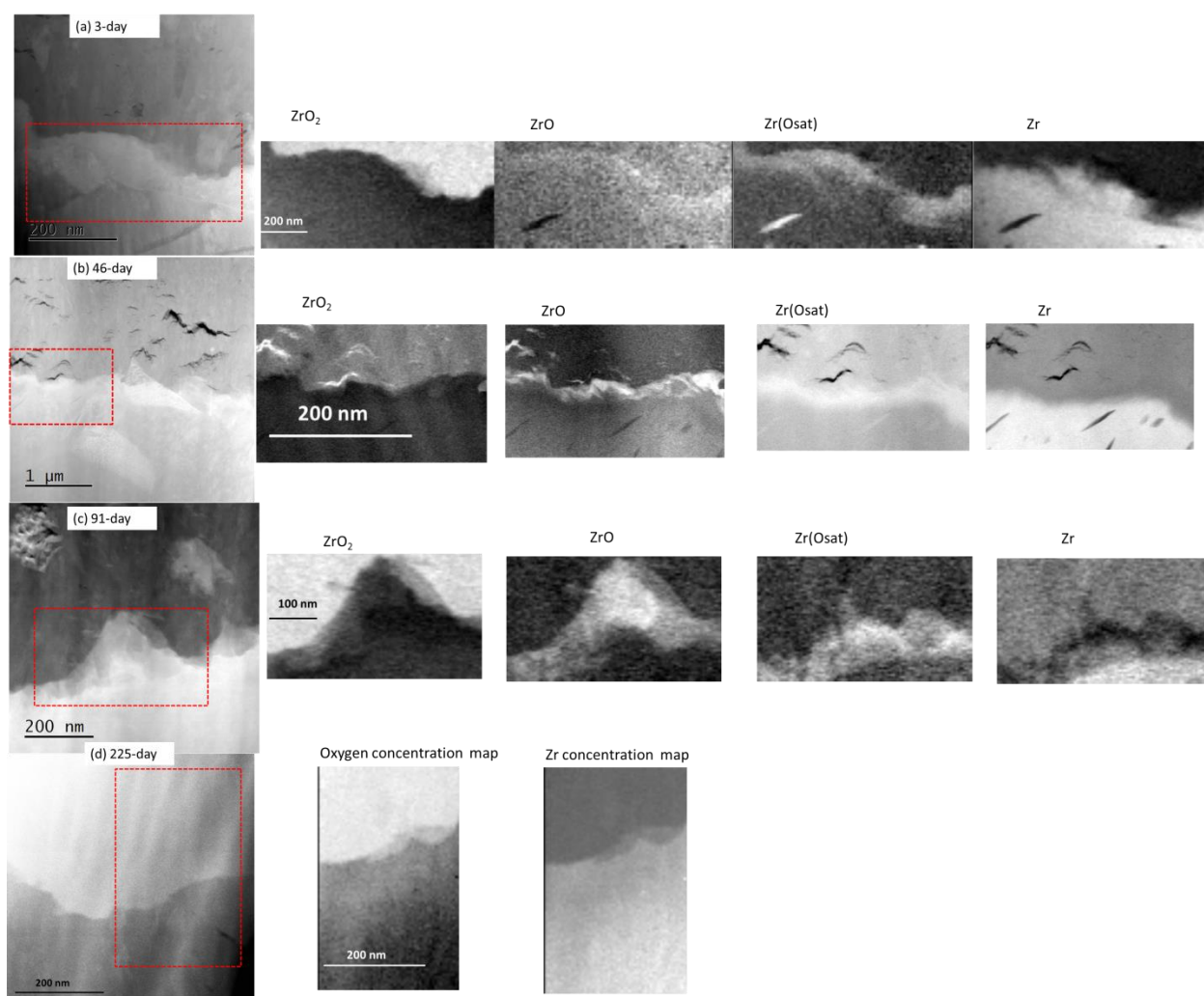


Figure 4-22: Detailed EELS analysis for 3-day, 46-day, 91-day and 225-day samples. (a-c) STEM HAADF images showing the area of low loss EELS mapping area with MLLS mapping for oxide, suboxide, oxygen saturated and metal on the right hand side. (d) STEM HAADF image of 225-day sample showing the area of core loss EELS mapping with oxygen and Zr concentration map on the right.

Figure 4-23 shows the thickness of suboxide, oxygen saturated region and the combination of these two as Zr-O region as a function of oxidation days. It is interesting to see that the three different lengths follow similar trends; they start as very thin suboxide, oxygen saturated layer and Zr-O layers in the early oxidation stage. Then when closer to the first transition at 46 days, the Zr-O layer grows to the highest thickness in the four samples. However, when transition happens, the protective layers in the 91-day sample drops to a thinner layer. It worth mentioning for the 225-day sample, although many transitions have happened as this stage, the suboxide layer is very thin, the Zr-O layer still remains at a similar thickness as pre and

post first transition samples. This can possibly explain why the hydrogen content in the sample remains growing linear during oxidation.

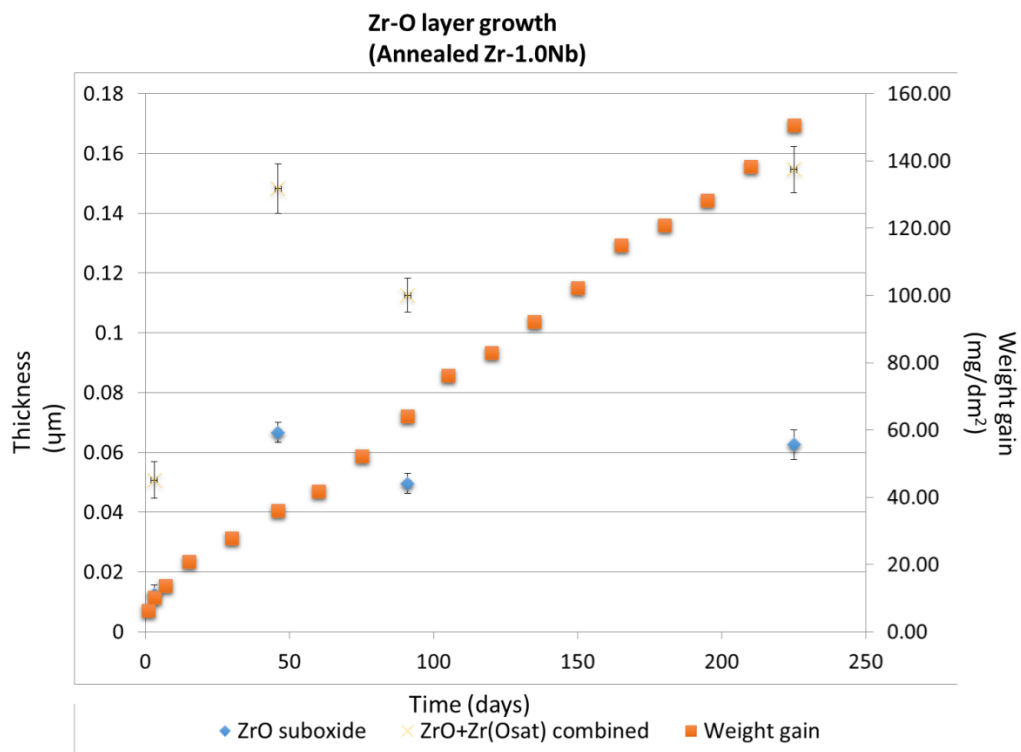


Figure 4-23: Suboxide and combined region growth with oxidation days.

5.1 SAMPLE DATA

To compare with the study of the autoclave-oxidised samples discussed in Chapter 3, two neutron irradiated samples were provided by the MUZIC project for detailed microstructural examination. These samples have a nominal composition Zr-1.0Nb-0.06Fe, and were fully recrystallized with equiaxed metal grains. They were manufactured by the same process as the autoclave samples previously described.

These samples were irradiated for one cycle (18months) in the Vogtle reactor in the US as a flat coupon, i.e. it was not part of a fuel rod. The estimated fast neutron fluence accumulated was 4.35×10^{21} n/cm², E>1 MeV, which can be considered around a third of the fluence that fuel cladding sees by the end of life. The sample was inserted to study oxide growth, thus it was not subjected to any stress.

First stage FIB in situ liftout was done in the active laboratories in Studvik, Sweden by Pia Tejlund. There was no prior oxide polishing before liftout, i.e. the whole oxide thickness was retained during liftout. Two TEM lamella were prepared in the size of around 10 μm $\times$ 10 μm $\times$ 2 μm , the activity value is very low due to the small sample volume, so that they can be easily transported in plastic sample box to Oxford for final FIB thinning and detailed analysis.

5.2 MICROSTRUCTURAL ANALYSIS

5.2.1 (S)TEM

Figure 5-1 shows the TEM BF (a) and STEM HAADF (b) overview images of one of the irradiated FIB lamelle. The sample has been oxidised in a reactor environment for around 540 days, but contains few cracks in the oxide, suggesting that no kinetic transition has occurred.

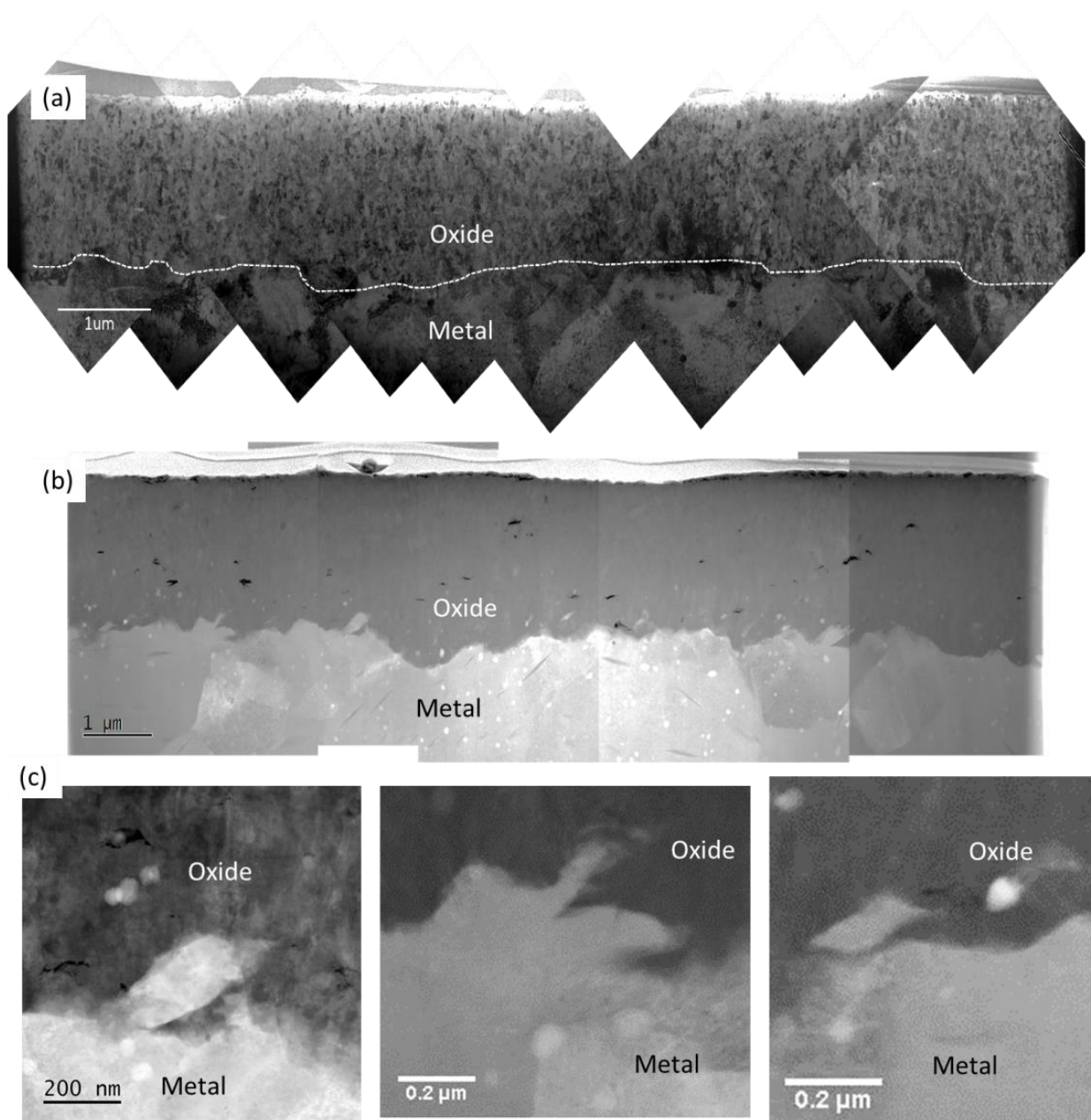


Figure 5-1: (a) TEM BF and (b) STEM HAADF images of the whole of one of the irradiated FIB lamelle; (c) Examples of STEM HAADF images of isolated metallic region penetrating into the oxide.

The metal-oxide interface is slightly uneven and the oxide thickness ranges from 2.3 μm to 1.7 μm, with an average thickness of 1.9 μm. It is interesting to see such a thin oxide despite its being in the reactor for 540 days, where as shown in Chapter 3.2, same sample in the autoclave for 120 day has 2.2 μm oxide and 540-day sample has 5.2 μm oxide. As discussed in Chapter 2.1, the temperature differences of the autoclave (360 °C) and reactor (305-320 °C)

can cause the oxide to be around 2.06 μm after the same time of 310 $^{\circ}\text{C}$, very close to the observed thickness of the irradiated sample. Comparing with the samples oxidised in the autoclave, there are more isolated metallic regions penetrating into the oxide like the areas shown in Figure 5-1 (c). This suggests that the variation in local oxidation kinetics at the metal-oxide interface is even greater than observed in the autoclave samples. It is unclear how they form, and worth mentioning that they are not associated with metal grain boundaries underneath, so the texture of the metal grains is not the reason of their existence.

Despite the fact that the irradiated samples do not have large cracks in the oxide, the HAADF images show that there is a layer of micro cracks parallel to the metal-oxide interface at the top surface of the oxide, just underneath the Pt protective layer, as seen from the top part of Figure 5-1 (b) and the higher magnification images in Figure 5-2(a) and (b). Noting that the sample has not been polished prior to the FIB sample preparation process, it is unclear why such cracks will exist on the top surface. In all the autoclave samples I examined in this thesis, I have not seen such parallel cracks at the top surface where equiaxed oxides are. Some micro cracks will develop into cracks perpendicular to the metal-oxide interface as seen in (a), and another irradiated lamella in (c) and (d) that has a big crack 1.6 μm in width and 1.1 μm deep. (c) is taken in FIB-SEM to show that the crack was not created during FIB process. TEM-BF image in (d) shows that this crack starts from the top surface and runs into the middle of the oxide. This kind of perpendicular crack provides the best pathway for water penetration and oxidation reaction, but the oxide thickness underneath such huge cracks seems relatively unaffected.

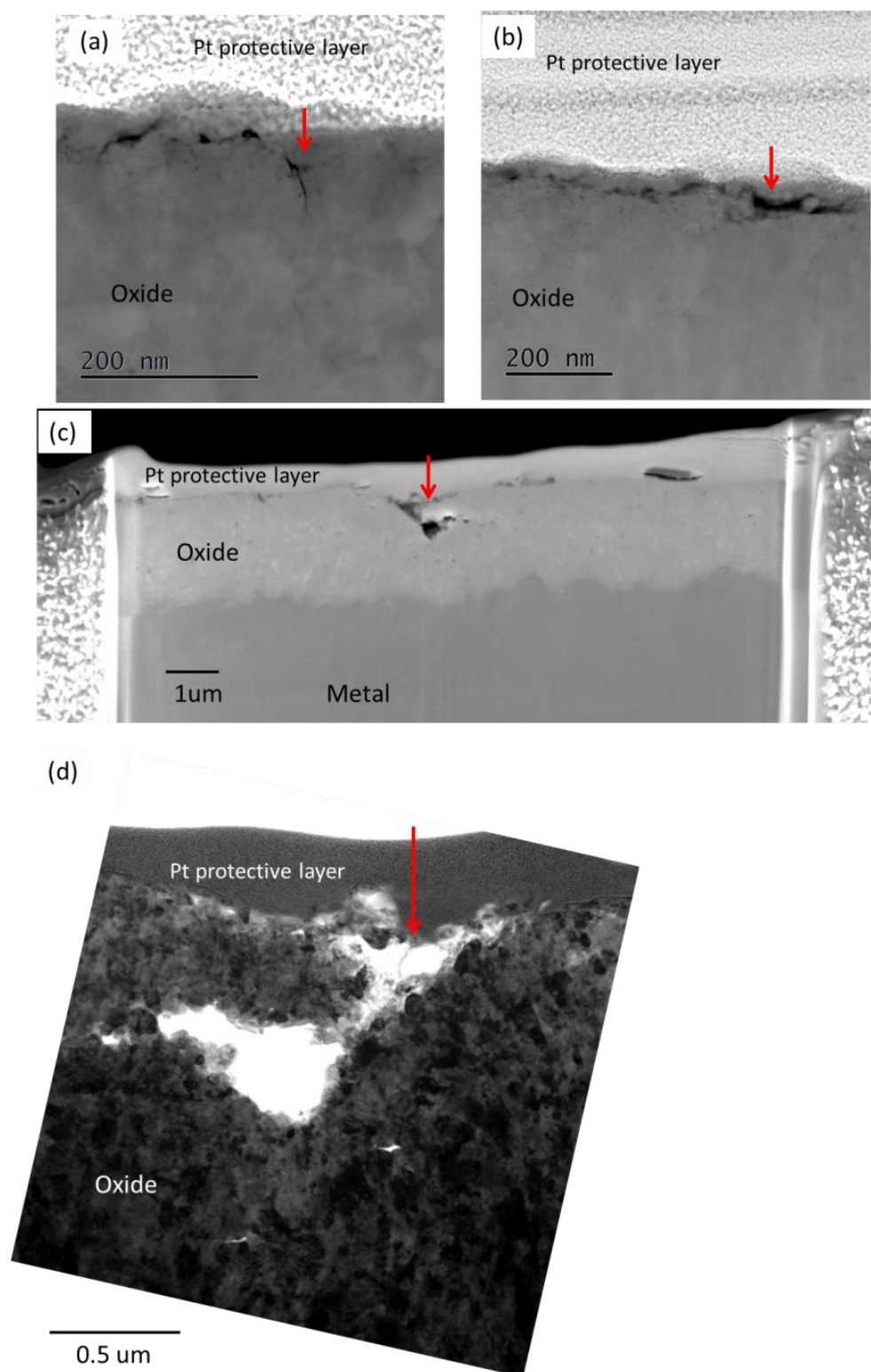


Figure 5-2: (a-b) higher resolution images of top surface micro cracks from the same sample in Figure 5-1 a) and (b). (c) SEM image of the overview of another irradiated FIB lamella with a huge crack coming from the top surface penetrating about half way down the oxide .Picture taken during the FIB milling process.(d) TEM-BF image of the crack in (c) after the FIB milling process, noting that the Pt protective layer remains after.

