Understanding corrosion and hydrogen pickup of Zr nuclear fuel cladding alloys-the role of oxide microstructure, porosity, suboxide and SPPs

Link to publication record in Manchester Research Explorer

Citation for published version (APA):

Published in:
18th International Symposium on Zirconium in the Nuclear Industry

Citing this paper
Please note that where the full-text provided on Manchester Research Explorer is the Author Accepted Manuscript or Proof version this may differ from the final Published version. If citing, it is advised that you check and use the publisher's definitive version.

General rights
Copyright and moral rights for the publications made accessible in the Research Explorer are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

Takedown policy
If you believe that this document breaches copyright please refer to the University of Manchester’s Takedown Procedures [http://man.ac.uk/04Y6Bo] or contact uml.scholarlycommunications@manchester.ac.uk providing relevant details, so we can investigate your claim.
Understanding Corrosion and Hydrogen Pickup of Zirconium Fuel Cladding Alloys: the Role of Oxide Microstructure, Porosity...
Understanding corrosion and hydrogen pickup of Zr nuclear fuel cladding alloys-the role of oxide microstructure, porosity, suboxide and SPPs

Jing Hu¹, Brian Setiadinata¹, Thomas Aarholt¹, Alistair Garner², Arantxa Vilalta-Clemente¹, Jonna Parteza³, Philipp Frankel³, Paul Bagot¹, Sergio Lozano-Perez³, Angus Wilkinson¹, Michael Preuss², Michael Moody¹, Chris Grovenor¹

1. Department of Materials, University of Oxford, Parks Road, Oxford, UK
2. Materials Performance Centre, School of Materials, University of Manchester, Manchester, UK
3. Westinghouse Electric Company, 1332 Beulah Road, Pittsburgh, USA

Abstract

We 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 from both autoclave and in-reactor conditions were available to compare, including ZIRLO™, Zr-1.0Nb and Zr-2.5Nb samples with different heat-treatments. (Scanning) Transmission Electron Microscopy ((S)TEM), Transmission Kikuchi Diffraction (TKD)¹ and automated crystal orientation mapping with TEM ²,³ were used to study the grain structure and phase distribution. Significant differences in grain morphology were observed between samples oxidised in the autoclave and in-reactor samples, with shorter, less well-aligned monoclinic grains and more tetragonal grains seen in the neutron irradiated samples. A combination of Energy Dispersion X-ray (EDX) mapping in STEM and Atom Probe Tomography (APT) analysis of SPPs can reveal the main and the minor element distributions respectively. 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 reveal the fully oxidised Nb⁵⁺ state in the SPPs deep into the oxide, but Nb²⁺ in the crystalline SPPs near the metal-oxide interface. EELS analysis and automated crystal orientation mapping with TEM have also revealed Widmanstatten-type suboxide layers in some samples with the hexagonal ZrO structure predicted by ab initio modelling⁴. 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 is part of the protective oxide that is rate limiting in the key in the transport processes involved in oxidation⁵. Porosity in the oxide has a major influence on the overall rate of oxidation, and there is much more porosity in the rapidly oxidising annealed Zr-1.0Nb alloy than found in either the recrystallised alloy or the similar alloy exposed to neutron irradiation.

Keywords: Zr alloys, corrosion, hydrogen pickup, (S)TEM, EELS, Atom Probe Tomography, Transmission Kikuchi Diffraction, automated crystal orientation mapping in the TEM

1. Introduction

Because of its use as the preferred nuclear fuel cladding material since the 1950s, a great deal of effort has been exerted in understanding the oxidation of zirconium alloys at temperatures of 300 ± 60 °C in pressurised water⁶-⁸. Recent demands to increase the burnup of fuels and reduce the number of fueling cycles has led to renewed interest in developing a detailed mechanistic understanding of aqueous corrosion⁹-¹¹ and hydrogen pickup in zirconium alloys, and in the design of improved
materials. There are several features of the complex oxide microstructure that have been suggested to offer clues to the rate-controlling mechanisms for oxidation, and these have recently been studied in particular detail; the shape, size and crystallographic texture of grains in the oxide grains, the influence of second phase particles (SPPs), cracking, nano-scale porosity in the oxide scale, and the local chemistry of the metal-oxide interface where the primary electrochemical oxidation reaction occurs.

The recent introduction of low tin Zr-Nb alloys has resulted in significant improvements in both the corrosion resistance, primarily by delaying the accelerated stage of oxidation (transition), and reductions in the level of hydrogen pickup. This improved corrosion resistance has been shown to correlate with a stronger oxide texture and improved oxide grain alignment compared to those observed in older alloys like ZIRLO™. Second-phase particles have been shown to undergo chemical changes as the zirconium oxide forms around them using EDX mapping. They often show a delayed oxidation rate relative to the surrounding zirconium metal, and during irradiation, Fe-containing SPPs show Fe-depletion from the SPP into the surrounding oxide grains. The SPP distribution has also been shown to affect crack formation in the oxide, but their role in affecting the corrosion rate remains uncertain, and although the size and nature of SPPs have been proposed as important factors controlling hydrogen pickup in these alloys, the specific mechanisms are not clear. The formation of a ZrO suboxide and oxygen-saturated metal (Zr(Osat)) region at the metal-oxide interface has been shown on several alloys, and has been proposed to contribute to key rate-limiting steps in the corrosion process. Finally, porosity throughout the oxide has also been suggested as a potential route for oxygen and hydrogen ingress for oxidising species down to the metal surface.

