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HIGH-RESOLUTION CHARACTERIZATION OF CORROSION AND HYDROGEN PICKUP OF ZR CLADDING ALLOYS

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ABSTRACT

As part of the MUZIC-2 project, several state-of-the-art high resolution analysis techniques are being used to study the microstructure of a range of commercial and developmental Zr alloys corroded under autoclave simulated PWR conditions. Samples were chosen to be representative of the early, pre-transition, transition and post-transition stages of the oxidation process. We have studied the development of the equiaxed-columnar-equiaxed grain structure, and observe that the columnar grains are both longer and show a stronger preferred texture in more corrosion-resistant alloys. Fresnel imaging revealed the existence of both parallel interconnected pores and some vertically interconnected pores along the columnar oxide grain boundaries, which become disconnected near the metal-oxide interface. Analytical (Scanning) Transmission Electron Microscope ((S)TEM) has been used to study two types of second phase particles (SPPs): β-Nb and Zr(Nb,Fe)$_2$. The Zr(Nb,Fe)$_2$ SPPs are present at a lower number density and tend to become amorphous quickly once incorporated into the growing oxide. Atom Probe Tomography (APT) was used to study finer Nb and Fe clusters in the suboxide and metal regions, Fe clusters are also found at the oxide grain boundaries. Electron Energy Loss Spectroscopy analysis (EELS) and automated crystal orientation mapping with TEM have also revealed Widmanstatten-type suboxide layers in some samples with compositions in different regions of either the hexagonal ZrO structure predicted with ab initio modelling or Zr$_3$O$_2$. Some of these layers are much thicker than observed previously in other oxidised zirconium alloys. Hydrogen pickup mechanisms have been studied by high resolution Secondary Ion Mass Spectrometry (NanoSIMS) analysis of deuterium-spiked samples, showing that at different stages of oxidation the penetration of deuterium occurs in quite different patterns. These observations are discussed in the context of current models for oxidation and hydrogen pickup in zirconium alloys.

1. Introduction

For the past five decades, Zr alloys have been selected for use as nuclear fuel cladding and major components of the fuel assembly in nuclear reactors. These alloys show a low thermal neutron absorption cross section and reasonable mechanical properties. However, the major problems associated with cladding applications are high temperature aqueous corrosion and hydrogen pickup (HPU)\(^1\).

The oxidation kinetics of Zr alloys start with an initial pre-transition period of parabolic growth kinetics followed by cycles of increased oxidation rate, and eventually an abrupt increase called “breakaway” to almost linear kinetics\(^2\). Some of the liberated hydrogen from the corrosion process is absorbed into the metal, which can lead to further problems such as delayed hydride cracking (DHC). Careful kinetics studies have shown that the hydrogen pickup(HPU) rate is related to the oxidation rate and alloying chemistry of Zr alloys\(^3\).

In recent years, developments of modern microscopy and sample preparation techniques have allowed us to understand the microstructural and microchemistry changes during the
oxidation and HPU processes in unprecedented detail. In this work, the same Zr-1.0%Nb alloys were treated in the autoclave with periodic measurements of oxidation weight gain. Samples from early, pre-transition, transition and post-transition stages were studied using state-of-the-art microscopy techniques including (Scanning) Transmission Electron Microscope((S)TEM), Electron Energy Loss Spectroscopy (EELS), Energy-dispersive X-ray Spectroscopy (EDX), automated crystal orientation mapping with TEM (ASTAR), Atom Probe Tomography (APT) and high resolution Secondary Ion Mass Spectrometry (NanoSIMS).

2. Materials and Method
In this work, Zr cladding tubes from a Westinghouse developmental alloy were selected. The composition of the alloys was measured by EDF using inductively coupled plasma atomic emission spectrometry (ICP-AES) as Zr-0.9Nb-0.01Sn-0.08Fe (wt%) and all samples were in the recrystallized state. The bulk Zr cladding tube samples 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 further 45 days. Details of autoclave testing and oxidation kinetics are reported elsewhere. The weight gain data in Fig.1 shows that the samples show no sign of transition, even after 360 days.