Figure 5-3 (a) shows a higher resolution montage of TEM BF images of the oxide microstructure and development from the top surface oxide in (b) to the middle part of oxide (c) to the metal-oxide interface (d). The oxide microstructure is significantly more complicated comparing with an autoclave sample, i.e. it does not show a well-defined equiaxed-columnar-equiaxed oxide grain structure like as seen in Chapter 3, such as Figure 3-4. It is very hard to see the precise location of some of the grain boundaries in the oxide, as seen in (a). The top surface oxide consists of equiaxed grains around 30-50 nm in diameter, but, it is less porous compared with the autoclave samples. In the middle part of the oxide, while there are fewer horizontal cracks, the columnar grain structure is unclear, with shorter and less well aligned grains around 150-200 nm in length and 40-60 nm in width. Hardly any amorphous or metallic SPPs can be seen in the TEM BF images of the middle part of the oxide, (a) and (c), however we discuss later how to use combined STEM HAADF, TKD and EDX analytics to locate SPPs in the oxide. The metal-oxide interface is hard to define, because there are no clear columnar oxide grains to show where the oxide stops at the metal-oxide interface. There are some metallic SPPs with crescent shape cracks on the top, circled in (d). There are no obvious to see saw-tooth shaped suboxide grains at the metal-oxide interface. In this study, basic TEM BF imaging analysis reveals that the microstructure in irradiated sample is significantly different from the autoclave samples, with a much more disorganised and not well defined oxide microstructure.

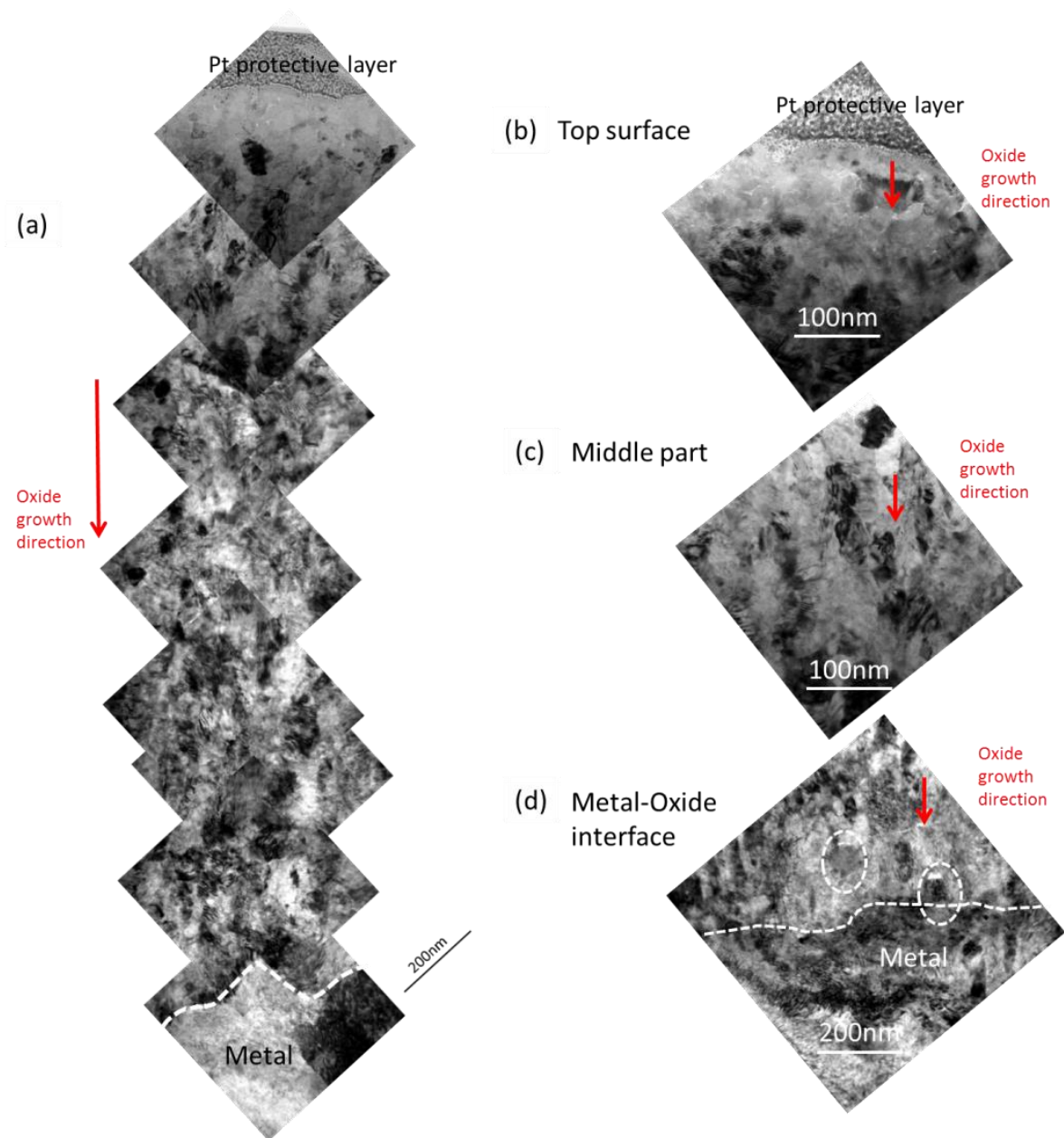


Figure 5-3: High resolution TEM BF images of the first irradiated TEM lamella (a) Montage of images from the top surface to the metal-oxide interface which show complicated oxide microstructure. Higher magnification examples are shown in (b) top surface (c) middle part and (d) metal-oxide interface.

5.2.2 ASTAR analysis

The second sample which has a crack from the top surface as shown in Figure 5-2 was analysed by TEM precession ASTAR mapping. The area for ASTAR mapping is identified in Figure 5-4(a) and the same area is also used for later TKD, EDX and EELS analysis. The area has a micro-crack in the middle of the oxide and a hydride right under the metal-oxide

interface, which can be used as reference points for position correlation. Figure 5-4 (b) and (c) show the pattern quality map and phase maps of the TEM lamella. The TEM sample was further thinned down to around 50 nm in order to do accurate ASTAR and EELS mapping resulting in some part of the Pt layer but not all disappearing and around the large crack being preferentially milled away more quickly than other parts of the oxide.

The pattern quality map in Figure 5-4 (b) agrees with the TEM BF observation of a more complicated oxide grain structure, with shorter and less organised columnar grains. It is interesting to note the gradual change of oxide grain size distribution throughout the oxide. At the top surface for around 500 nm, the average grain size is around 58 nm in width and 132 nm in length. In the middle part towards the metal-oxide interface, the oxide grains become larger, averaging around 74 nm in width, with some grains even being 100 nm in width. These grains also become longer as well, with an average length of 379 nm. The area around the surface cracks is full of equiaxed oxide grains 55 nm in diameter. The phase map in Figure 5-4 (c) shows that most of the columnar oxide grains are identified as having the monoclinic-ZrO₂ (m-ZrO₂) structure. However, comparing with the autoclave samples, the irradiated samples contain more tetragonal-ZrO₂ (t-ZrO₂) grains, some of them around 40-50 nm in size and scattered in the equiaxed oxide from the top surface throughout the oxide thickness. At the metal-oxide interface, there are more and larger columnar tetragonal grains with width around 50-70 nm and length of around 200-300 nm. At the metal-oxide interface, there are also smaller grains identified as a discontinuous layer of Widmanstätten-type suboxide with the hexagonal ZrO structure predicted with ab initio modelling, with P-62m symmetry and lattice parameters $a=5.31 \text{ \AA}$ and $c=3.20 \text{ \AA}$. Other grains match Zr metal with P 63/m symmetry and lattice parameters $a=3.23 \text{ \AA}$ and $c=5.14 \text{ \AA}$. However, compared with the autoclave samples, this irradiated sample has a much thinner suboxide of around 50-70 nm,

with some places without any detectable suboxide at all, and the shape of the suboxide grain has a less defined saw tooth shape in some locations.

5.3 POROSITY IN THE OXIDE

Using the Fresnel imaging technique, I was easily able to identify porosity in the autoclave oxidised samples, see images in Chapter 3.3 and Chapter 4.3. However in the irradiated sample, in TEM BF images as seen in Figure 5-5, it proved to be difficult even to see oxide grain boundaries, so porosity could not be confidently identified in the irradiated sample.

Another reason for not seeing too much porosity in this sample could be that the oxide is still protective at this stage in the oxidation, judging from the very dense oxide microstructure without many cracks and even the very dense equiaxed oxide layer, so it is also possible that the nature of porosity in this sample might be small, which makes it harder to see. In Chapter 3.3, I discussed how interconnected porosity can lead to fast transition and oxidation growth, and slow oxidation rate might relate with lack of porosity.

5.4 SECOND PHASE PARTICLES

5.4.1 SPP distribution from diffraction based techniques

Figure 5-6 (a) shows the TEM BF image from the same area as ASTAR maps. By doing diffraction contrast, it is very hard to spot SPPs. However, by doing TKD mapping of the same area, as seen from Figure 5-6 (b), not only the grain structure shows up clearly, it is easy to see some round areas with black contrast in, which indicates there are SPPs. The location of the SPPs are all over the oxide, from the top surface throughout the middle part of the oxide towards the metal-oxide interface. However, we tried matching β -Nb and Laves phase SPPs in the kikuchi patterns in the map, there was not any match with SPPs, which indicates the SPPs no longer have the anticipated crystal structure, they can still be crystalline.

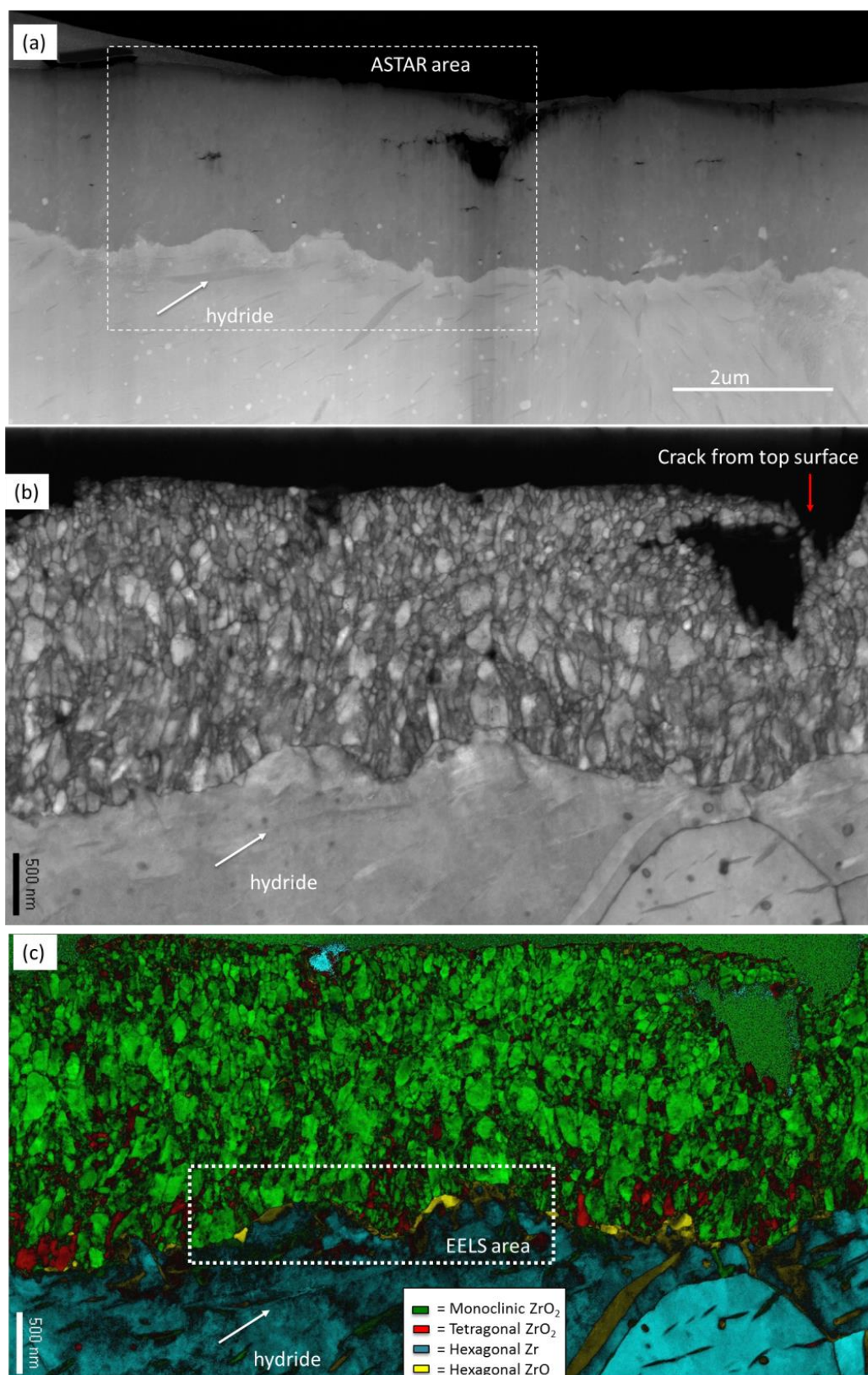


Figure 5-4: (a) STEM HAADF overview of the second irradiated TEM lamella with the position of the ASTAR mapping indicated. The pattern quality map (b) and phase map (c) of the second irradiated TEM.

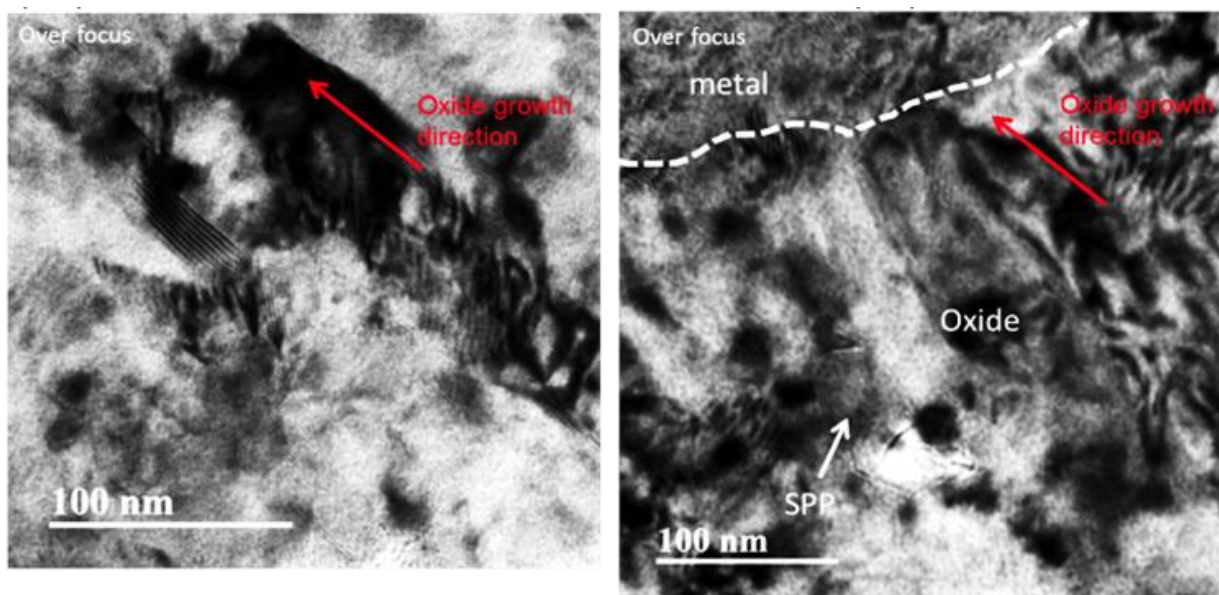


Figure 5-5: Over-focused TEM images in irradiated RXA Zr-1.0Nb. (a) in the oxide (b) near the metal-oxide interface.

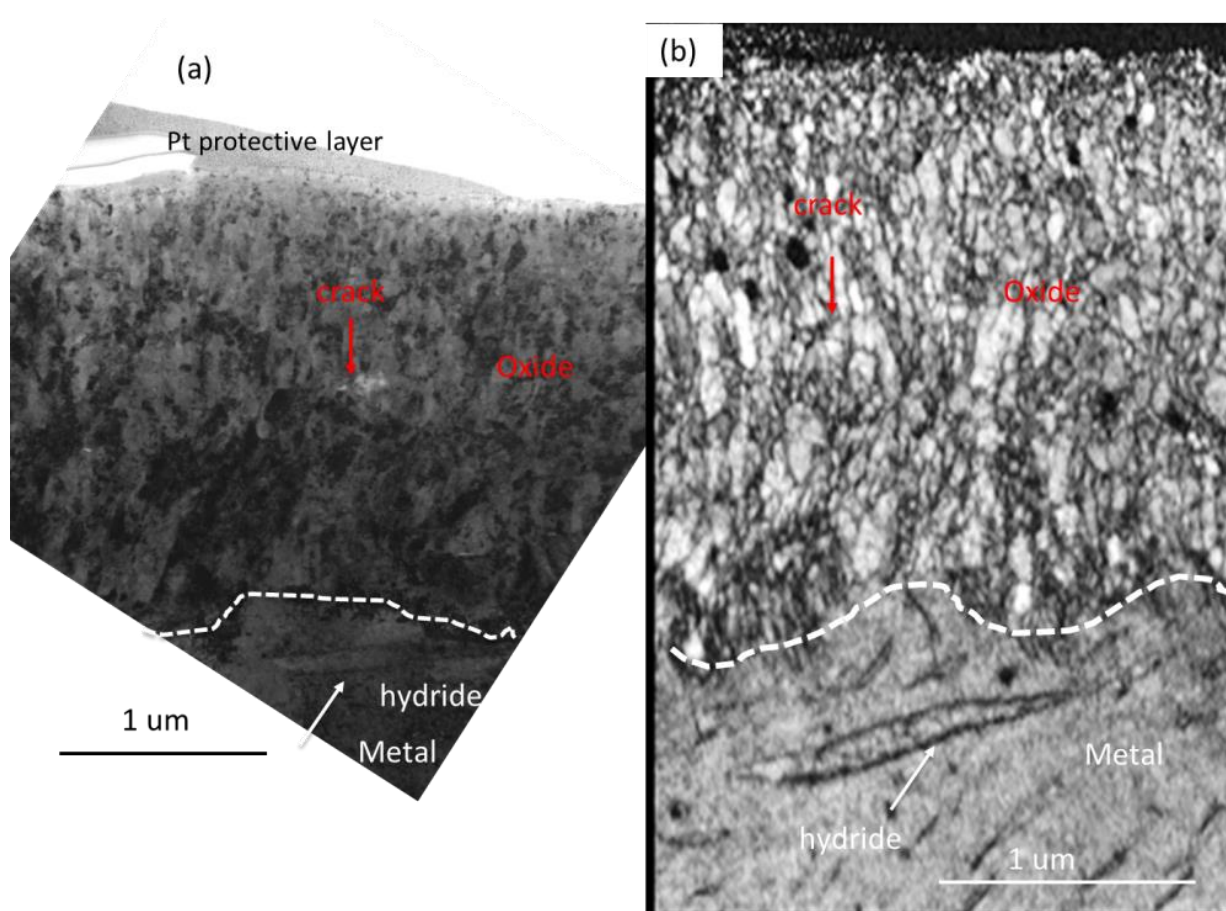


Figure 5-6: (a) TEM BF image (b) TKD map

5.4.2 EDX mapping of SPPs

Despite the difficulties of identifying SPPs using diffraction contrast, average atomic mass contrast (z-contrast) is able to differentiate between metallic and oxidised SPPs. Figure 5-7(a) shows the STEM HAADF image and EDX maps. When an SPP is oxidised, the overall atomic mass of the oxidised SPP is lighter than a metallic SPP, so in z-contrast, the oxidised SPPs appear darker, as seen by those circled in red in Figure 5-7 (a), while the metallic SPPs appear brighter compared with the oxide surroundings, as circled in yellow. Combining the Nb and Zr EDX maps with HAADF image in (b), it is possible to identify with confidence the location of some of the SPPs due to their different STEM HAADF contrast. The Nb K map in Figure 5-7 (c) shows that the β -Nb SPPs have a homogenous distribution from the surface towards the metal-oxide interface but that they oxidise gradually. The metallic/partially oxidised SPPs were found in the region around 700 nm above the metal-oxide interface. Above this region, the SPPs were all fully oxidised.