The availability of powerful new techniques like high-resolution Electron Energy Loss Spectroscopy (EELS), Transmission Kikuchi Diffraction (TKD), automated crystal orientation mapping in the Transmission Electron Microscope (TEM-ASTAR) and Atom Probe Tomography (APT) have allowed new measurements to be made on the nanoscale structure and chemistry of oxidised zirconium alloys. In this paper we present new results obtained from these techniques on ZIRLO™ and a variety of Zr-Nb alloys. We show that low loss EELS mapping can give an excellent, fast measure of the thickness of the suboxide and the oxygen-saturated metal (Zr(Osat)) regions, and show a relation between the thickness of these phases and the instantaneous oxidation rate of the alloy. SPP chemistry variations as they oxidise have been investigated using EELS and Atom Probe Tomography, and we attempt to correlate SPP type and density with the corrosion rate. Finally, we give a qualitative overview of the concentration and nature of porosity present in oxides grown on the different alloys, and also link this to oxidation rate.

2. Materials and Methods

Four types of materials were examined in this study: recrystallised Zr-1.0Nb (tube), annealed Zr-1.0Nb (sheet), ZIRLO™ (tube) and Zr-2.5Nb (tube), with their composition in Table 1. Both Zr-1.0Nb alloys contain ~0.1 at% Fe. The annealed Zr-1.0Nb was held at 720°C for 24 hours to obtain a larger precipitate size, but these precipitates were β-Zr rather than the small β-Nb precipitates found in the recrystallised alloy. Recrystallised Zr-1.0Nb was oxidised for up to 540 days in a static autoclave in simulated primary water with 2 wt. ppm Li added in the form of lithium hydroxide and 1000 wt. ppm Boron added as boric acid, at a saturation pressure of ~18 MPa at 360 °C. Both annealed Zr-1.0Nb and ZIRLO™ were oxidised for up to 225 days in an autoclave in light water at 360°C. The Zr-2.5Nb is a
CANDU pressure tube alloy that was oxidised in heavy water at 340°C. Two samples of the recrystallised Zr-1.0Nb and annealed Zr-1.0Nb received additional exposures in heavy water so the deuterium uptake could be measured by SIMS analysis. These samples are 180- and 540-day recrystallised Zr-1.0Nb which had 45-days of additional corrosion, and 30- and 60-day annealed Zr-1.0Nb with 31-days of additional corrosion.

The oxidation weight gain data from all these samples can be found in Figure 1. The recrystallised 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\textsuperscript{23,24,25}. The ZIRLO\textsuperscript{TM} transition point is between 120-135 days.

A few small samples were received of Zr-1.0Nb sheet coupons irradiated for one cycle (540 days) in the Vogtle reactor. The reactor temperature from the samples we had was between 305-315 °C and the estimated fast neutron fluence accumulated was $4.35 \times 10^{21}$ n/cm$^2$, 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.

Samples at different stages of oxidation were selected from this set of materials for TEM, STEM and APT analysis. TEM lamellae of the autoclave oxidised samples were prepared by the in-situ lift out method using an FEI FIB200. 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 lamellae were prepared in the size of around 10 μm × 10 μm × 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. All the TEM lamellae were further thinned down to a thickness below 100 nm in a Zeiss Nvision 40 dual beam FIB to create homogeneous and electron-transparent samples for TEM and STEM analysis. The samples were further thinned down to ~50 nm using low-voltage conditions in Nvision FIB for final EELS, TKD and automated crystal orientation mapping with TEM analysis on selected regions of interest. TEM and STEM analysis were performed on a JEOL 2100 microscope operated at 200 kV. EELS spectrum imaging was performed on a JEOL ARM200F TEM operated at 200 kV and equipped with a Gatan image filter. The convergence half-angle $\alpha$ was 20 mrad and collection half-angle $\beta$ was 30 mrad with an energy dispersion of 0.25 eV per channel and a step size of 1~5 nm. 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. Automated crystal orientation mapping with TEM 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. Data analysis was carried out using a NanoMEGAS ASTAR automated crystal orientation mapping system. APT specimens were also prepared by in-situ lift out using a Zeiss NVision 40 dual-beam FIB. Needle-like samples with tip diameter less than 100 nm were prepared for analysis near the oxide/suboxide-metal interface. The needles were analysed in a Cameca LEAP3000X with laser energy of 0.5 nJ and repetition rate of 200 kHz, and data reconstruction was carried out using IVAS 3.6.8 software.
Table 1: Composition in wt% of zirconium alloys used in this study.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Zr (wt%)</th>
<th>Nb (wt%)</th>
<th>Fe (wt%)</th>
<th>Sn (wt%)</th>
<th>Cr (wt%)</th>
<th>O (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Recrystallised Zr-1.0Nb</td>
<td>Balance</td>
<td>0.91</td>
<td>0.08</td>
<td>0.01</td>
<td>&lt; 0.01</td>
<td>~ 1</td>
</tr>
<tr>
<td>Annealed Zr-1.0Nb</td>
<td>Balance</td>
<td>0.91</td>
<td>0.08</td>
<td>0.01</td>
<td>&lt; 0.01</td>
<td>~ 1</td>
</tr>
<tr>
<td>ZIRLO™</td>
<td>Balance</td>
<td>0.87</td>
<td>0.09</td>
<td>0.92</td>
<td>&lt; 0.01</td>
<td>~ 1</td>
</tr>
</tbody>
</table>