In order to observe the microstructural changes during the oxidation process, four samples were selected for detailed analysis, as shown by the circles in Fig.1. Sample A from the early stage of pre-transition was oxidised for 120 days. Sample B which represents the early stage of pre-transition has been oxidised initially for 180 days and received an additional exposure to deuterated water for a further 45 days. Sample C is close to first-transition and was oxidised for 360 days. Sample D which represents the post-transition stage was initially oxidised for 540 days and then exposed to deuterated water for a further 45 days. The inserts in Fig.1 are Scanning Transmission Electron Microscope (STEM) High Angle Annular Dark Field (HAADF) images of the samples showing the general microstructural changes at different stages of the oxidation process.

![Corrosion kinetics of Zr-0.9Nb-0.01Sn-0.08Fe(wt%)](image)

Figure 1: Autoclave corrosion weight gain profiles showing averaged weight gain values for Zr-1.0Nb-0.1Fe samples. Samples selected for further study are circled in red, with STEM HAADF images of the samples inset (scale bar applies to all images).
The four tube samples around 30 mm long and 9.5mm in diameter were cut into small pieces with a diamond saw. TEM samples were prepared by the in-situ lift out method on an FEI FIB200 and further thinned down to a thickness below 100nm in a Zeiss Nvision 40 dual beam FIB to create a homogeneous and electron-transparent sample for TEM and STEM analysis. The samples were further thinned down to ~50nm using low-voltage conditions for final EELS analysis on selected regions of interest. TEM and STEM analysis were performed on a JEOL 2100 LaB₆ microscope operated at 200kV. EELS spectrum imaging was performed on a JEOL ARM microscope operated at 200kV and equipped with a Gatan image filter. The convergence half-angle α was 20mrad and collection half-angle β was 30mrad with an energy dispersion of 0.5eV per channel and a step size of 7.7nm. 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 5nm step size. Data analysis was carried out using a NanoMEGAS ASTAR automated crystal orientation mapping system.

APT specimens from 225-day and 585-day Zr-1%Nb samples were also prepared by in-situ lift out using a Zeiss NVision 40 dual-beam FIB. Needle-like samples with tip diameter less than 100nm were prepared for analysis near the oxide/suboxide-metal interface. The needles were tested in a Cameca LEAP3000X with laser energy of 0.5nJ and repetition rate 200kHz and the data reconstruction was carried out using iVAS 3.6.6 software.

The materials selected for NanoSIMS analysis were 225-day and 585-day Zr-1%Nb, samples were set in epoxy resin and metallurgically polished in cross-section to a 40nm colloidal silica finish to reveal the metal-oxide interface. Immediately thereafter, 5nm of platinum was deposited onto the surface to ensure conductivity and minimise oxidation of the metal surface.

Samples were analysed on a CAMECA NanoSIMS50 with a 16keV primary Cs⁺ beam. The $^{16}\text{O}$ signal was detected to indicate the exact location of the metal-oxide interface, and the $^2\text{H}$ signal was detected to show deuterium localisation. As hydrogen was present in the vacuum chamber, in carbon contaminants and in the previously oxidised material, the use of deuterium showed how hydrogenic species interact with the microstructure during the 45 days of deuterated oxidation. As deuterium is only present with a natural isotopic abundance of only 0.01%, it was assumed that any deuterium detected was from the 100% heavy-water oxidation stage.