For sizing of the SPPs, it is worth pointing out that most of the oxidised SPPs at the top of the oxide appear larger; some of the bigger SPPs are around 100 nm in length and 50 nm in width, while there are small round ones around 50 nm in diameter. The average size of these fully oxidised SPPs is 71 nm, and the shape tends to be more elliptical than round. By contrast, the average size of the metallic/partially oxidised SPPs is 63 nm; the shape is sometimes elliptical for the partially oxidised ones, but those with a crescent shape crack on the top always remain round. It seems that when an SPP starts to oxidise, it expands in the direction of oxidation growth as the oxygen atoms are incorporated. In the metal, the average size of these metallic SPPs is 63 nm, and they are mostly round.

It is also interesting to see from Figure 5-7 (b) and (c) that there are almost no Laves phase SPPs in the irradiated sample, except one large SPP at the far right side of the Fe map. The Fe

layer at the top surface of the oxide is believed to come from deposition of dissolved Fe from the reactor water.

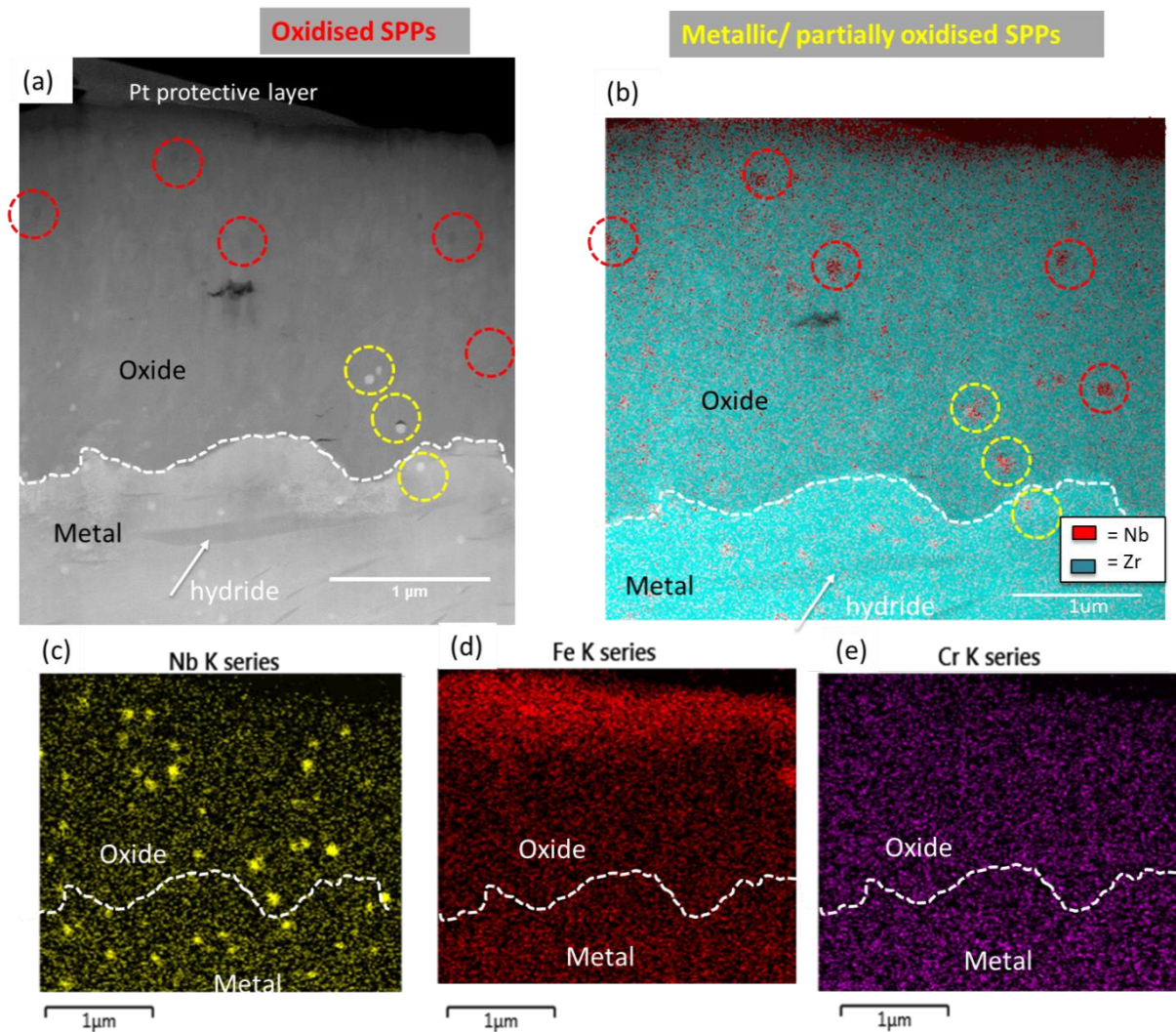


Figure 5-7: (a) shows the STEM HAADF image combined with EDX mapping in (b). Individual Nb Fe and Cr maps are in (c-e).

The TEM BF images in Figure 5-8(a) shows in detail an area at the top surface of the oxide where there is a crack. From the image alone it is unclear whether there are any SPPs in this region, while the EDX maps and HAADF image suggest there should be local oxidised SPPs. Figure 5-8 (b) shows as area at the metal-oxide interface. The oxidised SPP which is circled in red is shown to be amorphous in the TEM BF image, while the metallic SPPs are remain crystalline.

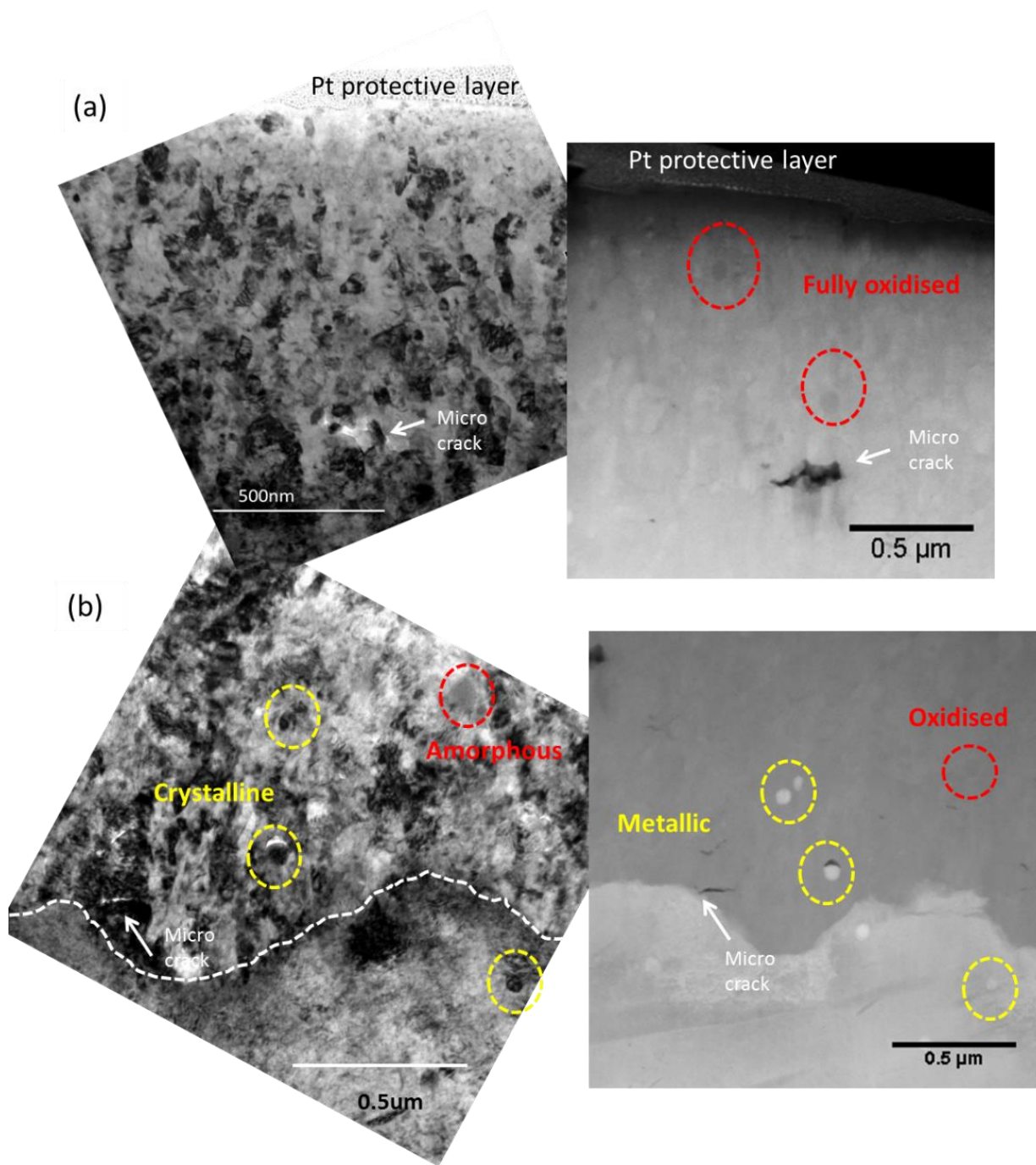


Figure 5-8: TEM BF and STEM HAADF comparison of (a) an area containing a micro-crack as seen in Figure 5-7 and (b) the metal-oxide interface region.

In a different area, a similar Fe layer on the top surface can be seen in EDX mapping. However, there are also two Laves phase SPPs as shown in Figure 5-9, both rich in Fe and Cr, and also larger than the β -Nb SPPs. In the Cr map, there are two SPPs, one near the metal-oxide interface and another unoxidised in the metal. Judging from their bigger size, it is speculated that they used to be Laves phase SPPs, while Fe and Cr have diffused out during

irradiation. In the Ni map, there is one Ni rich SPP at around 200 nm from the top surface of the oxide.

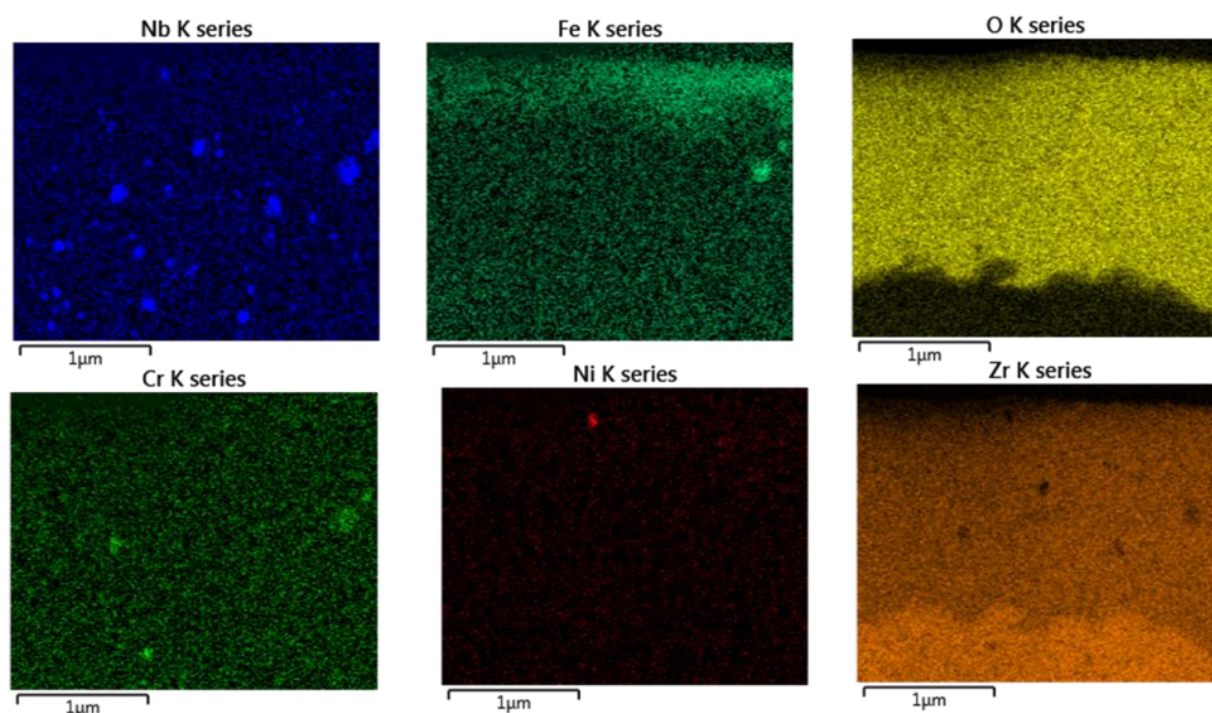


Figure 5-9: EDX mapping of another area in the oxide, this area is used for EELS analysis in chapter 5.4.3

Figure 5-10 shows the EDX mapping of SPPs in the metal substrate of the irradiated sample. B-Nb SPPs are homogenously distributed in the metal. While there are no SPPs containing Fe, there are three or more SPPs that contain Cr. This agrees with EDX maps in the oxide that during irradiation, Fe diffuses out of SPPs first, Cr diffuses at a slower rate while Nb stays within the SPPs. Compared with the EDX mappings in the autoclave samples, shown in Chapter 7.4, there are Laves phase SPPs with Fe, Nb and Cr in the oxide and metal, although at a lower number density than β -Nb SPPs. Irradiation affects the Fe and Cr in Laves SPPs, but it doesn't affect Nb in the Laves phase and β -Nb SPPs.

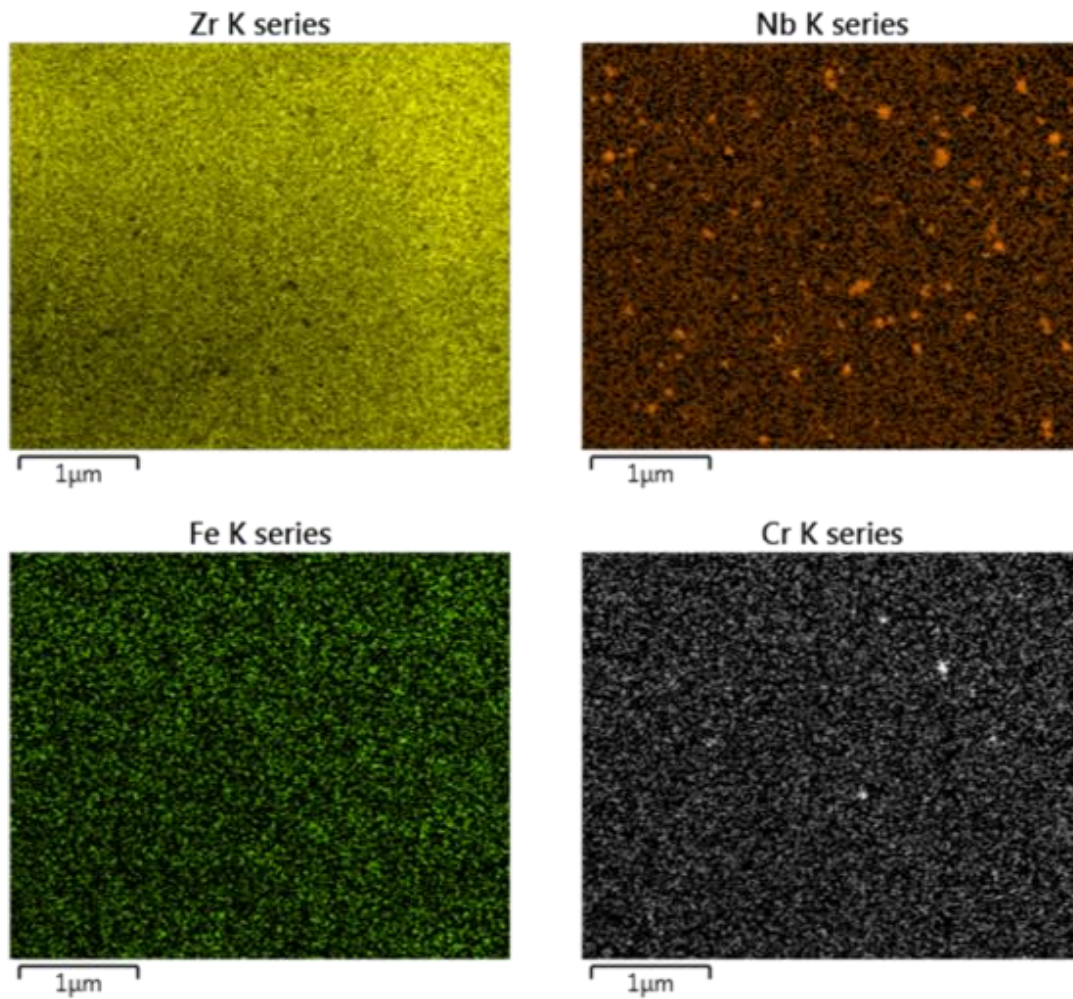


Figure 5-10: EDX mapping of SPPs in the metal substrate of the irradiated sample.