Figure 1. Weight gain evolution with time, for recrystallised Zr-1.0Nb, ZIRLO™, annealed Zr-1.0Nb and neutron-irradiated recrystallised Zr-1.0Nb. The neutron-irradiated sample was oxidised at a lower temperature than the other alloys.

3. Results and discussions

3.1. Sample overview

For recrystallised Zr-1.0Nb alloys, six samples were chosen for detailed study. The 3-day sample represents 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. The TEM Bright Field (TEM BF) image in Figure 2 (a-1) 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. It is worth pointing out that the lateral cracks may appear larger due to the release of stresses...
after the removal of the top Pt layer, however, these cracks exist before the final thinning process in the FIB. The 120-day sample (not shown) represents the early stage of oxidation with an average oxide thickness of 2.2 μm. The 225-day sample (also not shown) represents a stage before the first transition when the oxide has grown to around 2.5-2.7 μm. The 360-day sample is taken at approximately the first transition, and the oxide thickness has grown to around 3.2 μm in Figure 2 (b-1). The metal-oxide interface is relatively flat, with large cracks parallel to the interface. The 540-day sample (also not shown) represents at the second transition with an average oxide length of 5.2 μm. The 585-day sample is well past the second transition. As seen from the STEM High Angular Annual Dark Field (STEM HAADF) image in Figure 2 (c-1), after the second layer of cracks, another -900 nm of oxide has grown during the 45 days in deuterated water. The oxide thickness is around 6.1 μm.

For the annealed Zr-1.0Nb alloys, four samples were chosen for detailed study. It was noticed during the sample making procedure in the FIB that this set of samples had very uneven metal-oxide interfaces suggesting that the oxidation rate varies considerably at different locations in these samples as well. The 3-day sample represents the early stage of oxidation, Figure 2(a-2), and 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 oxide in Figure 2 (b-2) ranges in thickness 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. The 91-day sample (not shown) is post first transition with an average thickness of 5.2 μm. The 225-day sample in Figure 2 (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). It is worth mentioning that the high temperature annealing process not only makes the Zr-1.0Nb alloy oxidise much faster, but also changes the microstructure of the underlying metal. The metal grains are around 12-14 μm in diameter, compared with the 5 μm grain size in the recrystallised samples.

For the ZIRLO™ samples, 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. The 45-day sample shows significant lateral cracking, despite the weight-gain data for the ZIRLO™ samples in Figure 1 showing that this sample should not even be halfway to this point. The 225-day sample shows the beginning of 2nd transition cracking near the metal-oxide interface, and an oxide thickness of 4.5 -5.3 μm.

Figure 3(a) shows the STEM HAADF image of one of the FIB lamellae from the irradiated coupon. It contains very few cracks in the oxide, suggesting that no kinetic transition has occurred. The metal-oxide interface is slightly uneven, and the oxide thickness ranges from 1.7 μm to 2.3 μm, with an average thickness of 1.9 μm which is the entire oxide thickness during the 540-day reactor oxidation. It is interesting to see such a thin oxide despite this sample having been in the reactor for 540 days. The same alloy corroded in an autoclave for 120 day has 2.2 μm of oxide and 540-day sample 5.2 μm. Comparing with the samples oxidised in the autoclave, there are more isolated metallic regions isolated in the oxide (circled in Figure 3 (a)). This suggests that the variability in local oxidation kinetics at the metal-oxide interface is even greater than observed in the autoclave samples. It is unclear how these metallic protrusions form, but they are not associated with underlying metal grain boundaries.
so changes in the orientation of the metal grains cannot explain how they are produced during oxidation.

**Figure 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.

Despite the fact that the irradiated samples do not have large cracks in the oxide layer, at the top surface of the oxide, as highlighted by arrows in the HAADF image in Figure 3 (a) shows that there is a layer of micro cracks parallel to the metal-oxide interface, just underneath the Pt protective layer. Noting that the sample has not been polished prior to the FIB sample preparation process, it is unclear why such cracks are formed on the top surface. Some of these micro cracks develop into cracks perpendicular to the metal-oxide interface as seen in Figure 3 (b), and in another irradiated lamellae in (c) and (d) that has a large vertical crack 1.6 μm in width and 1.1 μm deep. (c) is taken of the bulk cross section in the FIB-SEM to show that the crack was not created during FIB thinning process. The TEM-BF image in Figure 3 (d) shows that this crack starts from the top surface and run into the middle of the oxide. 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.
Figure 3. TEM BF and STEM HAADF images of two FIB TEM lamellae from the neutron-irradiated Zr-1.0Nb alloy (a,b) first sample, (c,d) second sample.