### 3. Results and discussions

#### 3.1 Overview of Oxide Morphology

Fig. 1 shows STEM HAADF images of the four selected Zr-1.0%Nb samples. In the pre-transition samples oxidised for 120, 225 and 360 days, the oxide grows from 1.5 μm in overall thickness to about 3.0 μm overall when it reaches the transition point, and to 5.4 μm in the 585-day sample. In all the pre-transition samples, macro-cracks around 0.6-1.2μm in length parallel to the metal-oxide interface are scattered near the metal-oxide interface as reported in previous studies. In addition, much smaller micro-cracks or flake-like porosity 40-50nm in length cuts through the columnar grains or is located near the metal-oxide interface. In the post-transition 585-day sample, there are two distinct layers of cracks parallel to the metal-oxide interface, although the two layers are not exactly parallel which suggests the local transition happens at different times in different locations, in agreement with previous observation. Although there is no available autoclave data between 360 and 585 days, the two layers of cracks suggest that the sample has gone through two transitions. There is another 1.5 μm thick region with small oxide grains between the second layer of crack and the metal-oxide interface, showing that the sample may still be in the fast oxidation rate region after the second transition.
The top \~700nm layer of pre-transition samples consists of equiaxed grains with a grain size \~20nm. In the post-transition sample, equiaxed grains near the two layers of cracks were also observed. Cracks and pores are found around these small equiaxed grains near the sample surface. It is worth mentioning that at a much lower density there are vertical cracks from the sample surface about 400nm in length. This type of cracks provides the best paths for oxygen 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\(^8\). 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 50nm wide and 200nm in length.

### 3.2 Porosity in Fresnel Imaging

By using Fresnel imaging in the TEM, different types of porosity can be easily identified. The outer equiaxed part of all the oxides is very porous, with individual pores around 10nm in diameter at oxide grain boundaries. Around 500nm further into the oxide, small flake-like pores around 200nm in length start to appear parallel to the metal-oxide interface between equiaxed and columnar oxide grains. The columnar oxide grains have flake-like porosity 50nm wide at the top and 20nm wide across the middle of grains. There are also individual pores inside columnar grains, which suggests that bulk lattice migration is a possible path for oxygen transport. Some of the individual pores are connected, creating an interconnected array of nanocracks around 20nm in width as shown in Fig 2. (a) \~200 nm away from the metal-oxide interface of the 225-day sample. Near the metal-oxide interface, columnar grain boundaries are more commonly seen to be decorated with vertically interconnected pores, as seen in the Fig. 2(b) which is taken close to (a). Towards the end of the vertical connected porosity, the pores gradually become disconnected as we move closer the metal-oxide interface. In Fig. 2(c) there are disconnected pores along the columnar grain boundaries and also individual pores at the metal-oxide interface and the suboxide region underneath which is the oxygen sink for the most recent oxidation process. In Fig. 2(d), at the end of the columnar grains, another type of connected porosity is seen along the metal-oxide interface. This kind of complex interconnected porosity is proposed to play an important role in the rate determining oxygen diffusion process\(^9\).

![Figure 2: Through-focal imaging of fine pores (circled) close to the metal-oxide interface in the 225-day Zr-1.0Nb sample. The pores are invisible in the top in-focus images (Δf = 0 nm), but show Fresnel contrast in the middle under-focussed images (Δf = -980 nm) and in the lower over-focussed images (Δf = +980 nm). Three different types of porosity are revealed at different locations: (a) 100nm from](image)
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 Second Phase Particles
We have studied SPPs in some details because they are proposed to offer cathodic sites for hydrogen penetration and also become oxidised and release aliovalent elements which can affect the local electronic conductivity in the oxides.

3.3.1 EELS mapping of SPPs
Analytical (S)TEM revealed two types of second phase particles: β-Nb and Zr(Nb,Fe)₂. The Zr(Nb,Fe)₂ SPPs are present at a lower number density and tend to become amorphous quickly as the oxide grows.

EELS spectrum imaging was carried out on the 120-day sample. Fig. 3(a)-(d) shows the EELS core loss results. In Fig.3 (a), STEM HAADF image of three SPPs is taken around 300-500 nm from the metal-oxide interface where there is a parallel crack. EDX mapping of the same region has shown that both the top and middle SPPs (SPP1 and 2) contain Fe and Nb, and the bottom one (SPP3) contains Nb only. Fig.3 (b)-(d) shows different oxidation stages for 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.