5.4.1 EELS analysis of oxidation of SPPs

EELS analysis was performed on SPPs at different locations in the oxide. STEM HAADF images like those in Figure 5-11(a) provide a good way to use z-contrast to see oxidised and metallic SPPs, and EELS low loss spectrum imaging as seen in (b) is an easy way to give an overview of SPP distribution. Here we discuss the characteristics of the SPPs in terms of their relative distance from the oxide top surface.

- *SPP at the top surface of oxide*

As seen in the STEM-HAADF image Figure 5-12(a), there is one elliptical SPP around 100 nm in length and 55 nm in width lying around 200 nm from the top oxide surface. While the

TEM BF image in (c) hardly shows any diffraction contrast (despite the SPP is not amorphous), the higher magnification STEM HAADF image in (b) shows dark contrast of this SPP. Line profiles were drawn across the SPP and the EELS signal from 500 eV- 950 eV (d) identifies the O-K signal from both the SPP and oxide, indicating that the SPP has fully oxidised. From the analysis presented above, one can be sure of its fully oxidised state from such a location in the oxide. The Fe-L edge exists both in the SPP and oxide. This is presumably due to the Fe- rich layer present at the top surface, as shown in the EDX mapping in Figure 5-9. Ni-L edge at 855.1 eV is only detected inside the SPP, suggesting that there is no Ni in the surrounding oxide. It is considered that both Fe and Ni come from the water chemistry in the reactor core, however Fe concentrates at the surface while Ni concentrates in the SPP.

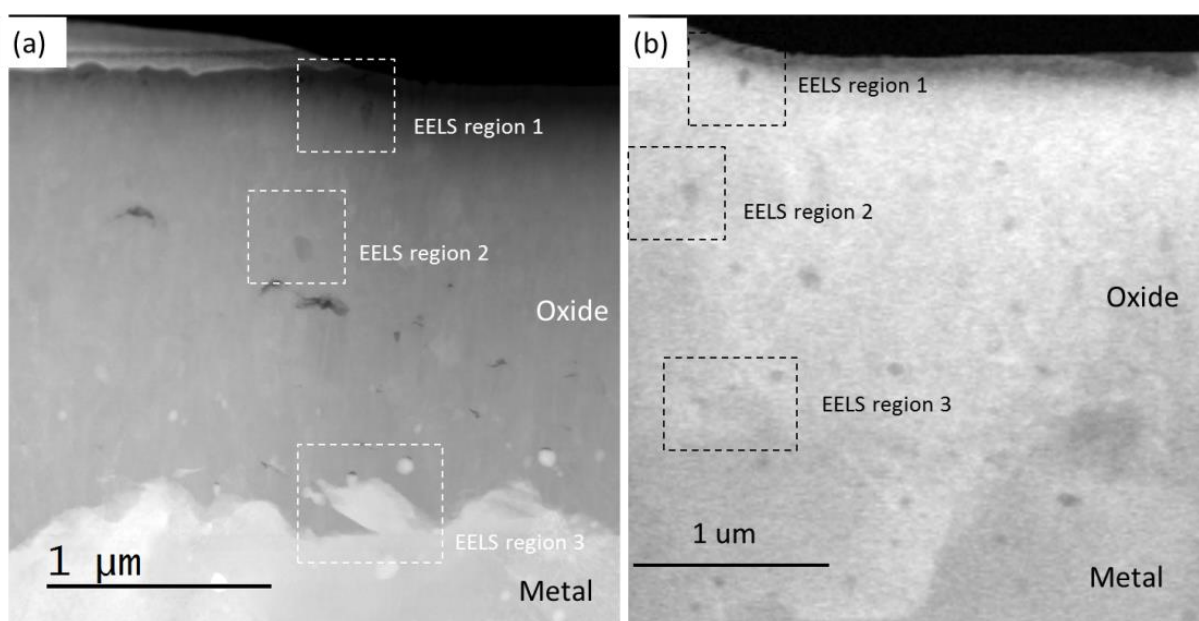


Figure 5-11: SPP distribution in the oxide and metal in the second irradiated TEM sample. (a) STEM HAADF image and (b) EELS low loss spectrum imaging

The core loss spectrum in (e) shows the Zr-L and Nb-L edges. Inside the SPP, there are Nb-L peaks with the Nb-L₃ peak at 2382.8 eV, possibly the oxidised Nb⁵⁺ peak. It seems that as the SPP oxidises, the Zr concentration drops as seen from (e), so that there is a much larger Zr-L

peak at 2233 eV in the oxide than in the SPP. The concentration profile in (f) shows the central part of SPP consists of 30% Zr and 70% Nb, which has a slightly lower Nb concentration than 80 % Nb in β -Nb. Several other fully oxidised SPPs (containing only Zr and Nb)were analysed as well, and the Nb peaks all lie around 2382.7 to 2381.6 eV, indicating the Nb⁵⁺ oxidation stage in fully oxidised SPPs.

- *SPPs in the middle of the oxide*

In the middle part of the oxide, there are several oxidised SPPs as shown in Figure 5-13 which are around 0.85 μ m away from the top surface of oxide. There is one elliptical SPP around 110 nm in length and 75 nm in width, and another two smaller SPPs around 60 nm length and 40 nm width. While the TEM BF image in (b) hardly shows any diffraction contrast (suggesting that the particles are not amorphous), the STEM HAADF image in (a) shows dark contrast from these SPP.

The core loss spectrum from the larger SPP using a 1 nm step size and 0.25 eV channel per pixel in (e) shows the Zr-L and Nb-L edges. Inside the SPP, there are Nb-L peaks with Nb-L₃ peak at 2382.3 eV, possibly oxidised Nb⁵⁺. It seems that as the SPP oxidise, the Zr concentration drops as seen from (e) as there is much more Zr-L peak at 2232.5 eV in the oxide than the oxidised SPP. The concentration profile in (d) shows the top 60 nm of SPP consists of 20% Zr and 80% Nb, while the bottom 45 nm gradually falls to 50% Zr and 50% Nb which indicates Zr/Nb ratio increases closer to the metal-oxide interface. Judging from the size of the SPP, it is likely to have started as a Laves phase SPP, even though in the lower energy range that there is no Fe from this SPP at 710 eV. Similarly, core loss spectra for the two smaller SPPs in (e) also have Nb-L peaks at 2383.3 eV and 2383.0eV, respectively.

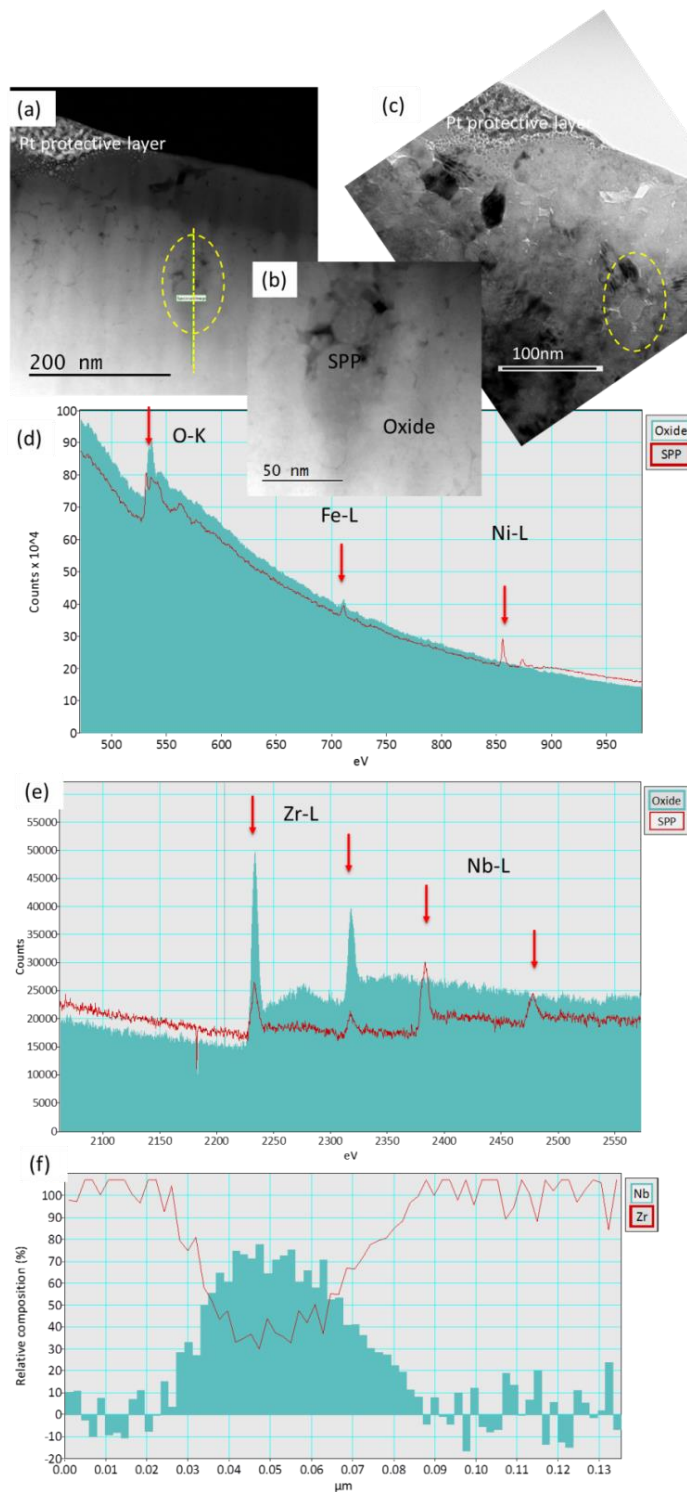


Figure 5-12: Example of EELS analysis of an SPP at the top surface of oxide in the first irradiated TEM sample: (a) STEM HAADF image shows the location of the SPP 200 nm from the top oxide surface, (b) higher mag STEM HAADF image shows darker contrast of SPP, (c) TEM BF of SPP, (d) comparison of EELS spectrum of SPP and oxide over a range containing the oxygen, Fe and Ni signal, (e) comparison of EELS spectrum of SPP and oxide over a range containing Zr and Nb signal, (f) concentration of Zr and Nb across the SPP (horizontally).

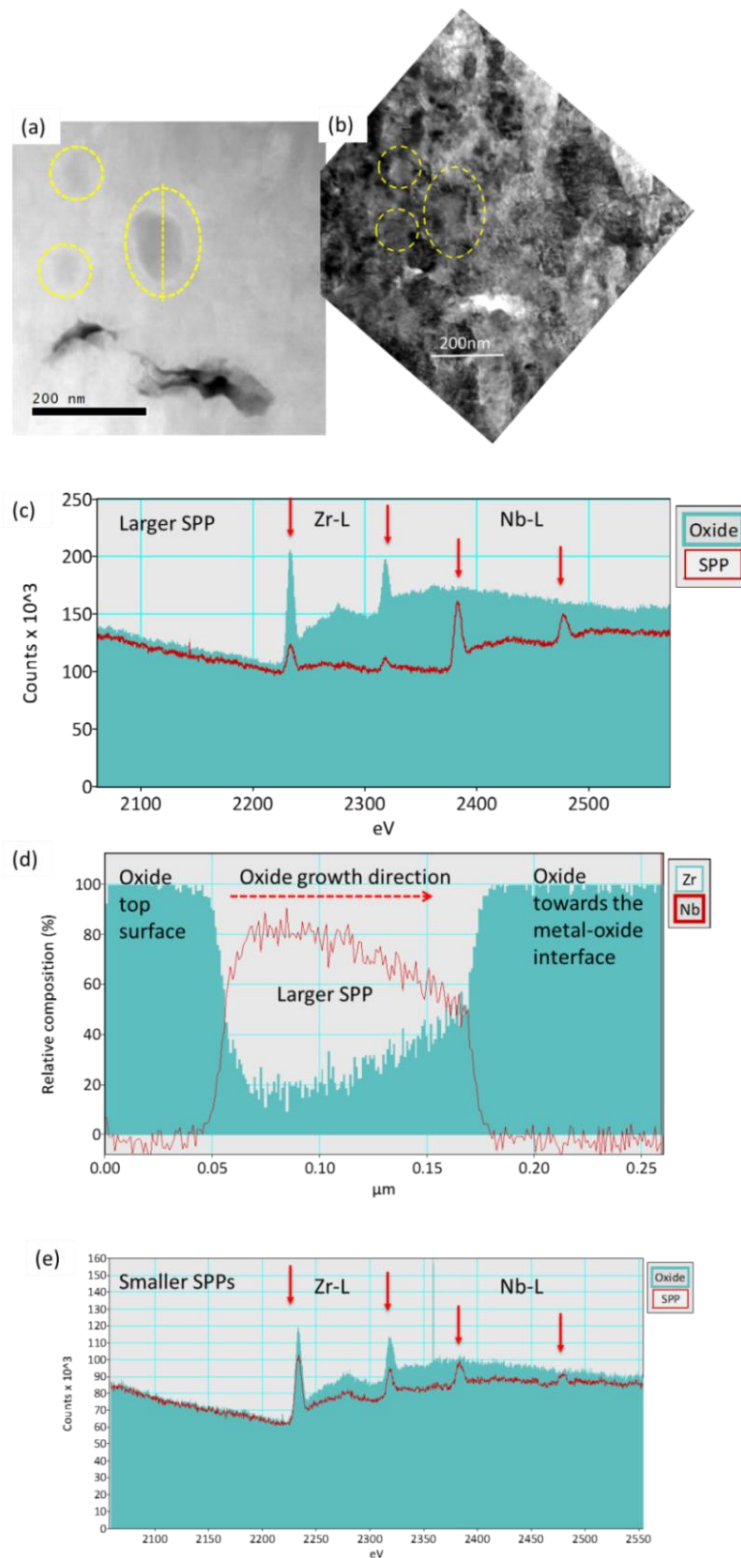


Figure 5-13: Example of EELS analysis of SPPs in the middle of oxide from the first irradiated TEM sample: (a) STEM HAADF image shows the location of the SPPs 0.85 μm from the top oxide surface, (b) TEM BF image of the SPPs, (c) comparison of EELS spectrum of bigger SPP and oxide over the range containing Zr and Nb signal, (d) concentration of Zr and Nb across the bigger SPP (vertically). (e) Comparison of EELS spectrum of bigger SPP and oxide over the range containing Zr and Nb signal

- *SPPs near the metal-oxide interface*

Figure 5-14 shows an example of several SPPs near the metal-oxide interface. The metal-oxide interface in this case has an unusual shape, with a protruding segment of unoxidised Zr metal and several SPPs near the interface. There are two SPPs with crescent shape crack on top, one is around 50 nm in diameter and another one 80 nm in diameter. These two SPPs can be easily spotted in the TEM BF image in (c). However, all the other smaller SPPs with 30-40nm in diameter in the oxide are very hard to find in the TEM BF image due to low diffraction contrast. Several metallic SPPs in the metal can be seen in the STEM HAADF image, but the TEM BF image covers a smaller so it does not include those. The majority of the SPPs are 30nm in diameter while there is one bigger one that is 100nm in diameter.

EELS analysis was done on one elliptical SPP around 40 nm in length and 35 nm in width. This SPP is around 450 nm from the interface. The higher magnification STEM HAADF image in (b) shows a slightly darker contrast than the bigger metallic ones but still shows lighter contrast than the oxide, which suggests it might be partially oxidised. The oxygen peak in 510 eV range shows that there is oxygen in the SPP, although it can be from the oxide surrounding the SPP or surface oxide created after final thinning. The core loss spectrum of the SPP using a 3 nm step size and 0.25 eV channel per pixel in (d) shows the Zr-L and Nb-L edges. Inside the SPP, there are Nb-L peaks with Nb-L3 peak at 2378.8 eV, which corresponds well with our earlier calibration of Nb metallic peak at 2378.5 eV. The Zr-L peak is at 2232.6 eV. The concentration profile in (e) shows a concentration of 80% Zr and 20% Nb, suggesting that there should be some Zr from the surrounding oxide and the SPP is not the full thickness of the TEM sample.

In Figure 5-14 (f), I analysed one elliptical SPP around 85 nm in length and 50 nm in width, right at the interface with the top part in the oxide and bottom part in the metal. By comparing the core loss spectrum from line profiles across oxide, SPP and metal, it is found that the SPP

has the Nb-L3 peak at 2378.2 eV which is very different from the oxidised Nb⁵⁺ peak 2383eV, suggesting it is either partially oxidised or remains metallic. It is interesting to see the Zr-L peak of SPP and oxide lies at 2231.8eV while in the metal it is at 2229.4 eV. Both of these examples suggest that the Nb in the metallic/partially oxidised SPPs near the metal-oxide interface is not oxidised.

- *Conclusions*

In this section, EELS and HAADF imaging have provided a good way to analyse the oxidation states of individual SPPs and how this changes with its position in the oxide layer.

The SPPs started as β -Nb and Laves phase SPPs in the metal, and while undergoing neutron irradiation most of the Fe has diffused out of the Laves phase SPPs in both the oxide and the Zr matrix and some of the Cr as well. The average size of these metallic SPPs is 63 nm, and they are mostly round.

At around 700 nm from the metal-oxide interface, most SPPs remain metallic/ partially oxidised. The average size of these metallic/partially oxidised SPPs is 63 nm. EELS core loss spectra show that Nb in these SPPs remains metallic or in the 2+ oxidation state.

When SPPs begin to oxidise, such as the SPPs at the top surface of oxide, the shape becomes elliptical, some of the bigger SPPs are around 100 nm in length and 50 nm in width, while there are also small round ones around 50 nm in diameter. The average size of these fully oxidised SPPs is 71 nm. EELS core loss spectra show that Nb in these SPPs is fully oxidised to the 5+ state.