### 3.2 Higher resolution microstructural analysis

Although detailed microstructural analysis was carried out on all these samples by conventional TEM, the grain structure in the oxide, and especially the characteristic periodic pattern of equiaxed-columnar-equiaxed-columnar grains observed in most of the samples after one or more kinetic transitions, is most easily revealed by TKD, Figure 4. As seen in the (a) 360-day, (b) 585-day and (c) neutron irradiated 540-day Zr-1.0Nb alloys, the top of the oxide has a layer around 700 nm thick of small equiaxed grains, 20-30 nm in diameter. Under this equiaxed layer, there are large, elongated columnar grains oriented parallel to the oxide growth direction. These columnar grains are around 50 nm in width and 350-450 nm in length, and are the characteristic microstructure that forms during the slower stages of cyclic oxidation. In the recrystallised Zr-1.0Nb samples, it is noticed that the thickness of the layer of equiaxed grains on the top surface also increases with oxidation time; 150 nm in the 3-day sample, 500 nm in the 120-day sample, up to 650-750 nm in the 225-day sample. Similar observation on equiaxed oxide growth was also reported by Ni et al.\(^{26}\)

There are scattered parallel cracks in the pre-transition samples which break up the columnar grains. As is commonly reported, the number of layers of lateral cracks appears to be correlated with the number of kinetic transitions; one in the 360-day sample, and two in the 585-day sample. In this later sample, the 900 nm thick layer of oxide under the second layer of cracks shows a more disorganised oxide grain structure, highlighted in the magnified images on the right of Figure 4(b), with shorter columnar grains only around 150-200 nm in length. This may be associated with the fast oxidation stage after the second transition.
Figure 4. TKD band contrast images of the typical microstructure in (a) recrystallized Zr-1.0Nb (b) annealed Zr-1.0Nb and (c) neutron irradiated recrystallized Zr-1.0Nb samples, with the higher resolution image on the right hand side.
Figure 4 (c) shows a more complicated oxide grain structure in the neutron irradiated sample, with a shorter and less organised columnar grains. It is interesting to note the gradual change of grain size distribution throughout this oxide layer. The area around the surface cracks is full of equiaxed oxide grains 30-50 nm in diameter. Near the top surface, the average columnar grain size is 60 nm wide and 130 nm long. Nearer the metal-oxide interface the oxide grains become larger, 70 - 100 nm in width and with an average length of 380 nm.

The TKD technique allows for simultaneous acquisition of both phase and local orientation information. The phase maps in Figure 11 (a) show that most of the columnar oxide grains can be identified to have the monoclinic-$\text{ZrO}_2$ ($m$-$\text{ZrO}_2$) structure. In the recrystallised Zr-1.0Nb samples there are a few tetragonal-$\text{ZrO}_2$ ($t$-$\text{ZrO}_2$) grains, around 20 nm in size, in the equiaxed oxide and scattered 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% at the 360-day sample, while in the post-transition 585-day sample the fraction drops to 0.1%. However, the irradiated samples contain more $t$-$\text{ZrO}_2$ grains as seen in Figure 10(c), they scattered from the equiaxed oxide on the top surface throughout the oxide thickness, at the metal-oxide interface, there are larger columnar tetragonal grains 50-70 nm wide and around 200-300 nm in length. It is worth mentioning that the tetragonal phase fraction measurements in TKD give lower values than the 3%-5% measured on the recrystallised Zr-1.0Nb alloy at a similar oxidation stage using synchrotron X-Ray Diffraction (XRD)\(^1\). 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 TKD\(^1,3\).

### 3.3 SPP analysis

The distribution, chemistry and stability of second phase particles (SPPs) have been studied in detail in the recrystallised, annealed and neutron-irradiated Zr-1.0Nb alloys, since they are proposed to offer cathodic sites for hydrogen evolution\(^27\). They also oxidise when incorporated into the growing $\text{ZrO}_2$ oxide and may release aliovalent elements which can affect the local electronic conductivity. Crystalline SPPs near the metal-oxide interface and amorphous SPPs in the middle oxide are easy to image using diffraction contrast in the TEM BF Figure 5(c-e), the SPPs in the oxide top surface is very hard to image using diffraction contrast, Figure 5(b), but HAADF imaging (based on Z-contrast\(^28\)) is able to differentiate between metallic and oxidised SPPs, Figure 5(b). When an SPP is oxidised, the overall atomic mass of the oxidised SPP is lower than in a metallic SPP, so in HAADF images the oxidised SPPs appear darker while the metallic SPPs appear brighter compared with the oxide surroundings. Combining EDX elemental maps with HAADF images, it is possible to identify with confidence the location of the SPPs in TEM specimens. APT analysis was also used to study SPP chemistry at the nanoscale in some of these samples.