![STEM HAADF image of an area containing three SPPs about 300nm away from the metal-oxide interface. (b)-(d) Core loss EELS mappings 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.](image)

3.3.2 Atom Probe Tomography of SPPs
We have used APT to study the chemistry of the metal-oxide interface at the atomic scale. The sensitivity of this technique means that the distribution of even dilute impurity elements like Fe can be studied in detail.

The APT results in Fig. 4 show the presence of two β-Nb particles. These particles have similar concentration profiles, containing ~85at% Nb and ~13at% Zr at the core. Fe atoms
decorate the precipitate-metal interface with a maximum concentration of ~0.9 at%, but very little Fe is found inside the precipitates.

A partially-oxidised Nb-rich particle similar to those observed in Fig. 3 is observed in the ZrO suboxide adjacent to the metal-oxide interface. This particle is about ~4nm in diameter with the core containing ~50 at% Nb, ~30 at% Zr, and ~20 at% O. Fe is now present inside the precipitate rather than at the periphery of the particle, with maximum Fe concentration of ~3.5 at%.

Figure 4: Atom map showing Nb and Fe distributions near the suboxide-metal interface of the 225-day Zr-1% Nb sample. Two β-Nb particles are found in the metal with similar concentration profiles across the precipitate-metal.

Group of Nb clusters have also been observed in the ZrO and metal regions, as seen in Fig. 5 (a) and (b), but only a few of them was found in the bulk ZrO. Many Fe clusters were found in O-saturated metal (Fig. 5 (c)) and only a few in ZrO. This indicates that both Fe and Nb clusters can be dissolved into bulk oxide during oxidation. In addition, it has been observed that grain boundaries were found to be enriched in Fe, as has been observed by other authors. 

Figure 5: a) Fe (pink) and Nb (blue) concentration profiles in the O-saturated metal showing Fe (green arrows) and Nb (red arrows) clusters, b) Nb clusters in the ZrO region, and c) Fe clusters in bulk ZrO.
3.4 Suboxide growth

3.4.1 EELS and ASTAR mapping

EELS analysis and automated crystal orientation (ASTAR) mapping in the TEM have been used to study the metal-oxide interface in order to provide a comprehensive view of microstructure and micro-chemistry.

Fig.6 (a) shows the HAADF STEM image of a 120-day Zr-1.0%Nb sample after further thinning down to around 50nm in order to do accurate ASTAR and EELS mapping. Fig.6 (b) shows a phase map of the TEM lamella. Columnar oxides with monoclinic-ZrO$_2$ (m-ZrO$_2$) structure are clearly seen, and scattered equiaxed tetragonal-ZrO$_2$ (t-ZrO$_2$) grains. The top layer of t-ZrO$_2$ is considered to be a result of FIB damage. At the metal-oxide interface, there is a continuous layer of Widmanstatten-type suboxide with the hexagonal ZrO structure predicted with *ab initio* modelling, which agrees with previous findings using Transmission Kikuchi Diffraction but with a higher matching rate. The undulating area under a parallel crack shows a more uniform saw-tooth shape with metal underneath intact. This same area was analysed in the EELS mapping in Fig. 7.

Figure 6: (a) HAADF STEM image of the 120-day Zr-1.0%Nb 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 Fig.6 is shown in Fig. 7(a). The Z-contrast in the image shows the saw-tooth shaped suboxide as seen in the ASTAR map, and the Oxygen and Zr concentration maps in Fig. 7 (b1, b2) confirm an ~86nm thick ZrO suboxide followed by oxygen saturated metal with ~25 at% oxygen.

Figure 7: (a) HAADF STEM image of the area for EELS mapping of the 120-day Zr-1.0Nb sample, (b-1) Oxygen concentration map, (b-2) Zr concentration map.
EELS mapping of the suboxide was carried out on a series of Zr-1.0%Nb samples. The suboxide thickness grows with oxidation time before transition. Some of these suboxide layers are much thicker than observed previously in other oxidised Zr alloys. We concluded that the suboxide forms only during the slow stages of oxidation and is rapidly consumed at transition as the metal-oxide interface moves much faster to consume the underlying metal.