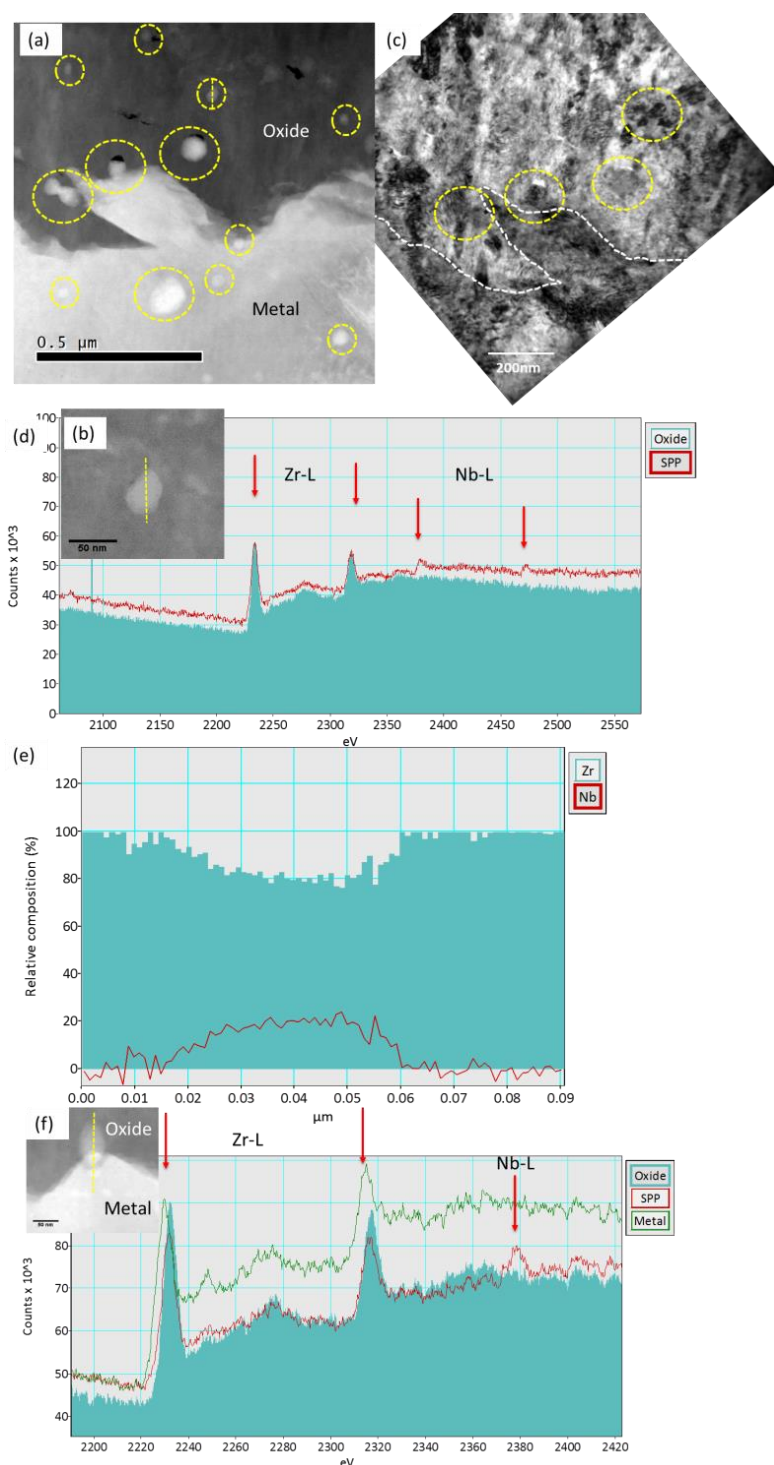


Figure 5-14: Example of EELS analysis of SPPs near the metal-oxide interface (a) STEM HAADF image shows the location of the SPPs from the first irradiated TEM sample, (b) higher magnification STEM HAADF image of the elliptical SPP around 450 nm away from the metal-oxide interface, (c) TEM BF image of SPPs, (c) comparison of EELS spectrum of SPP and oxide over the range containing Zr and Nb signal, (d) concentration of Zr and Nb across the bigger SPP (vertically). (f) higher magnification STEM HAADF image of the SPP at the metal-oxide interface from the second irradiated TEM sample, and comparison of EELS spectrum of SPP, oxide and metal over the range containing Zr and Nb signal

5.5 SUBOXIDE

Low-loss EELS mapping was done in the region highlighted in the ASTAR map in Figure 5-4(c) from the second irradiated TEM sample. The step size is 4 nm and acquisition time is 10^{-5} s. Several reference spectra were acquired from ZrO_2 , ZrO , $\text{Zr}(\text{Osat})$, metal, hydride and SPP phases.

After MLLS fitting over the energy range 10-60 eV, the results are shown in Figure 5-15. As seen in the STEM HAADF image in (a) and part of the ASTAR map in (b), most of the fitting works very well in (c), such that the oxide, metal, SPPs and hydrides. However, it is interesting to see that although the reference spectra of ZrO and $\text{Zr}(\text{Osat})$ have different peak shapes and positions, the fitting was not very successful in separating them unlike in the autoclave oxidised samples, seen from Chapter 3.5. Instead, the suboxide and oxygen saturated metal area are combined together to form an almost uniform layer around 100-120 nm thickness, except at one undulation area as highlighted in the STEM HAADF image, ASTAR map and ZrO map, there is around 160nm thickness suboxide. ASTAR mapping indicates the ZrO suboxide is very discontinuous with regions of around 50-100 nm in length.

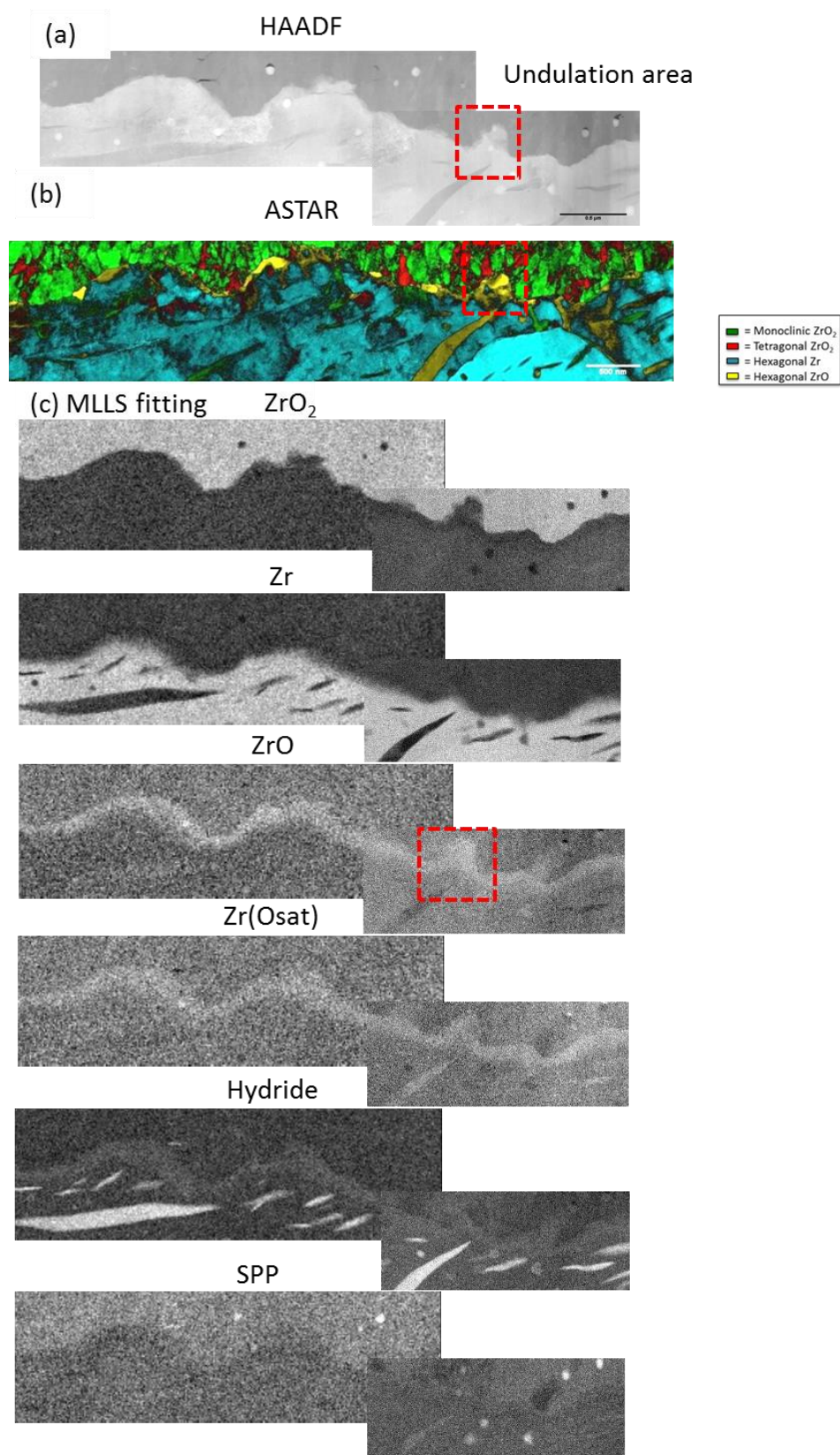


Figure 5-15: (a) STEM HAADF image of an area from the second irradiated TEM sample (b) ASTAR map of the same area (c) MLLS fitting of the reference spectra from low loss EELS mapping, for the ZrO_2 , ZrO , $Zr(Osat)$, metal, hydride and SPP phases, respectively.

6 CHAPTER 6 DISCUSSION

6.1 Effect of macro structure of oxide – macro cracks, metal-oxide evenness and their relationship with oxide phases

In this study, detailed macrostructure analysis on different samples with different oxidation rates reveals the importance of macro cracks on the oxidation and hydrogen pickup in corroding Zr alloys. The relationship between macro crack distribution and metal-oxide evenness and oxide phases will be discussed in this section.

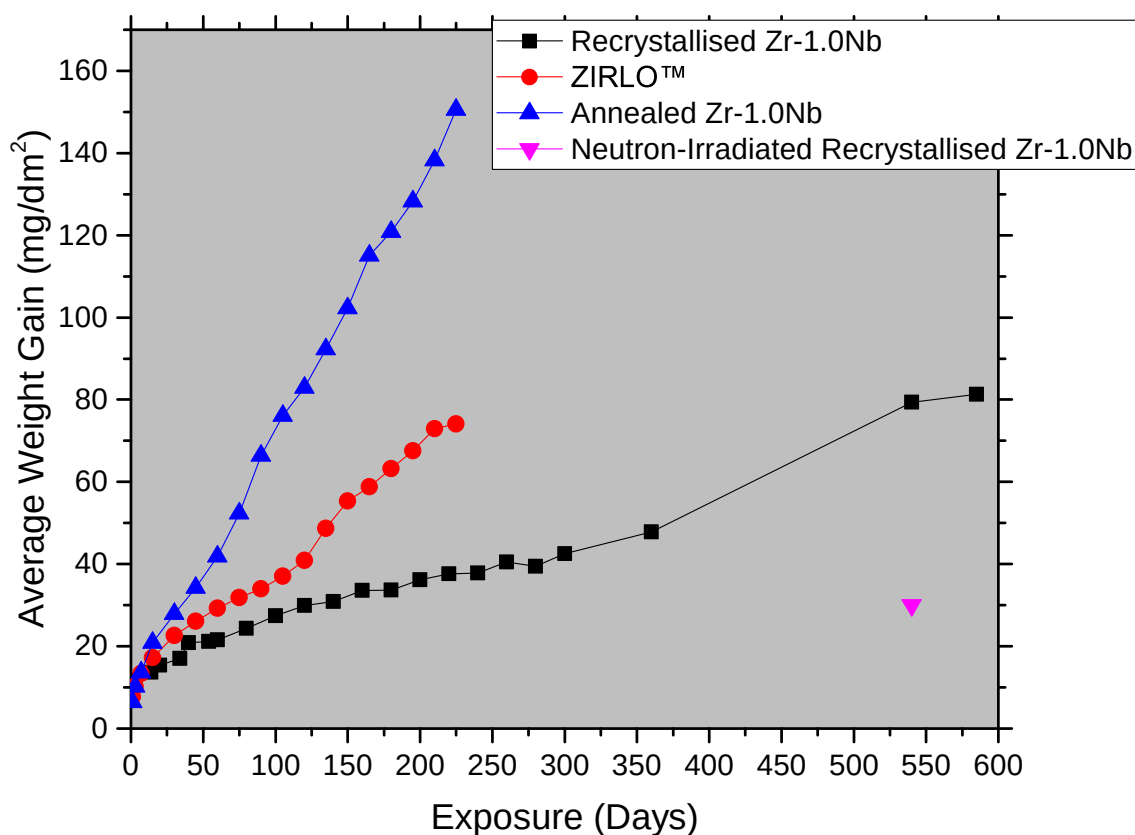


Figure 6-1: Weight gain data for RXA Zr-1.0Nb, ZIRLO[®], annealed Zr-1.0Nb and neutron-irradiated RXA Zr-1.0Nb. The neutron-irradiated sample was oxidised at a lower temperature than the other alloys.

Here I compare the RXA and annealed Zr-1.0Nb alloys that I studied with data from another student, Thomas Aarholt who worked in parallel on ZIRLO[®] alloys. The weight gain data for all these samples is shown in Figure 6-1. The RXA Zr-1.0Nb undergoes a kinetic transition in the corrosion rate at around 360 days. Even though it has the same composition, the annealed

Zr-1.0Nb alloy showed a much earlier acceleration in corrosion rate between 45 and 60 days, and much faster overall oxidation kinetics^{70,47,119}. The ZIRLO® transition point is between 120-135 days. It is also noticed that in these three samples, the initial oxidation rates were very fast.

The macro crack distribution is shown of the overview of the samples in Figure 6-2. The 3-day samples represent the very beginning of the corrosion process where the sample has a very fast oxidation rate. It is interesting to note that the oxide thickness varies considerably in different regions, and this feature is seen across the three different samples. The TEM Bright Field (TEM BF) image in (a-1) of RXA Zr-1.0Nb which has a good corrosion resistance in general, shows that on the right side the oxide has a uniform thickness of 0.65 μm but on the left the oxide becomes uneven with the thickest part >1.3 μm . Around 400 nm from the top surface there is a continuous layer of parallel cracks running over a 5 μm wide region. The 3-day sample of annealed Zr-1.0Nb in (a-2) shows the oxide thickness ranges from 0.5 μm to 0.9 μm . There is one big crack 600 nm in length about 50 nm from the metal-oxide interface. For the ZIRLO® samples in (a-3), the 3-day sample emphasises the observations of local variation in oxidation kinetics. The oxide thickness varies strongly, ranging from 0.5 μm at the thinnest to 1.0 μm at the thickest.

When oxide continues to grow to the first transition, the slower oxidising RXA Zr-1.0Nb shows a much more even metal-oxide interface and fewer cracks at the interface with denser oxide as seen in the 360-day sample in (b-1) comparing with annealed Zr-1.0Nb and ZIRLO®. For the much quicker oxidising annealed Zr-1.0Nb sample after 46 days, (b-2), the oxide thickness ranges from 2.5 μm to 4.2 μm . In a region about 700 nm above the metal-oxide interface there are several parallel cracks around 500 nm in length, and at the metal-oxide interface on the right hand side where the oxide is thicker a single 500 nm crack suggests

another transition is just about to happen locally. Similar uneven metal-oxide interfaces and a high density of cracks are observed in ZIRLO[®] as well, (b-3).

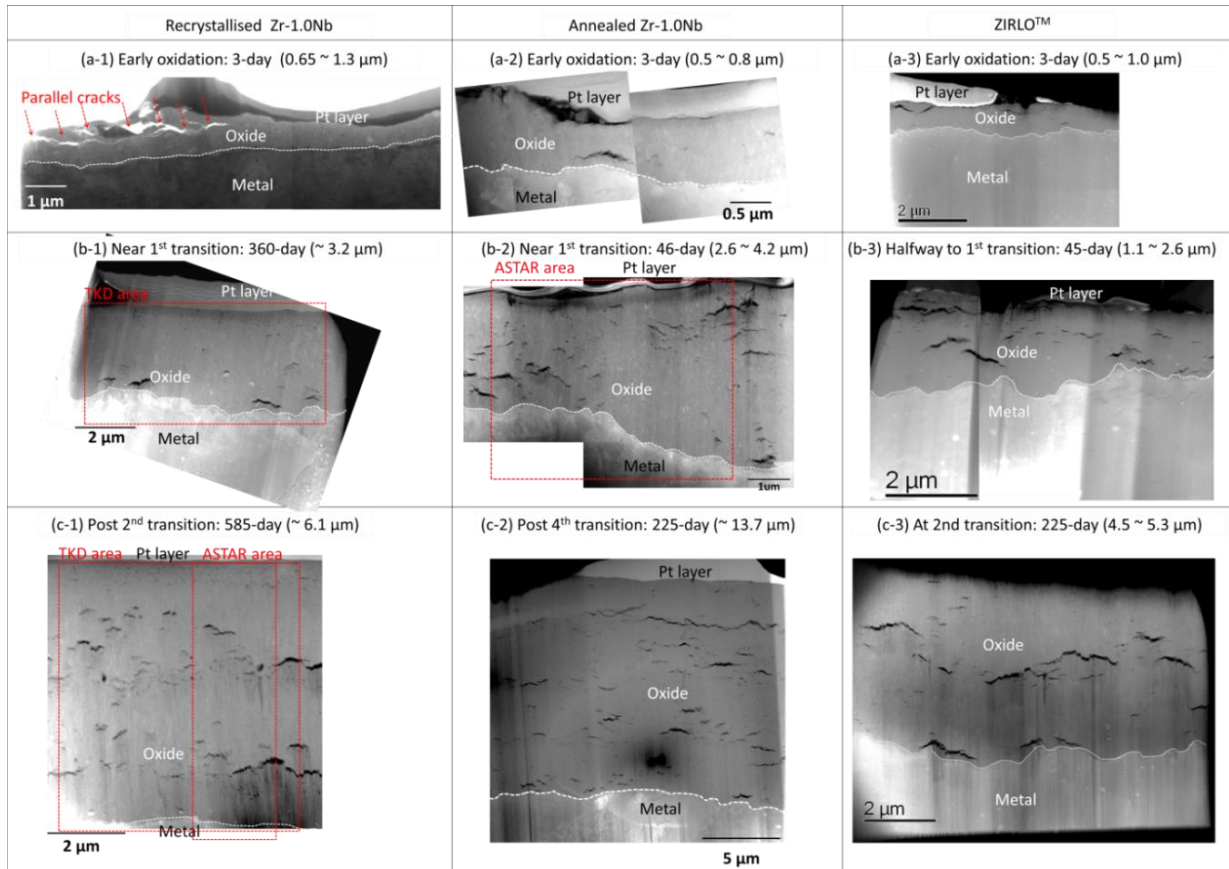


Figure 6-2: TEM BF and STEM HAADF images of autoclave oxidised samples chosen for the study: recrystallized Zr-1.0Nb annealed Zr-1.0Nb and ZIRLO[®]. Only examples of early oxidation, near 1st transition and post transition samples are shown. (All ZIRLO[®] images courtesy of Thomas Aarholt)¹⁵².