#### 3.3.1 Recrystallised Zr-1.0Nb

In the recrystallised Zr-1.0Nb samples, two types of SPPs were observed, $\beta$-Nb and $\text{Zr(Nb,Fe)}_2$ Laves phase particles. The second type is larger in size and have a lower number density, and tend to rapidly become amorphous once incorporated into the growing oxide. 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\(^29,5\). As oxidation progresses, the $\beta$-Nb SPPs start to become amorphous about 1.5 $\mu$m from...
the metal-oxide interface, but earlier for the Laves phase SPPs at just 0.8 μm. A typical data set showing these features is shown in Figure 5. Several SPPs near the oxide-metal interface in the 360-day sample can be identified in the TEM images and the majority elements shown in the EDX maps. The β-Nb SPPs in Figure 5(c) are crystalline but the one shown in (d) 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 5(b) shows a set of TEM BF and STEM HAADF images of fully oxidised SPP at the top surface. STEM HAADF image shows 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.

EELS analysis was also performed on SPPs at different locations in the oxide and in samples at different stages of oxidation. The aim of this set of experiments was to determine if the oxidation state of the different SPP alloying elements could be measured. EELS core loss line profiles were acquired at the step size was 1 nm and channel width per pixel 0.25 eV which makes it possible to see the slightest energy shift of Zr and Nb. A typical data set from the 360-day Zr-1.0Nb sample is shown in Figure 6. Several β-Nb SPPs in the oxide located at a range of distances from the interface can be identified. By comparing spectra from line profiles across each SPP with a reference spectrum from an unoxidised β-Nb SPP in the metal, it is 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 SPP near the metal-oxide interface, Zr-L3 edge remains at 2228.8 eV in the metallic, unoxidised condition. Both amorphous SPP and SPP at the top surface have similar edge shifts, as shown in (b) to 2231 eV in the oxidised condition. Comparing the Nb-L3 edge in different SPPs, it is interesting that the Nb L3 edges also show a similar shift from the metallic position at 2376.8 eV to 2377eV in the crystalline SPP, suggesting Nb in the β-Nb SPPs near the metal-oxide interface may already be partially oxidised. However, in the top and bottom part of crystalline SPP, the Nb L3 edge is shifted to 2378.5 eV, which suggests that it has been oxidised to a higher state, possibly Nb^{5+}. For amorphous SPP, is further from the interface shows Nb-L3 edge at lies at 2378.5 eV, and the fully oxidised SPP at the oxide top surface suggests that Nb is oxidised into 2380.3 eV, possible Nb^{5+}. Figure 6 (d) summarises the Nb-L3 edge of some of the SPPs analysed and their distance to the metal-oxide interface. 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 Nb ions to the surrounding oxide. The cracks on top of these SPP may also be influential in controlling the rate of local oxidation.

We have also used APT analysis to study the distribution of Fe in and around β-Nb SPPs near the metal-oxide interface in several different materials. Figure 7(a) shows a concentration profile for Fe around a crystalline/metallic (unoxidised) 50 nm β-Nb SPP in the oxide on a 3 day Zr-1.0Nb sample. The Fe concentration in the surrounding oxide is ~ 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. Comparison will be made below to similar results on the other alloys in Chapter 3.3.3-4.
Figure 5. SPP distributions in the 360-day recrystallised Zr-1.0Nb sample: (a) STEM HAADF, with the positions marked from which the higher magnification TEM images in (c), (d) and (e) were taken, (b) TEM BF and STEM HAADF images of SPPs on top surface, (f) EDX mappings.
Figure 6. An example of EELS analysis of beta-Nb SPPs in the 360-day Zr-1.0Nb sample: (a) comparison of the EELS spectra of fully oxidised, amorphous, crystalline SPP and β-Nb in the metal over the range containing the Zr-L and Nb-L edges, high magnification in (b) and (c). Inset in (c) showing top and bottom of crystalline SPP oxidises first. (d) Nb-L3 edge position in SPPs with their distance to the metal-oxide interface.
3.3.2. Annealed Zr-1.0Nb