3.4.2 Atom Probe Tomography of ZrO layers
ZrO suboxide layers were found by APT in both 225-day and 585-day samples. In both cases, a ZrO layer of 100nm or more in thickness was found. This initially contradicts the observations by Ni et al., showing that no suboxide is present in post-transition specimens. However, our TEM results also found a suboxide in the 540-day sample, indicating that these regions may still be in pre-transition state. In the 225-day sample, as illustrated in Fig. 5, Fe-decorated dislocation lines were found at the metal adjacent to the suboxide-metal interface. They are oriented in the direction perpendicular to the oxide growth direction. These may form due to the compressive stress in that region originating from volume expansion during oxidation. As the deformed metal transforms to ZrO and the dislocation lines disappear, but the Fe atoms often remain decorating linear features.

In the 585-day sample, as seen in Fig.8, a thick ZrO layer was also found. This particular saw-tooth shaped suboxide-metal interface had a composition profile similar to that reported in previous atom probe studies: 68at% Zr and 32at% O. The presence of Fe accumulation along the suboxide-metal interface suggests that Fe is rejected from the suboxide to the metal during oxidation.

Figure 8: a) Fe distribution in oxide, suboxide, and O-saturated metal with saw-tooth shape suboxide-metal interface in the 585-day sample, b) arrows showing Fe segregation to the interface.

3.5 NanoSIMS analysis of deuterium distribution
SIMS results from the 225-day and 585-day Zr-1%Nb show higher intensities of deuterium in the oxide as seen in Fig. 9. Linescans drawn across the metal-oxide interface of the 225-day sample show particularly high intensities of deuterium in the top 1 μm of the oxide, rapidly dropping off further towards the metal-oxide interface. The 585-day sample, whilst still showing the initial strong peak in the first micron of oxide, shows significantly more deuterium throughout the bulk oxide, suggesting that the transition event enables the propagation or trapping of deuterium while the pre-transition sample is a good barrier to deuterium penetration. In the metal, the 225-day sample shows very low deuterium counts, whilst the 585-day sample shows regions of strong intensity which can be identified as zirconium deuterides.

The high deuterium signal at the oxide surface is thought to be due to trapping in the extensive porosity seen by TEM in the equiaxed top layers. The relatively dense bulk oxide in the 225-day sample then offers few preferential sites for trapping deuterium and the
measured ratio is not much higher than natural isotopic background. The more cracked and porous 585-day sample offers a much easier route for deuterium penetration down to the zirconium metal.

4. Conclusions

Here we present a detailed microstructural and microchemistry study of oxidised Zr-1.0%Nb alloys. Samples were chosen to represent the early, pre-transition, transition and post-transition stages of oxidation.

1. Fresnel imaging revealed the existence of both parallel interconnected pores and some vertically interconnected pores along the columnar oxide grain boundaries, which become more disconnected near the metal-oxide interface. For the first time, we report similar porosity at the metal-oxide interface itself.

2. Analytical (S)TEM revealed two types of second phase particles: β-Nb and Zr(Nb,Fe)2. The Zr(Nb,Fe)2 SPPs are present at a lower number density and tend to become amorphous quickly as the oxide grows. APT was used to study finer Nb clusters and Fe clusters in the suboxide and metal regions. Fe clusters are also found at the oxide grain boundaries. These observations help us understand how different aliovalent elements (Nb5+, Fe3+, Fe2+) can be redistributed in the oxide during oxidation and potentially alter the electronic conductivity.

3. APT, EELS and automated crystal orientation mapping have revealed Widmanstatten-type suboxide layers in some samples with compositions in different regions of either ZrO structure or Zr3O2. Some of these layers are much thicker than observed previously in other oxidised zirconium alloys. And this may be an important feature in understanding the different overall corrosion rates on the basis of local environment in oxidation kinetics at the micron scale.

4. Hydrogen pickup mechanisms have been studied by high resolution SIMS analysis, showing that at different stages of oxidation the penetration of deuterium occurs in quite different patterns. This data can be correlated to the overall oxide microstructure revealed by ASTAR mapping in the TEM.
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