The post transition samples have a more even metal-oxide interface. The post-second-transition RZA Zr-1.0Nb sample shows two layers of transition cracks parallel to each other and to the metal-oxide interface in (c-1). The oxide thickness is 6.1 μm and the layers of cracks are separated by around 2.5 μm . In the annealed Zr-1.0Nb samples, the 225-day sample in (c-2) contains four layers of cracks and an average oxide thickness of 13.7 μm . Each layer of cracks is separated by around 3.2-3.5 μm (as is frequently observed in thick oxides on Zr alloys^{6,17}). Similar observations can be made in ZIRLO[®] as well, however with shorter crack separation between transitions, (c-3). This agrees well with previous findings

that alloys with good oxidation resistance have thicker layers of oxide before transition, thicker oxide between the transition cracks⁶⁹.

Previous authors have reported the relationship between crack formation and oxidation rate. Tejlund¹⁵³ reported a much higher crack density for Zircoloy-2 alloys with smaller SPPs and a higher oxidation rate. Ni¹²¹ used 3D FIB sectioning to study ZIRLO[®] alloys, which showed on the same sample that the thicker grey oxide has a higher crack density comparing with the thinner black oxide. Ni also shows that the inhomogeneity of the metal-oxide interface is formed in the pre-transition samples, and suddenly at transition period the interface tends to become flatter. After transition, the inhomogeneity continues to grow until another transition happens. This agrees well with the observations found in this study. Among all the 3-day samples as shown in (a-1~3), the oxidation rate is very high, the oxide thickness varies a lot even over small regions and large cracks are often seen in the oxide. In the pre-transition period, the RXA Zr-1.0Nb alloy which has a slower oxidation rate has fewer cracks in the oxide, and also a flat metal-oxide interface. The annealed Zr-1.0Nb and ZIRLO[®] alloys have much faster oxidation rates, more cracks in the oxide and also more inhomogeneous metal-oxide interfaces in pre-transition samples (b-2) (b-3). When these samples go through transition, the metal-oxide interface tends to become flatter, (c-3), until the oxidation breaks away. Especially in (c-2) when the oxide has gone through several transitions, it was noticed during the sample making process in the FIB that the metal-oxide interface was surprisingly flat.

Due to the large Pilling-Bedworth ratio of 1.55, the volume increase on forming the oxide has introduced stresses in both axial and hoop directions. When the metal-oxide interface is flat, the compressive stress in the oxide and the tensile stress in the metal are relatively small due to the big differences of thickness of oxide and metal¹⁵⁴. Also the axial stress is small¹⁵⁴. However, when the metal-oxide interface is wavy, finite element modelling shows that much

larger stresses are developed in both axial and hoop directions^{154,155}. Parise et al¹⁵⁴ have modelled the local stress at the metal-oxide interface, and Figure 6-3 shows the schematic distribution of stresses around the undulated area which suggests that in both concave and convex regions of the oxide, the hoop stress is compressive, while the axial stress is tensile when the interface is concave and compressive when it is convex. The axial stress that is perpendicular to the metal-oxide interface can be the reason for the preferential formation of parallel cracks above the undulation, as observed in this study (Figure 3-3 and Figure 3-6) and previous literature^{121,153}.

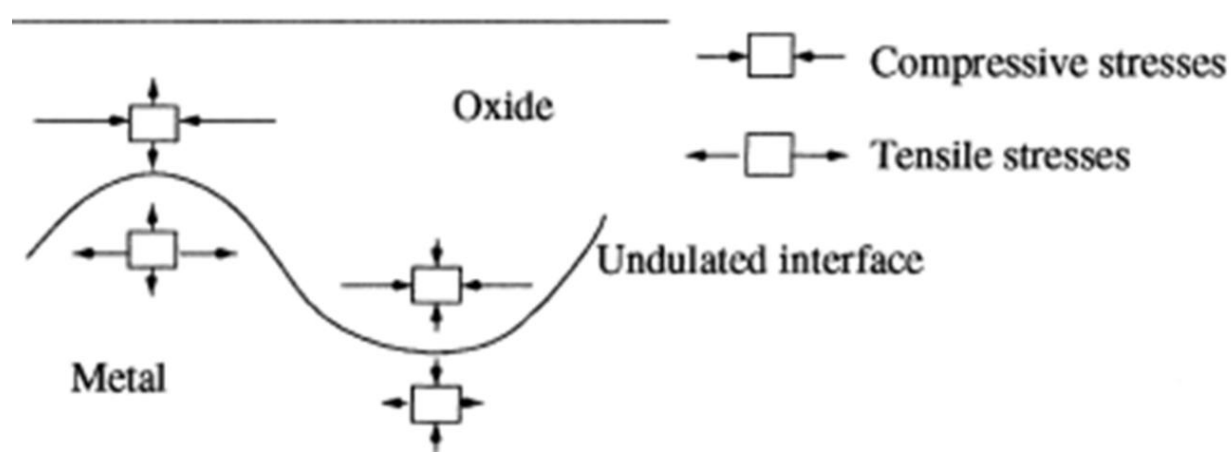


Figure 6-3: Schematic distribution of stresses around the undulated area¹⁵⁴

Another outcome of this work is the correlation of crack distribution and metal-oxide interface evenness with the metal grain texture underneath. In the RXA Zr-1.0Nb and ZIRLO[®] alloys the metal grain size is around 3~5 μm (Figure 3-3), however after anneal at 720°C the metal grain size almost triples (Figure 4-6). It seems that the metal grain size does not influence the metal-oxide interface evenness since both ZIRLO[®] and annealed Zr-1.0Nb have uneven metal-oxide interfaces. Another proof is that the uneven metal-oxide interface does not always happen above different metal grains (b-2) shows the uneven part lies above one single metal grain. Garner et al¹⁵⁶ studied Optimised ZIRLO[®] by looking at one sample at

three different orientations, and while the metal texture is different in each case the oxidation rate is similar, which suggests that metal texture should not play a role influencing the oxide growth rate. The effect of SPPs on cracking and the influence on oxidation rate will be discussed in section 6.4.

Although the majority of the cracks are parallel to the metal-oxide interface in this study, it is worth mentioning that at a much lower density there are vertical cracks from the sample surface about 400 nm in length or penetrating from top surface to the metal (Figure 3-6 and Figure 4-3). This type of crack provides the best paths for oxygen penetration towards the metal-oxide interface. Since this type of cracking is observed very rarely, we do not believe that it is a general feature of FIB-prepared TEM samples. Other authors have observed similar vertical cracks in Zircalloys which is linked to a local accelerated corrosion rate¹⁴⁹. Yardley et al¹⁵⁷ reported using NanoSIMS that the vertical cracks from the top surface to the metal-oxide interface in low tin ZIRLO[®] samples are the path way for oxygen ingress, while the parallel cracks near the metal-oxide interface are obstacles. In the RXA Zr-1.0Nb alloys, most of the vertical cracks are shorter, only running through the top equiaxed layer which should not influence the oxidation of the metal below, however, Y-shaped cracks have been found in 120-day sample that are connected from the top surface to an undulation of the oxide (Figure 3-6). In annealed Zr-1.0Nb samples, the vertical cracks are seen more often, and are longer in length (Figure 4-3). In FIB-SEM images, some of these vertical cracks are connected with an advanced metal-oxide interface, and this can introduce crystallographic mismatch between different parts of the oxide, which increases cracking and corrosion rate. It is worth mentioning that Westinghouse^{TM158} has commented that surface cracks can come from material processing procedures, however the samples compared in this work have been through similar manufacturing process so there should not be any significant difference between RXA and annealed Zr-1.0Nb. The extreme structure of surface vertical cracks in the

annealed sample has not been cold worked, and should therefore not have a high risk of defect formation during fabrication.

6.2 Effect of ZrO₂ oxide phases

Although detailed microstructural analysis was carried out on all these samples by conventional TEM, the grain structure in the oxide and their phase distribution is most easily revealed by TKD, as seen in Figure 3-7 in chapter 3.

The slower corroding RXA Zr-1.0Nb has a more characteristic periodic pattern of equiaxed-columnar-equiaxed-columnar grains, which is observed in most of the samples after one or more kinetic transitions. The large, elongated columnar grains are oriented parallel to the oxide growth direction, around 50 nm in width and 350-450 nm in length. There are scattered parallel cracks in the pre-transition samples which break up the columnar grains. Disorganised oxide grains under the second layer of cracks are smaller and shorter than those columnar grains higher up, only around 150-200 nm in length (Figure 3-8). This may be associated with faster corroding after the second transition. Comparisons of columnar grains in 360-day and 585-day samples above and below the second layer of cracks are shown in Figure 3-8.

The faster corroding annealed Zr-1.0Nb shows a more complicated oxide microstructure. It is interesting to see the top of the oxide has columnar grains around 20-25 nm in width (Figure 4-8). This is seen at multiple different locations and the top oxide has Pt protective layer intact during FIB process, unless the oxide has spalled off before making the sample. It is very unusual to see an oxide with columnar grains right up to the oxide-water interface, but some literature^{6,159} has shown that unalloyed zirconium alloys after oxidation at 650°C in atmospheric pressure air for periods of up to 67 h can grow very long columnar grains of 10 µm without too many cracks (Figure 1-17). A similar observation shows Zircaloy-4 alloys after steam corrosion at 1300°C also grow long columnar oxide from the oxide-water

interface towards the metal-oxide interface¹⁶⁰. The author also suggested that porosity development in this case can contribute to the oxidation process. The porosity content in annealed Zr-1.0Nb is much higher than RXA Zr-1.0Nb which, as will be discussed in section 6.3. Detailed TEM studies on Zircaloy-4, ZIRLO[®] and Zr-2.5Nb alloys⁶⁴ show that there is a trend for more complicated oxide grain structure with higher corrosion rate, which agrees well with this study.

Apart from the oxide morphology, the phase distribution is an important factor controlling oxidation resistance^{130,161,162}. Comparison of the ASTAR mappings between Figure 3-11 and Figure 4-7 illustrates the differences between slow oxidising and fast oxidising Zr-1.0Nb alloys. The RXA Zr-1.0Nb sample has a lower tetragonal phase fraction. In the pre-transition samples, the TKD mapping detects around 2.7% tetragonal grains in the 225-day sample, and 0.7% in the near-transition 360-day sample¹²⁸, while in the post-transition 585-day sample the fraction drops to 0.1%. The tetragonal grains in this sample are mostly near the metal-oxide interface so presumably they are mostly stress-stabilised¹⁶³. The annealed Zr-1.0Nb sample has much more tetragonal grains (Figure 4-7), some of them around 40-50 nm in diameter and scattered in the equiaxed oxide from the top surface throughout the oxide thickness. Previous authors^{63,129,130} have argued that the addition of Sn can stabilise the tetragonal phase, however in neither of these alloys is there any Sn, so this effect cannot explain the increasing tetragonal phase fraction. There are two primary mechanisms for tetragonal phase stabilisation. One is by stress^{163,164}, but the FIB process used to make the TEM samples studied here will reduce the stress in the oxide, which should destabilise those tetragonal grains^{129,165,166} which makes the tetragonal fraction in TEM samples much lower than observed in Raman spectroscopy and X-ray analysis¹⁶². It is interesting to see that more tetragonal oxide exists where there are no cracks (Figure 4-7), and this might be associated with stress stabilisation of tetragonal oxide, while at some locations there are tetragonal oxide grains around the cracks as well. It is

possible that there was initially a higher fraction of tetragonal grains in the equiaxed grain region around the cracks, but that they are destabilised by the cracking of the oxide. Another mechanism for stabilising tetragonal grains is by size¹⁶³. The grain size in annealed Zr-1.0Nb alloys is much smaller than in RXA Zr-1.0Nb alloys, so they can be size stabilised as well.

6.3 Effect of protective oxide layer porosity and suboxide

By using Fresnel imaging in the TEM, different types of porosity can be easily identified^{61,71,167,168}. Comparing different samples, there is a correlation between porosity content and oxidation rate. Annealed Zr-1.0Nb which has the most disorganised microstructure and fastest oxidation also has the highest porosity content. The RXA Zr-1.0Nb alloy has very organised microstructure with less porosity.

Many examples in Chapter 3.3 (Figure 3-14, Figure 3-15, Figure 3-16 and Figure 3-17) shows the distribution of porosity near the metal-oxide interface in the RXA Zr-1.0Nb alloy. There are several different kinds of porosity in this small area. The different types of pores detected include; individual pores in columnar oxide grains, some of these individual pores are connected creating an array of flake-like porosity around 10-15 nm in length parallel to the metal-oxide interface, and vertically interconnected porosity along some of the columnar oxide grain boundaries. There is also continuous porosity directly at the metal-oxide interface underneath some of the columnar grains. This kind of complex interconnected porosity is expected to play an important role in the oxygen diffusion processes that control the local rate of oxidation⁷¹.

The annealed Zr-1.0Nb alloy which has a much faster oxidation rate than the RXA material also contains significantly more porosity in the oxide, as seen in Chapter 4.3 (Figure 4-9 and Figure 4-10). These images show a high concentration of isolated pores, around 2-4 nm in diameter, inside columnar grains and continuous porosity along many columnar grain

boundaries. This vertically interconnected porosity forms a continuous path for the transport of oxidising species through the oxide scale.

HAADF and EELS analysis and automated crystal orientation mapping in the TEM have been used to study the metal-oxide interface in order to provide a comprehensive view of local microstructure and micro-chemistry (Chapter 3.5 and Chapter 4.5). I concentrated on this region because this is where the primary corrosion reaction occurs between zirconium metal and inwardly diffusing oxidising species. As well as the bulk zirconium oxide (which can have grains of both tetragonal and monoclinic crystal structures) and the underlying Zr metal, the metal-oxide interface contains a complex mixture of fine suboxide grains and oxygen-saturated metal ($\text{Zr}(\text{Osat})$)^{60,61,97,128,148,169–171}. Figure 3-50 shows that during the pre-transition, the suboxide and combined layer keep growing thicker, and that after the transition the layer becomes thinner and starts another cycle of growth.

By combining this kind of low loss EELS mapping and APT analysis of metal-oxide interfaces^{61,170,171} I have, with two other students working on the same set of samples, been able to correlate the total thickness of the suboxide and $\text{Zr}(\text{Osat})$ regions in a large number of different samples at different stages of oxidation (Chapter 3.5 and Chapter 4.5). This data is brought together in Figure 6-4. The error bars show the standard error for the measurements on each sample. Looking at all the alloys as one, the data suggests that during rapid oxide growth there is a thinner layer of suboxide and $\text{Zr}(\text{Osat})$. However, for individual alloys the trend is similar. Considering that RXA Zr-1.0Nb has a better corrosion resistance than ZIRLO[®], this implies that alloys with better corrosion resistance have more formation of suboxide and the combined Zr-O region (suboxide + $\text{Zr}(\text{Osat})$).

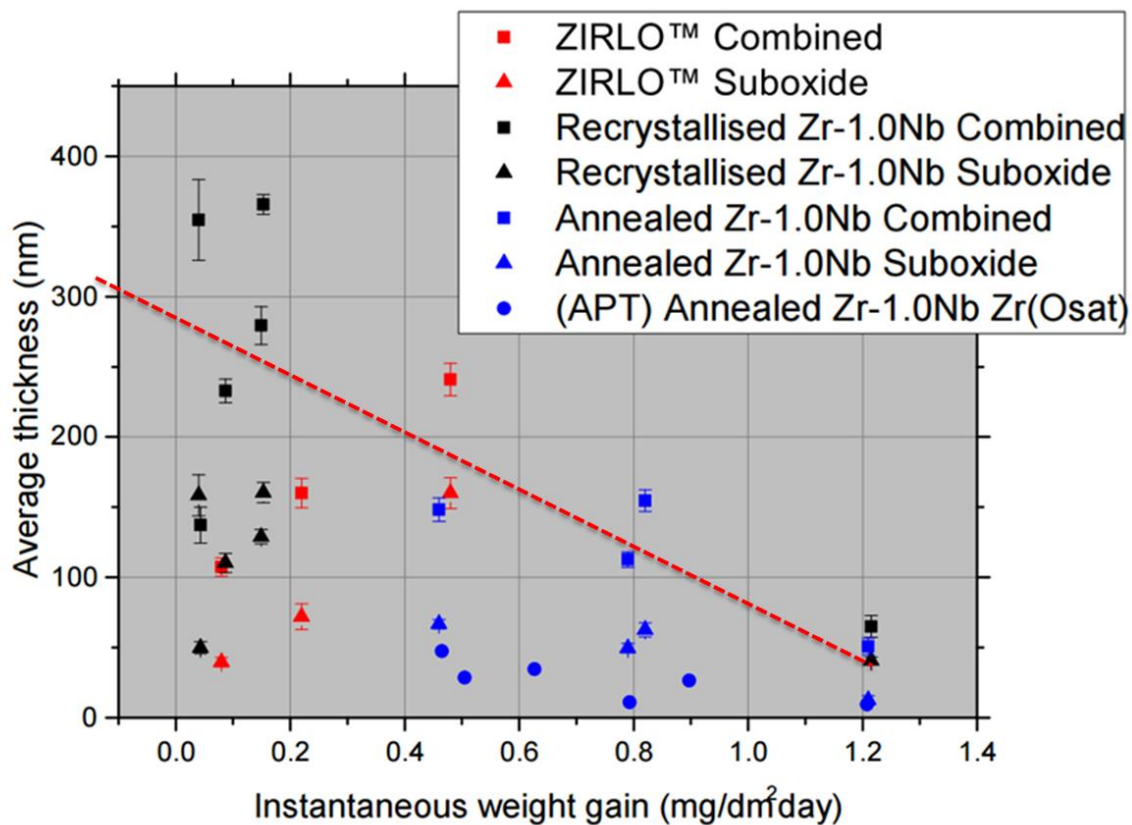


Figure 6-4: Correlating Zr-O with instantaneous oxidation rate. Includes data from Brian Setiadinata and Thomas Aarholt¹⁵².

Figure 6-5 illustrates our new interpretation of protective oxide combining the porosity based on Ni's⁷¹ work and our work on combined Zr-O layers. In the pre-transition stage when oxidation is slow, the porosity is not interconnected, the suboxide and combined O-rich layer grow thicker with oxidation time. After transition when oxidation is faster, the porosity becomes interconnected, and the suboxide and combined O-rich layer is thinner.