The Nb-Zr binary phase diagram suggests that after an anneal at 720°C for 24 hours, the alloy will contain β-Zr as the majority second phase\(^{30}\), and in our annealed Zr-1.0Nb sample we found this phase with a range of shapes and sizes. Figure 8 shows one example of a large intergranular beta-Zr SPP in the metal. EDX maps revealed that this SPP is rich in Nb as expected but also contains some Fe. The SPP has a very complicated internal microstructure as shown in the higher magnification STEM HAADF and TEM BF images. EELS line profiles are used to study the changes in concentration of Zr and Nb in different parts of this particle, 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. EELS MLLS fitting also confirms the distribution of these two phases in SPP. Presumably this microstructure is formed by decomposition of the β-Zr during cooling from the annealing process at 720°C\(^{31}\).
It is worth mentioning that from atom probe analysis, in both recrystallised 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. Although the \( \beta \)-Zr is intergranular and larger in size, it only contains 20% Nb and has a much lower number density compared with the \( \beta \)-Nb SPPs in recrystallised 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 \( \beta \)-Zr SPPs are associated with Fe due to the high solubility of alloying elements like Fe in \( \beta \)-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 detrimental influence on oxide growth of \( \beta \)-Zr SPPs is not clear in the microstructure of the oxide, since it is observed that when \( \beta \)-Zr is seen at the metal-oxide interface, it does not accelerate the local oxide growth. Also the micro cracks on top of the crystalline \( \beta \)-Zr particles near the metal-oxide interface are very small, so these SPPs do not encourage additional crack growth. There are also several examples of oxidised \( \beta \)-Zr in the oxide with no clear correlation of the \( \beta \)-Zr location with cracks nearby. 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

Figure 8. A large \( \beta \)-Zr particle at a metal grain boundary. STEM HAADF overview image of the SPP, with (b) EDX maps of Nb and Fe (c) higher magnification STEM HAADF and TEM BF images and (c) EELS MLLS fitting for two phases.
oxidation. 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.

3.3.3. Recrystallised Zr-2.5 Nb
We have used APT to analyse the compositions of several individual SPPs in the higher Nb material to compare to the results from the Zr-1.0 Nb alloy already described, and typical data is shown in Figure 7. Examination of four unoxidised β-Nb SPPs in the oxide in this alloy show that the average Fe content inside the particle is ~0.28 at%, rather similar to the value measured in the recrystallised Zr-1.0Nb material (Figure 7), and there was strong interfacial segregation of Fe (an interfacial excess of 1.8 atoms/nm²). 6 partially oxidised SPPs in the oxide were also analysed (with O contents from 18.8 at% to 36.8 at%), and contained Fe contents ranging from 0.14 at% to 0.40 at% (average 0.28 at%) similar to that found in the metallic particles. However, there is no sign of interfacial segregation of Fe in the oxidised particles, suggesting that the segregated Fe is redistributed to the oxide matrix as the SPPs oxidise.

3.3.4 Neutron irradiated Zr-1.0Nb
Figure 9 shows an overview of the TEM analysis of SPPs in a typical region of this irradiated material. The Nb map in (c) shows that the β-Nb SPPs are distributed fairly uniformly from the metal-oxide interface towards the sample surface. Metallic or partially oxidised SPPs were found in the region of the oxide less than 700 nm from the metal-oxide interface. Above this region, the SPPs were all fully oxidised as shown by the change in contrast in the HAADF image in (a). The TEM bright field image in (b) shows that we can be sure that that these oxidised β-Nb SPPs are indeed amorphous, however, they seem to have a different contrast as the amorphous SPPs in autoclave recrystallised Zr-1.0Nb Figure 5(e). These SPPs have approximately the same size as those found in the recrystallised alloy in Figure 5 (60 – 70 nm) and there is some evidence that as the SPPs start to oxidise they expand in the direction of oxide growth as the oxygen atoms are incorporated.

It is interesting to note that there are almost no Laves phase SPPs in this region of the irradiated sample, except one large particle at the right side of the Fe map. No Cr was found in any of the particles. 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. Comparing Figure 5 and Figure 9, the most significant feature of these microstructures is that the β-Nb SPPs are not dissolved faster under irradiation than in autoclave conditions. 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.
Figure 9. SPP distributions in the 540-day neutron irradiated recrystallised Zr-1.0Nb sample: (a) STEM HAADF image identifying crystalline SPPS near the metal-oxide interface (yellow circles) and oxidised SPPs higher up the oxide (red circles). Higher magnification (b) STEM HAADF and (c) TEM BF image of oxidised SPPs. The Nb, Fe and Cr EDX maps of the same region are shown in (d-f).

3.3 Suboxide analysis

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. We 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))\(^{1,5,32-34}\). EELS core loss mapping provides accurate quantitative analysis of the oxygen concentration across this interface, identifying local regions of stoichiometric ZrO and oxygen-saturated metal (Zr(Osat)) with varying thicknesses\(^{1,34}\). We have more recently shown that EELS low loss mapping offers a quick way to overview the distribution of phases at the metal-oxide interface. TKD and ASTAR mapping can be used to confirm the location of suboxide grains by indexing with the hexagonal ZrO structure predicted ab initio by Nicholls et al\(^4\). All these techniques can map relatively large regions of the metal-oxide interface, and we have studied several TEM samples extracted from different regions of the original sample, so that a more complete picture of the ‘average’ structure can be gained. We have been particularly interested in exploring if there any
systematic relationship between the thickness of the suboxide and oxygen-saturated metal (Zr(Osat)) regions and the instantaneous oxide growth rate in samples at different oxidation stages.