6.4 Effect of SPPs

In the RXA Zr-1.0Nb samples, two types of SPPs were observed, β -Nb and $\text{Zr}(\text{Nb},\text{Fe})_2$ Laves phase particles. The second type is larger in size and has a lower number density, and tends to rapidly become amorphous once incorporated into the growing oxide (Figure 3-25). In the oxide close to the metal-oxide interface most SPPs remain crystalline, and often have

crescent-shaped voids on the top created as the surrounding zirconium metal preferentially oxidises and expands around the relatively noble particles^{61,64}.

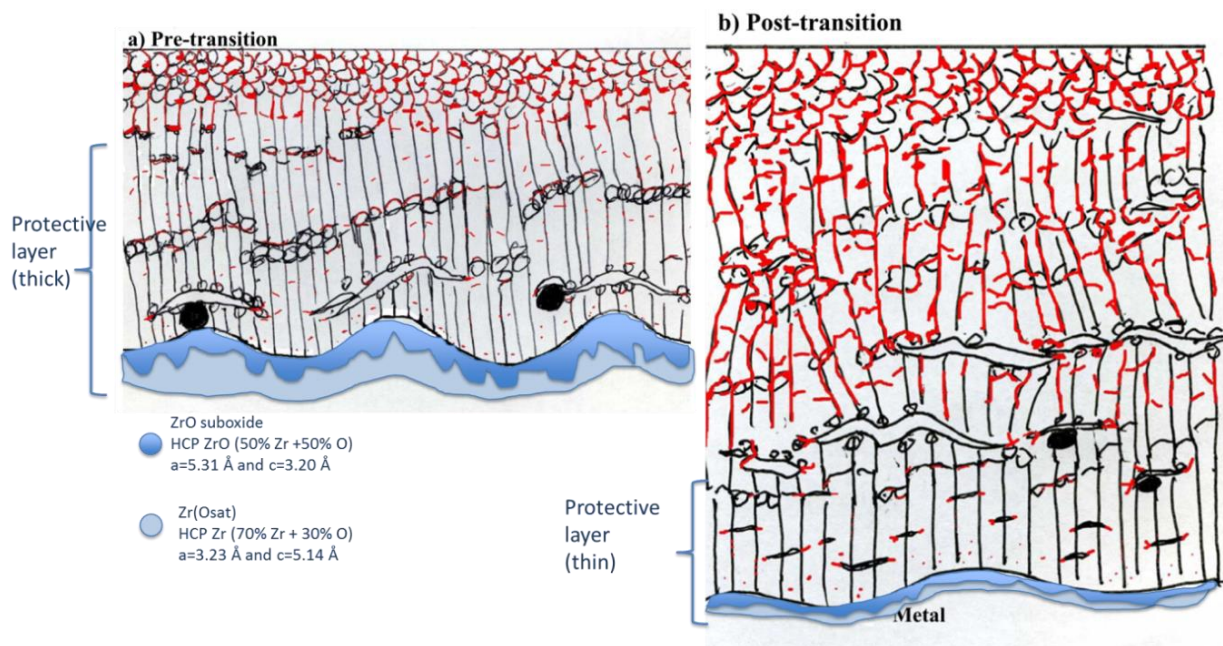


Figure 6-5: Illustration of protective layer in pre and post transition samples, based on the illustration from Ni^{66,71}.

As oxidation progresses, the β -Nb SPPs start to become amorphous about 1.5 μm from the metal-oxide interface, but earlier for the Laves phase SPPs at just 0.8 μm Figure 3-24. It is noticed that the thickness of the oxide where crystalline β -Nb SPPs can be found is thicker than previously reported in ZIRLO[®] alloys¹⁷². The β -Nb SPPs are crystalline but the one shown in Figure 3-22 has oxidised and become amorphous. The Laves phases near the interface are larger than the ones near the top surface and still contain Cr (Figure 3-26), while the ones near the top surface (in contact with the oxide for longer) have lost all the Cr. There is thus clear evidence for changes in the SPP chemistry as they spend more time in the growing oxide.

STEM HAADF images of the fully oxidised SPPs show a clear darker contrast, due to its higher oxygen content resulting in a lower atomic weight, while in the TEM BF image, there is hardly any diffraction contrast (Figure 2-6). It is often assumed that most SPPs become

amorphous and dissolve into the surrounding oxide matrix when they undergo oxidation, however, both Ni⁶⁶ and Gabory¹⁷³ have recently reported oxidised SPPs still remain crystalline in Zircaloy-4, either on the top surface of the oxide by Ni⁶⁶ or 300 nm away from the metal-oxide interface by Gabory¹⁷³. The fully oxidised SPPs on the oxide top surface in my RXA Zr-1.0Nb samples (Figure 3-36) are also crystalline, in a good agreement with these studies. The reason for the previous conclusions is perhaps because of the limitation of sample making techniques which makes producing a full TEM sample of the whole oxide difficult, many of them only looked at the area around 1 μ m above the metal-oxide interface, where it is more common to see amorphous SPPs than the top surface of the oxide. With the STEM HAADF and EDX mapping techniques that I have used, it is much easier to see all the different conditions of SPPs and their distribution through the oxide thickness.

APT analysis of the same samples was used by another student, Brian Setiadinata, to study the distribution of Fe in and around β -Nb SPPs near the metal-oxide interface in several different materials. This technique allows the analysis of trace element distributions with a higher sensitivity than can be achieved by TEM analysis. Figure 6-6 shows a concentration profile for Fe around a crystalline/metallic (unoxidised) 50 nm β -Nb SPP in the oxide in a 3 day RXA Zr-1.0Nb sample. The Fe concentration in the surrounding oxide is $\sim$ 0.0015 at%, and in the β -Nb SPP itself increases to about 0.2 at% with some indication of Fe segregation to the interface between the particle and the oxide matrix. Recent APT data has also shown that a small number of the columnar grain boundaries are also decorated with Fe and Ni in Zircaloy-2 samples¹⁷⁴.

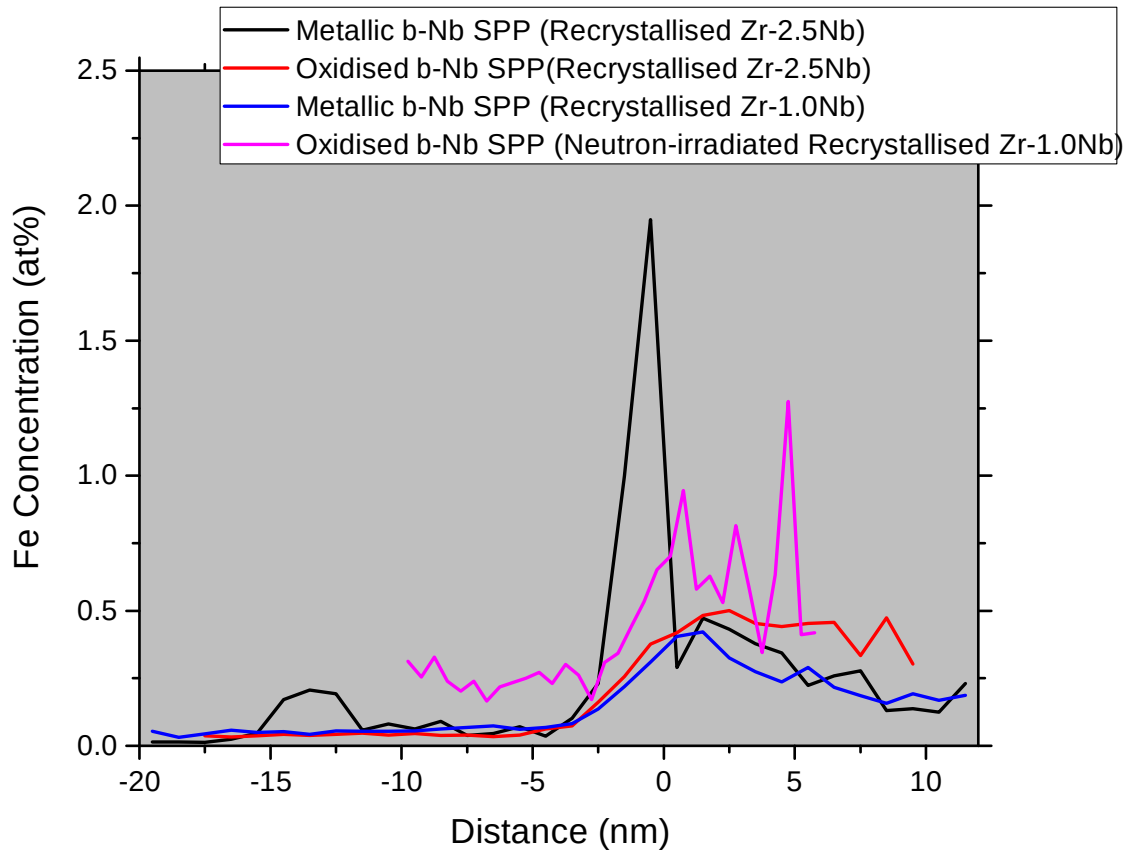


Figure 6-6: APT analysis of the distribution of Fe in and around β -Nb particles in the oxide in Zr-1.0Nb, Zr-2.5Nb and irradiated Zr-1.0 Nb samples. 0 nm is the SPP-oxide interface. Black: Metallic β -Nb in the metal (RXAZr-2.5Nb). Red: Oxidised β -Nb in the oxide (RXA Zr-2.5Nb). Blue: Metallic/partially oxidised β -Nb in the oxide with 5 at% Oxygen (RXA Zr-1.0Nb). Pink: Oxidised β -Nb in the oxide (neutron irradiated RXA Zr-1.0Nb)¹⁷⁵. Data courtesy of Brian Setiadinata.

Another interesting finding in this study is regarding the Laves phase SPPs in the oxide (Figure 3-27). EDX mapping of post-transition RXA Zr-1.0Nb samples has found that the top layer of oxide has the highest proportion of Laves phase SPPs, 50% out of all the SPPs, while the number gradually drops to 14% in the columnar oxide region where there are almost no Laves phase SPPs. Closer to the metal-oxide interface, the ratio of Laves phase SPPs seems to be similar to that found in the metal, around 20%.

The oxidation state of the SPPs has for the first time been analysed in Zr alloys. EELS analysis was performed on SPPs at different locations in the oxide and in samples at different

stages of oxidation refer to a fig in previous chapter. By comparing spectra from line profiles across each SPP with a reference spectrum from an unoxidised β -Nb SPP in the metal, it was possible to determine the oxidation states of both Nb and Zr, which are characterized by a shift of the edges towards higher energy losses (higher oxidation states). It seems that in the crystalline SPPs near the metal-oxide interface, Zr is in the metallic, unoxidised condition, but Nb is partially oxidised to the Nb^{2+} state. Both amorphous SPPs and SPP at the top surface which remains crystalline have similar edge shifts, suggesting Zr is now in the oxidised condition and Nb inside the SPPs has been oxidised to a higher state, possibly Nb^{5+} . This suggests that the oxidation of β -Nb SPPs is a dynamic process during the corrosion of Zr-alloys, with parts of the same SPP being at different stages of oxidation and releasing aliovalent ions to the surrounding oxide^{176–178}. XANES studies^{179,180} confirm the findings of $\text{Nb}^{2+}/\text{Nb}^{3+}$ states by probing the Nb L edge, and similar observations are found on Fe^{2+} as well, which can influence the electron and hydrogen pickup by changing the local charge state. Some authors say that these dopants can stabilise the tetragonal phase as well, which will make the oxide more protective^{32,181}. The cracks on top of these SPP may also be influential in controlling the rate of local oxidation.

In this study, a lot of comparisons have been made between the RXA and annealed Zr-1.0Nb samples, and one of the most obvious differences is the SPP size distribution (Figure 3-26 and Figure 4-13). By undergoing the 720°C heat treatment for 24 hours, the annealed Zr-1.0Nb developed big β -Zr SPPs at the metal grain boundaries instead of small β -Nb SPPs in RXA Zr-1.0Nb alloys³⁹. Previous studies have shown the detrimental effects of β -Zr on corrosion resistance¹⁸², suggesting that it forms ridges of oxide that are the reason for oxide break away. However, the current study shows that β -Zr SPPs do not have a detrimental influence on oxide growth, since several examples in SEM and TEM images show that when β -Zr is seen at the metal-oxide interface, it does not accelerate the local oxide growth (Figure 4-4, Figure

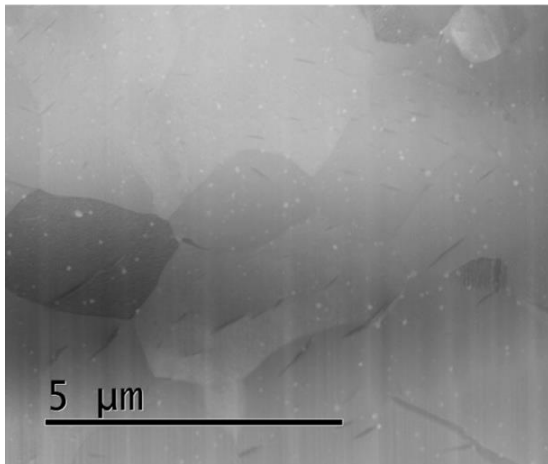
4-14 and Figure 4-16). Also the micro cracks on top of the crystalline β -Zr particles near the metal-oxide interface are very small (Figure 4-15), so these SPPs do not encourage additional crack growth. There are also several examples of oxidised β -Zr in the oxide (Figure 4-14, Figure 4-16 and Figure 4-17) with no clear correlation of the β -Zr location with cracks nearby.

Another hypothesis for the detrimental effect of β -Zr is that it changes the matrix concentration; the lower Nb concentration in the matrix the lower the corrosion rate. It is true that β -Zr SPPs are larger in size (1-5 μm) around the metal grain boundaries, but this does not necessarily result in a change in the matrix concentration of Nb (Figure 2-3). The APT data in Table 6-1 suggests that in annealed and RXA Zr-1.0Nb the matrix of these two alloys has almost the same concentration of Nb. A sketch in Figure 6-7 shows that although the β -Zr is intergranular and larger in size, it only contains 20%Nb and has a much lower number density compared with the β -Nb SPPs in RXA Zr-1.0Nb alloys which contain 80% Nb and have a much higher number density. So the Nb in solid solution is the same in both alloys. Some of the β -Zr SPPs are associated with Fe (Figure 4-14 and Figure 4-16) due to the high solubility of alloying elements like Fe in β -Zr. However, APT data of the matrix in annealed and RXA Zr-1.0Nb shows that the matrix of these two alloys have the same concentration of Fe.

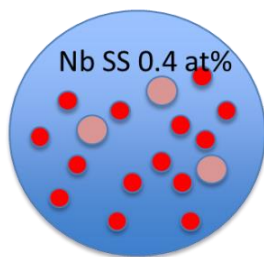
The β -Zr particles have a very complicated internal microstructure with phase separation at 50 nm scale (Figure 4-12 and Figure 4-18). EELS line profiles were used to study the changes in concentration of Zr and Nb in different parts of these particles, showing that the dark areas in the HAADF images are ~ 75 at% Zr and 25 at% Nb (β -Zr), while the light areas are 50 at% Zr and 50 at% Nb, Figure 4-18. Presumably this microstructure is formed by decomposition of the β -Zr during cooling from the annealing process at 720°C ⁴³. The corrosion data of Zr-2.5Nb alloys in CANDU reactor shows that after a period of time, the β -Zr will decompose to β -Nb and the corrosion resistance will improve¹⁷.

RXA Zr-1.0Nb

Small Beta-Nb and Zr-Nb-Fe SPPs
in large quantity, inside the grain



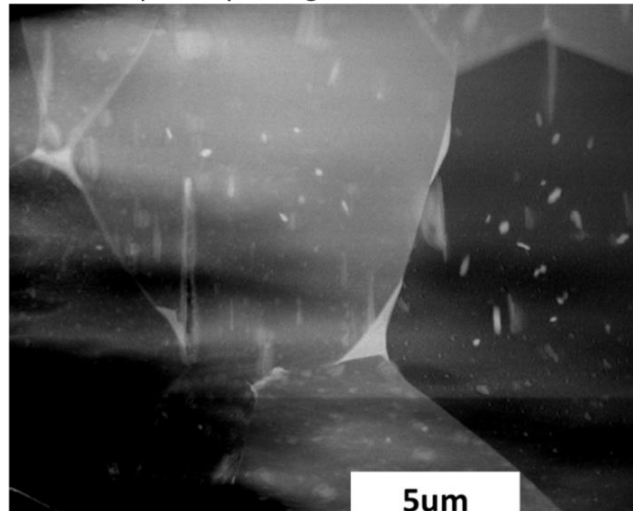
- beta-Nb (80 % Nb+ 20% Zr)
- Zr-Nb-Fe



Small metal grain

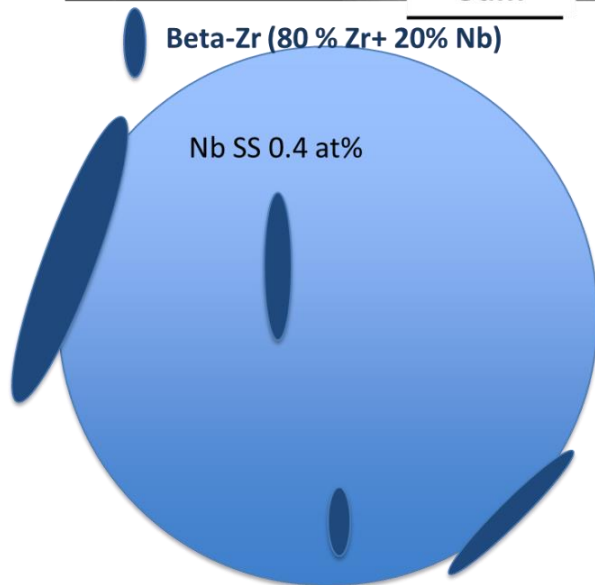
Annealed Zr-1.0Nb

Large Beta-Zr SPPs
in small quantity, along GB



Beta-Zr (80 % Zr+ 20% Nb)

Nb SS 0.4 at%



Big metal grain

Figure 6-7: TEM and schematic diagrams of SPP distribution in RXA and annealed Zr-1.0Nb. The optimum SPP size and distribution is important to the performance of Zr alloys, and it could be that both number density and SPP size have an impact on the cracking of the oxide and therefore make it less protective. Barberis et al¹⁸³ showed that in Zr binary alloys such as Zr-Fe, Zr-Cr and Zr-Ni alloys, increasing the SPP density regardless of the SPP type can improve the corrosion resistance in autoclave testing at 415 and 500°C. In the samples studied in this work, by increasing the number density of SPPs from β -Zr to β -Nb increases

the Zr-1.0Nb corrosion resistance. The size of the SPPs is also important in corrosion performance. Tejlund^{153,184,185} compared two different Zry-2 samples, one with small (20 nm) but more SPPs which creates a lot of cracks in the oxide and corrodes faster, with another that had larger (80 nm) but fewer SPPs which has a better corrosion resistance. This is due to the different oxidation rate for the Zr matrix and the relatively cathodic SPPs, which will create voids above the SPP and potentially more cracks in the oxide. In my annealed Zr-1.0Nb samples, although the large SPPs by themselves should not generate a network of cracks, the large SPP size can connect together all the small cracks that are generated by the huge amount of tetragonal to monoclinic phase transformation during oxidation⁶³. This can potentially provide a transport path between the metal and porous oxide since their size is much larger than the barrier layer, decrease oxide strength and promote and oxygen diffusion through defects.

The annealed Zr-1.0Nb material also has high hydrogen content, partially due to the high corrosion rate. It is speculated that the size of the β -Zr SPPs (much larger than commonly observed SPPs) can also provide a pathway to connect all the porosity in the oxide, which provides a highway for hydrogen entering the metal. A similar example was given¹⁵⁸ that a high Si containing Zr alloy with 0.25w%Si and 0.1w%Ni contained μm size silicides that were not dissolved during beta quenching. This results in a silicide that has a surface covered with Ni. This alloy was heavily hydrided and failed after a second cycle in the reactor due to excessive hydriding. The high concentration of hydrogen content in the metal can also give a volume expansion which can also be a reason for the extensive cracking of the oxide. The hydride in the metal can increase corrosion rate as well^{163,110}.

Table 6-1: Element concentrations (at%) from APT studies of the metal matrix in annealed and RXA Zr-1.0Nb. Noted Nb and Fe contents are very similar. Data courtesy of Brian Setiadinata.

Annealed									
Sample no.		Zr	O	Nb	Fe	Al	C	N	Total
1	No. of atoms	28401062	239557	120525	2877	2470	18981		28785471
	Conc. (at%)	Balance	0.83%	0.42%	0.010%	0.009%	0.066%		
2	No. of atoms	4632100	81729	18198	508	389	4122	357	4737046
	Conc. (at%)	Balance	1.73%	0.38%	0.011%	0.008%	0.087%	0.008%	
3	No. of atoms	4825443	78165	19743	1000	377	6562		4931290
	Conc. (at%)	Balance	1.59%	0.40%	0.020%	0.008%	0.13%		
4	No. of atoms	1399562	18006	6480	205	141	2311		1426704
	Conc. (at%)	Balance	1.26%	0.45%	0.014%	0.010%	0.16%		
5	No. of atoms	1207462	18972	4229	339	169	2654		1233824
	Conc. (at%)	97.86%	1.54%	0.34%	0.027%	0.014%	0.22%		
Total	No. of atoms	40465629	436429	169174	4929	3545	34630	357	41114335
	Conc. (at%)	98.42%	1.06%	0.41%	0.012%	0.009%	0.084%	0.001%	
As-recrystallised									
Sample no.		Zr	O	Nb	Fe	Al	C	N	Total
1	No. of atoms	2010696	15473	8299	365	255	926		2036014
	Conc. (at%)	Balance	0.76%	0.41%	0.018%	0.013%	0.045%		
2	No. of atoms	3235181	26331	13978	865	602	1933	458	3278891
	Conc. (at%)	Balance	0.80%	0.43%	0.026%	0.018%	0.059%	0.014%	
3	No. of atoms	1500167	17884	5508	175	279	901		1524914
	Conc. (at%)	Balance	1.28%	0.43%	0.011%	0.073%	0.015%		
4	No. of atoms	18990061	303318	80411	2097	3177	9904	461	19388968
	Conc. (at%)	Balance	1.56%	0.41%	0.011%	0.016%	0.051%	0.002%	
Total	No. of atoms	25736105	363007	108196	3502	4313	13664	918	26228788
	Conc. (at%)	98.12%	1.38%	0.41%	0.013%	0.016%	0.052%	0.004%	

6.5 Effect of irradiation

Although only two neutron irradiated coupons were received towards the end of this study, the systematic analysis of these two samples has shed some light on the effect of irradiation on microstructure and microchemistry of the RXA Zr-1.0Nb samples. The 540-day neutron irradiated sample has $\sim 2 \mu\text{m}$ oxide and in pre-transition, while 540-day in autoclave sample has $\sim 5.2 \mu\text{m}$ oxide and post-second-transition. Careful consideration has to be taken before drawing any conclusions when comparing these two samples.

The first question regarding the differences between neutron irradiated and autoclave samples is that apart from the neutron irradiation, there may be other differences such as the temperature of the oxidation environment and geometry of the samples. The neutron irradiated sample spent 540 days in a commercial nuclear reactor, and the temperature of the PWR is estimated to be below 320 °C, while the autoclave samples are oxidised using simulated PWR water at 360 °C for 585 days. As discussed in Chapter 2.1, the temperature differences of the autoclave (360 °C) and reactor (305-315 °C) can cause the oxide to be around 2.06 µm after the same time of 310 °C, very close to the observed thickness of the irradiated sample. Another difference is that the neutron irradiated sample is a flat coupon (without any fuel in and it is not subjected to stress) and the autoclave sample is a tube.

Many studies on ZIRLO[®] and Zircalloys have shown that irradiation increases the rate of corrosion¹¹⁰⁻¹¹⁴, however there are many previous studies on similar Zr-1.0Nb alloys showing that Zr-Nb alloys do not undergo accelerated corrosion. The Russian alloys E110¹¹⁵ and French Areva alloy M5TM ¹¹⁶ have been used as the fuel rod for cladding of WWERs and RBMKs and French PWR for many years, respectively. They both show very good corrosion resistance and low hydrogen pickup fraction, with very few cases reported for abnormal corrosion in reactor^{116,117}. The studies by Markelov et al¹¹⁵ focused on changing the Nb and Fe contents in model alloys and analysing its in-reactor corrosion resistance.

The geometry of the samples can also influence the corrosion rate, but certainly cannot explain a halving or even less of corrosion rate after irradiation. So in this study, the comparison between irradiated and autoclave samples must take into account not only the reactor temperature or sample geometry, but can also reflect the effect of irradiation on corrosion.

The detailed microstructure analysis shows much fewer cracks in the oxide comparing with autoclave samples (Figure 5-1, Figure 5-4), and similar observations have been made on the E110 samples¹⁸⁶. As mentioned earlier, there is a strong correlation between crack number density and corrosion rate, so this agrees with the low corrosion rate of this sample under irradiation. Comparing with the samples oxidised in the autoclave, there are more isolated metallic regions in the oxide (Figure 5-1), however it is worth pointing out that the metal-oxide interface is still relatively uniform comparing with other neutron-irradiated Zircaloy samples^{187,188}. This is the first time that the layer of micro cracks on the top surface of the oxide, parallel to the metal-oxide interface, has been reported (Figure 5-2), and it is clear that these are not coming from the sample making process. The samples were not polished before the FIB sample preparation process, so it is unclear how such cracks are formed on the top surface. Some of these micro cracks develop into cracks perpendicular to the metal-oxide interface, and in another irradiated lamella has a large vertical crack 1.6 μm in width and 1.1 μm deep (Figure 5-2). This kind of perpendicular crack provides the best pathway for water penetration to accelerate the oxidation reaction, but the oxide thickness underneath even such large cracks seems relatively unaffected.

The oxide microstructure is significantly more complicated comparing with an autoclave sample, i.e. it does not show a well-defined equiaxed-columnar-equiaxed oxide grain structure (Figure 5-4 and Figure 5-6). The average size of the columnar grains in the irradiated sample is shorter in length but greater in width (Figure 5-4 and Figure 5-6). There are also much more equiaxed grains in the oxide, similar to irradiated Zry-4^{112,113}. It is sometimes very hard to see the precise location of some of the grain boundaries in the oxide, which makes Fresnel contrast in imaging porosity more difficult, but in general the porosity content in the irradiated sample is much lower than the autoclave (Figure 5-5). Together with its lack of cracks, this correlates well with the good corrosion resistance of this irradiated sample⁷¹. By

using automated crystal orientation mapping in the TEM (Figure 5-4), I observe a high tetragonal grain fraction comparing with autoclave samples. In the neutron irradiated sample, besides the scattered equiaxed tetragonal grains, I observe that at the metal-oxide interface there are more, larger columnar tetragonal grains 50-70 nm wide and around 200-300 nm in length (Figure 5-4). I have never observed t-ZrO₂ grains this large in any of the autoclave-oxidised samples. Simeone et al^{189,190} used Raman microprobe and grazing X-ray diffraction to simulate the neutron irradiation on monoclinic oxide, and the results show increasing tetragonal phase fraction under irradiation. An early study by Adam¹⁹¹ also suggested that increasing impurities in the monoclinic oxide may link to increasing transformation to the tetragonal phase. A study on neutron irradiated Zircaloy-4³² shows that increasing Fe content may contribute to the stabilisation of tetragonal phase, however in this case the Fe is not only coming from dissolution of the SPPs but also from the crud from the oxide-water surface.

The metal-oxide interface is hard to define in bright field TEM images, however STEM HAADF and EELS analysis and automated crystal orientation mapping in the TEM have been used to study the metal-oxide interface in order to provide a comprehensive view of local microstructure and micro-chemistry (Figure 5-15). I have concentrated on this region because this is where the primary corrosion reaction occurs between zirconium metal and inwardly diffusing oxidising species. As well as the bulk zirconium oxide (which can have grains of both tetragonal and monoclinic crystal structures) and the underlying Zr metal, the metal-oxide interface contains a complex mixture of fine suboxide grains and oxygen-saturated metal (Zr(Osat))^{60,61,97,128,169}. EELS core loss mapping provides accurate quantitative analysis of the oxygen concentration across this interface (Figure 5-15), identifying local regions of stoichiometric ZrO and oxygen-saturated metal (Zr(Osat)) with varying thicknesses^{128,169}. The neutron irradiated sample has a much thinner suboxide layer, around 50-70 nm, with some places without any detectable suboxide at all. The oxygen saturated area

is also very thin, as observed from EELS low loss mapping, around 50 nm (Figure 5-15). Previously I showed that there is a correlation between instantaneous oxidation rate with suboxide and oxygen saturated area thickness, and if a similar trend is followed for the slow oxidation rate in the neutron irradiated sample, it should have developed a thicker suboxide and oxygen saturated area than is actually observed. Abolhassani et al^{188,192} studied three different alloys (Zry-4, low tin ZIRLO[®] and Zr-2.5 Nb), and EDX profiles across the metal-oxide interface shows the thinnest oxygen diffusion layer of 200 nm while others are thicker. Diffusion models suggested diffusion coefficients in the metal in the range of $6 \times 10^{-20} \text{ m}^2 \text{ s}^{-1}$ for Zry-4 and 1×10^{-20} and $0.8 \times 10^{-20} \text{ m}^2 \text{ s}^{-1}$ for the more corrosion-resistant cladding alloys, which may help explain why the Zr(Osat) layer varies in thickness in different alloys. There is a lack of data in the literature reporting similar observations, so it still unclear how irradiation could inhibit suboxide growth. It might be also be that this sample is still in the early stage of suboxide growth, so that the Zr-O layer is still developing. Further analysis on other neutron irradiated samples at different exposure times is needed to answer this question.

Analytical studies on SPP distribution have shown that β -Nb SPPs remain stable after neutron irradiation, which is in agreement with French studies on M5TM^{19,97,116,181} and Russian studies on E110¹⁹³⁻¹⁹⁶. Comparing my autoclave and neutron irradiated samples, the most significant feature of these microstructures is that the β -Nb SPPs are not dissolved faster under irradiation than in autoclave conditions (Figure 5-10). The SPPs do not become amorphous as in Zircalloys samples¹⁹⁷. In both cases the SPPs oxidise gradually as they spend longer in the growing oxide, but the localisation of the Nb to the oxidised particles is similar in both materials. Doriot et al¹⁹⁸ studied the differences in fluence with regard to β -Nb particle size and number density, and found an increase from 35 nm to about 50 nm at a fluence of $4 \times 10^{25} \text{ n/m}^2$. The number density showed continuous decrease during irradiation. It would be

interesting to determine if this microstructure change resulted in a change in the metal matrix composition.

Several studies focus on radiation introduced precipitates (RIP)^{20,191,198}, arguing that these RIPs should come from precipitation of the Nb in solid solution in the metal matrix, thus the concentration of Nb falls in the metal matrix which leads to a better corrosion resistance. However, these authors also report that the Nb concentration in β -Nb has dropped from 85% to 55% after irradiation using T-XRD¹⁹⁸. Without careful calculation of the Nb in solid solution in the irradiated metal matrix using techniques such as APT, the conclusions on what controls the corrosion rate remain unconvincing.

However, it is clear to see in the EDX mapping that Fe leaks out of the Laves phase SPPs with higher speed than Cr (Figure 5-9 and Figure 5-10). It is interesting to note that there are almost no Laves phase SPPs in the analysed region of the irradiated sample, except one large particle at the right side of the Fe map. Some Cr is still left in the Laves phase SPPs. The apparent Fe-rich layer at the top surface of the oxide may be a result of deposition of dissolved Fe from the reactor water. Lefebvre et al¹¹² suggested that the redistribution of Fe is associated with oxidation of $Zr(Fe,Cr)_2$ SPPs, and he argued that the release of Fe can have a chemical stabilisation effect on the tetragonal phase. This effect will not happen near the metal-oxide interface since SPPs still remain metallic in this region. This may explain the higher tetragonal phase fraction in the irradiated sample, the tetragonal phase is stabilised by stress near the metal-oxide interface, while above the metal-oxide interface it is stabilised by Fe. Another effect of Fe redistribution from the SPPs can be changing the local charge state by doping the oxide or reducing the space charge build up. XANES studies^{179,176,204} have shown that both Nb and Fe in solid solution and in SPPs show delayed oxidation comparing with bulk oxide, which can explain the good corrosion resistance and HPU performance.

7. Chapter 7 Conclusions and suggestions for further work

I have used a range of advanced microscopy techniques to study the microstructure, the nanoscale chemistry and the porosity in a range of zirconium alloys at different stages of oxidation. Samples exposed in both autoclave and in-reactor conditions were available to compare. The following observations were made:

- TKD and automated crystal orientation mapping with TEM can be used very effectively to reveal both the morphology and the crystallography of these nanoscale oxides.
- RXA Zr-1.0Nb alloys which have good corrosion resistance and HPU has a better well-aligned equiaxed-columnar-equiaxed grain structure, fewer macro cracks and a more even metal-oxide interface. Annealed Zr-1.0Nb alloys which have a bad corrosion resistance and HPU have more disorganised microstructure, higher tetragonal oxide grain fraction, more macro and micro cracks, and an uneven metal-oxide interface.
- RXA Zr-1.0Nb alloys show significant differences in microstructure and microchemistry after being neutron irradiated for 540 days. Significant differences in grain morphology were observed between samples oxidised in the autoclave and in-reactor samples, with longer, better aligned monoclinic grains seen in the autoclave samples. The irradiated sample contains many fewer cracks, more tetragonal oxide grains and a relatively even metal-oxide interface.
- A combination of EDX and EELS analysis of SPPs can reveal the main and the minor element distributions respectively. In RXA Zr-1.0Nb alloys, Nb from β -Nb SPPs undergo gradual oxidation from the 2+ state in the crystalline SPPs near the metal-oxide interface to 5+ in the amorphous and fully oxidised SPPs towards the oxide-water interface. Neutron irradiation seems to have little effect on promoting fast

oxidation or dissolution of β -Nb precipitates in RXA Zr-1.0Nb alloys, but encourages dissolution of Fe from Laves phase precipitates. In annealed Zr-1.0Nb alloys, β -Zr does not show direct link with the detrimental major cracking in the oxide or the uneven metal-oxide interface, however, the large SPP size can connect together all the small cracks that are generated by the huge amount of tetragonal to monoclinic phase transformation during corrosion and provides pathway for corrosion and hydrogen pickup. In both RXA and annealed Zr-1.0Nb, the Nb in solid solution in the metal is 0.4 at%, and so cannot explain the differences in corrosion performance.

- The combined thickness of the ZrO suboxide and oxygen-saturated layers at the metal-oxide interface correlates well to the estimated instantaneous oxidation rate (Figure 6-4). , the suboxide and Zr(Osat) thickness keeps increasing prior to the transition, until it reaches the transition point and drops to a thinner thickness, also comparing with different alloys, during rapid oxide growth there is less formation of suboxide and Zr(Osat). This suggests that the presence of this oxygen rich zone is part of the protective oxide that is key in the transport processes involved in oxidation.
- Porosity in the oxide has a major influence on the overall rate of oxidation, and there is much more porosity in the annealed Zr-1.0Nb alloy than found in either the RXA alloy or the similar alloy exposed to neutron irradiation.
- The presence of this oxygen-rich zone combining the porosity is part of the protective oxide that is key in the transport processes involved in oxidation. In the pre-transition, the porosity is not interconnected, the Zr-O region grows with oxidation days until reach transition, when porosity becomes interconnected and the Zr-O layer drops to the minimum thickness.

In order to complete the study on Zr-Nb samples, below are suggestions for future work:

- In order to further understand the influence of Nb and Fe, it will be important to look at some alloys with higher or lower Nb and Fe content, such as Zr-0.4 Nb where the Nb will be in solid solution, Zr-2.5 Nb, Zr-1.0Nb with higher Fe content etc. It will be interesting to see what is the influence of SPPs on corrosion and hydrogen pickup rate in these alloys.
- Further study on the annealed Zr-1.0Nb alloys should include non-destructive methods such as XRD for studying the tetragonal phase fraction in the oxide. 3D FIB-SEM-EDX imaging of oxide in order to double check the β -Zr effect on cracking in the oxide might also provide useful information.
- It would be useful to study the annealed Zr-1.0Nb base metal before autoclave treatment in order to see whether the decomposition of β -Zr happens during cooling or during autoclave testing. There is doubt on the HPU data on this alloy, so it will be valuable to run Thermal Desorption Spectroscopy (TDS) testing to see whether hydrogen is trapped in the cracks of the oxide, or really absorbed by the metal matrix.
- Further study on neutron irradiated samples should include APT analysis on the Nb and Fe concentrations in the oxide and metal matrix. Defect analysis and radiation introduced precipitate analysis should be done on clean electro-polished samples or ion thinning TEM samples.
- NanoSIMS analysis on samples from pre and post transition on RXA and annealed samples could be carried out in order to track the location of deuterium/hydrogen pickup of the samples, and combined with higher resolution techniques to correlate microstructure to HPU.

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