By using automated crystal orientation mapping with TEM, we were able to determine precisely the distribution of different nanoscale phases. Figure 10 shows typical ASTAR phase maps of TEM lamellae for (a) the 120-day recrystallised Zr-1.0Nb sample, (b) the 91-day annealed Zr-1.0Nb sample and (c) the neutron irradiated recrystallised Zr-1.0Nb sample. In (a) columnar grains with the monoclinic-ZrO$_2$ (m-ZrO$_2$) structure are clearly seen, and scattered equiaxed tetragonal-ZrO$_2$ (t-ZrO$_2$) grains. The annealed and neutron irradiated samples contain more t-ZrO$_2$ grains, some of them around 40-50 nm in diameter, and scattered throughout the more equiaxed bulk oxide. In the annealed sample (b), it is interesting to see that more tetragonal oxide grains are detected where there are no cracks, which might suggest stress stabilisation of the tetragonal oxide. In the neutron irradiated sample (c), besides the scattered equiaxed tetragonal grains, we 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. We have never observed t-ZrO$_2$ grains this large in any of the autoclave-oxidised samples.

At the metal-oxide interfaces in all the samples we observe layers of suboxide grains with the hexagonal ZrO structure predicted by ab initio modelling. These ZrO grains often show Widmanstatten-type acicular shapes, suggesting a strong crystallographic relationship between the suboxide and underlying O-saturated Zr crystals. The thickness of the suboxide layers is easy to measure from these images, and can be seen to vary considerably across imaged regions only a few μm wide. For instance, in Figure 10(b) there is a clear continuous layer of ZrO suboxide on the left hand side where the oxide thickness is about 3 μm, but on the right hand side where the oxide is much thicker and about to go through a transition as seen in STEM HAADF Figure.2(b-2), the suboxide layer is both thinner and less continuous. The neutron irradiated sample also has a thin suboxide layer, around 50-70 nm, with some places without any detectable suboxide at all.

However, we know from EDX and APT analysis that as well as a stoichiometric ZrO suboxide phase there are also regions of oxygen-saturated Zr metal (Zr(Osat)), in these interfaces. Because they are crystallographically indistinguishable from the bulk hexagonal metal, we cannot detect them in ASTAR or TKD mapping. We have thus developed low loss EELS spectrum imaging to provide a quick and easy way to identify oxide, suboxide, Zr(Osat) and metal regions in a TEM sample. As an example of this kind of analysis, Figure 11 shows a TKD map from a region of the Zr-1.0Nb 360-day sample. Zero loss EELS mapping with a step size of 4 nm and acquisition time of $10^{-5}$ s was used to acquire unique spectra from regions with all the possible Zr-O combinations, Figure 11(b). For example, bulk ZrO$_2$ has three peaks at 15 eV, 26.7 eV and 43 eV while Zr(Osat) has two peaks at 17.8 eV and 41.2 eV and Zr metal has two peaks at 16.9 eV and 40.8 eV. After multiple linear least squares (MLLS) fitting over the energy range 10-60 eV, the mapping results for oxide, suboxide, Zr(Osat) and bulk metal are shown in (c). The 4 phases are clearly separated in these maps, and so the morphology and thickness of the different interfacial phases can be easily determined over the whole width of the images. It is easy to see that even over a distance of a few μm the phase distribution is rather variable.
Figure 10. ASTAR mappings of (a) 120-day recrystallised Zr-1.0Nb, (b) 46-day annealed Zr-1.0Nb, (c) 540-day neutron irradiated recrystallised Zr-1.0Nb.
Areas 1 and 2 in Figure 11 (b) both have a relatively flat metal-oxide interface, but it is interesting to see the difference in suboxide distribution. Area one has a very thin suboxide, 60-100 nm, but the oxygen saturated region is thick, ~250 nm. What we will now define as the combined Zr-O region is around 310 nm thick. In area two, there are several very well defined saw-tooth suboxide grains with very variable thickness. The Zr(Osat) region fills the gaps between the suboxide grains, and the combined Zr-O region is ~350 nm thick. Similar differences can be seen in areas 3 and 4.

By combining this kind of low loss EELS mapping and APT analysis of metal-oxide interfaces5,35,36 we 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. This data is brought together in Figure 12. The error bars show the standard error for the measurements on each sample. Looking at recrystallised Zr-1.0Nb in (a), the suboxide and Zr(Osat) thickness keeps increasing prior to the transition, until it reaches the transition point and drops to a thinner thickness. Comparing all the alloys as one with the instantaneous oxidation rate in (b), the data suggests that during rapid oxide growth there is less formation of suboxide and Zr(Osat). This suggests that the suboxide is formed when the oxide growth is slow and allows some oxygen diffusion in the base metal, 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™ and annealed Zr-1.0Nb (Figure 1), this implies that alloys with better corrosion resistance have more formation of suboxide and the combined Zr-O region (suboxide +Zr(Osat)).

3.2 Porosity

By using Fresnel imaging in the TEM, different types of porosity can easily be identified in oxide scales, and we have used this technique to study the development of porosity at different stages of oxidation. Figure 13 (a) shows an over-focus image of the distribution of porosity near the metal-oxide interface in the 225-day recrystallised Zr-1.0Nb alloy. There are several different kinds of porosity in this small area that show dark Fresnel contrast in the over-focussed images (Δf = +980 nm), identified more clearly in the higher magnification over focus images in (b - d). 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 (arrowed), 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. The metal underneath the metal oxide interface also has large amount of isolated pores. This kind of complex interconnected porosity is expected to play an important role in the oxygen diffusion processes that control the local rate of oxidation.

The annealed Zr-1.0Nb alloy, which has a much faster oxidation rate than the recrystallised material (Figure 1) also contains significantly more porosity in the oxide, as seen in Figure 14(a). These over-focus images were taken around the region between 1 μm away and the metal-oxide interface, and 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.
Figure 11. TKD mapping (a) and MLLS fitting results (b) EELS low loss mapping reference spectra (c) and for oxide, suboxide, Zr(Osat) and metal for 360-day recrystallised Zr-1.0Nb
Figure 12. The thickness of suboxide (triangles) and the combined region (suboxide + Zr(Osat)) (squares) against (a) oxidation days and weight gain data of recrystallised Zr-1.0Nb; (b) the instantaneous oxidation rate for ZIRLO™, recrystallised Zr-1.0Nb and annealed Zr-1.0Nb. The circles represent individual measurements on the Zr(Osat) region using APT.
In the neutron irradiated sample, which had a surprisingly thin oxide scale after 540 days in the reactor, it proved extremely difficult to see any porosity at all. At the metal-oxide interface, the over focus images in Figure 14(b-1 and b-2) there is some dark contrast around a SPP with crescent shape crack on top, but there is no obvious porosity near the grain boundaries or inside the grains. This lack of porosity is consistent with the slow overall oxidation rate for this sample, as well as the very dense oxide microstructure without many cracks shown in Figure 3.
Conclusions

We 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. Low loss EELS mapping is used to map a large area across the metal-oxide interface showing suboxide and 

Figure 14. Over focus images of different kinds of porosity in (a) 91-day annealed Zr-1.0Nb and (b) the 540-day neutron irradiated Zr-1.0Nb sample.
Zr(Osat) area distribution. Atom Probe and EDX is used to study the microchemistry and distribution of SPPs. Core loss EELS is used to study the oxidation state of Nb and Fe in the amorphous and crystalline SPPs in different locations of the oxide and metal. Fresnel imaging is used to image porosity in the oxide and metal underneath the interface.

- Significant differences in grain morphology were observed between samples oxidised in the autoclave and in-reactor samples. Recrystallised Zr-1.0Nb alloys which have good corrosion resistance and HPU have 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.

- Recrystallised Zr-1.0Nb alloys show significant differences in microstructure and microchemistry after being neutron irradiated for 540 days, with longer, better aligned moniclinic grains seen in the autoclave samples. The irradiated sample contains many fewer cracks, more tetragonal oxide grains and a relatively even metal-oxide interface. The sample also contains fewer macro and micro cracks in the oxide.

- A combination of EDX and EELS analysis of SPPs can reveal the main and the minor element distributions respectively. In recrystallised 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 recrystallised 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 recrystallised 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.

- Comparing with different alloys with different overall oxidation rate and instantaneous oxidation rate, it is found that alloys with better corrosion resistance have more formation of suboxide and the combined Zr-O region (suboxide +Zr(Osat)), their thickness correlates well to the estimated instantaneous oxidation rate. The suboxide is formed when the oxide growth is slow and allows some oxygen diffusion in the base metal, when oxidation rate is fast, there is enough oxygen to develop zirconium oxide directly without going through suboxide stage. Throughout the oxidation process from early days to transition to post transition, the suboxide and Zr(Osat) thickness keeps increasing prior to the transition, until it reaches the transition point and drops to a thinner thickness. 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 with higher oxidation rate than found in either the recrystallised alloy or the similar alloy exposed to neutron irradiation. Neutron irradiated sample has very few porosity, possibly related with the low oxidation rate.

- The presence of this oxygen-rich zone: combined Zr-O region (suboxide +Zr(Osat)) together with 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 \textit{combined Zr-O region (suboxide +Zr(Osat))} grows with oxidation days until reach transition, when porosity becomes interconnected and \textit{combined Zr-O region (suboxide +Zr(Osat))} drops to the minimum thickness.

\textbf{Acknowledgements:}

This project is part of the MUZIC-2 collaboration studying oxidation and hydrogen pickup in Zr alloys. The authors gratefully acknowledge support from EDF, Westinghouse, EPRI and Rolls Royce, and many useful discussions within the consortium. Jing Hu is supported by the China Scholarship Council. The ARM was funded by the EPSRC, grant EP/K040375/1. The authors wish to acknowledge Pia Tejland from Studvik, Sweden who did the FIB lift out from the neutron irradiated samples, also Allan Hart and Matthew Topping from Manchester, UK who helped with automated crystal orientation mapping with TEM experiment setup, without which the work would not have been possible.

\textbf{References}


13. de Gabory, B., Dong, Y., Motta, A. T. & Marquis, E. A. EELS and atom probe tomography study


