1 **Determination of the Initial Oxidation Behavior of Zircaloy-4 by *In-***
2 ***Situ* TEM**

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Abstract

The corrosion behavior of Zircaloy-4 (Zry-4), specifically by oxidation, is a problem of great importance as this material is critical for current nuclear reactor cladding. The early formation behavior and structure of the oxide layer during oxidation was studied using *in-situ* TEM techniques that allowed for Zry-4 to be monitored during corrosion. These environmental exposure experiments were coupled with precession electron diffraction to identify and quantify the phases present in the samples before and after the oxidation. Following short-term, high temperature oxidation, the dominant phase was revealed to be monoclinic ZrO_2 in a columnar structure. These samples oxidized *in-situ* contained structures that correlated well with bulk Zry-4 subjected to autoclave treatment, which were used for comparison and validation of this technique. By using *in-situ* TEM the effect of microstructure features, such as grain boundaries, on oxidation behavior of an alloy can be studied. The technique presented herein holds the potential to be applied any alloy system to study these effects.

Keywords: Zircaloy-4, in-situ TEM, precession diffraction, oxidation, corrosion

1. Introduction

Zirconium-based alloys have long been used as nuclear fuel cladding, due to their resistance to corrosion and low neutron cross section [1–4]. In particular, the Zircaloy series of alloys have been the most widely implemented in reactors, with much attention focused on the oxidation behavior of Zircaloy-2 and Zircaloy-4. Zircaloy-2 and Zircaloy-4 are distinguished mainly by the lower Ni and Fe content of Zircaloy-4[3]. While these alloys possess moderate corrosion resistance, uniform corrosion, along with the associated hydrogen pick up, remains a life-limiting factor for fuel rod service[5,6]. Zircaloy-2 is commonly used in Boiling Water Reactors (BWRs), where hydrogen pickup is less of a concern than in Pressurized Water Reactors (PWRs), in which Zircaloy-4 is more commonly found. More recently, the Zircaloy series of alloys is being replaced with alloys such as ZIRLO and M5, which have better corrosion resistance due to the additions of niobium[2,7,8]. As the push to increase nuclear reactor efficiency continues, an improved understanding of the oxidation behavior of these alloys is necessary for prolonged fuel service and for use in harsher environments that are dictated to achieve higher burn-up. In particular, Generation IV reactors will provide higher temperatures that will accelerate cladding oxidation, in turn limiting the achievable burn-up and thus efficiency[9].

The in-service lifetime of fuel rods is limited by material behavior, which is very dependent on microstructure and composition. In the case of the Zircaloy family of alloys, it has been shown that corrosion behavior is dependent on both alloying additions and on base metal phase. Past studies have shown that Zircaloys that are beta-quenched are more corrosion resistant than traditionally prepared Zircaloys[10–12]. Other studies have shown that crystallographic orientation has an effect on the oxidation behavior of zirconium-based alloys, with the base metal affecting the orientation of the oxide formed[13–15]. Grain boundary engineering techniques that alter microstructure are a viable method for increasing corrosion resistance[16–20]. In zirconium-based alloys, it has been shown that phenomena connected to oxidation, such as hydride formation, are very dependent on microstructure such as grain boundaries and precipitates, and in-situ TEM can be used to study the initial mechanisms resulting in hydride formation[21]. The base metal microstructure has also been shown to have significant effects on the microstructure of the oxide formed during oxidation[22].

The oxidation behavior of these alloys has been extensively studied by a variety of methods. These methods include microbeam synchrotron diffraction[23–25], transmission electron microscopy (TEM)[14,26–28], scanning electron microscopy (SEM)[12,14,23–25,29], optical microscopy[23,30], and x-ray diffraction[25,29,30]. These techniques have provided an extensive knowledge base for the morphology and structure of the oxides formed on these alloys, including cracking behavior[23,26], crystal structure[23,25,26,29], and the start of breakaway corrosion[9,31]. A variety of oxidation environments for zirconium-based alloys have been studied as well, including oxygen[32,33], steam[7,8,34,35], water[7,9,25], water vapor[32], air[36–38], with all studies showing similar oxide structures and appearance, with only changes in kinetics of oxidation being noted. The majority of these experiments, however, have been done using autoclave or reactor corroded samples over long periods of time, which has not allowed for the study of the initial steps of corrosion. As such, while the oxide structure on corroded zirconium-based alloys is known to be composed of both of tetragonal and monoclinic ZrO_2 , the structure of the initially formed oxide is not yet known. It is known that the oxide structure formed on zirconium-based alloys is highly textured, and that this may affect the corrosion rate of the base alloy[9,23,27,39]. It is thought that the texture in the monoclinic phase is the result of stress minimization, but the effect of this texture on oxidation rate is unknown[9,39]. Changes in texture of the oxide have also been attributed to the reformation of the protective oxide layer, but once again the effect on oxidation rate is not discussed[23]. More recently, it has been found that more strongly textured oxides provide better corrosion resistance, and there are preferred growth directions in both monoclinic and tetragonal oxides[27]. By studying the initial growth of the oxide in zirconium-based alloys, it may be possible to identify factors that lead to a slower oxide growth rate, such as low angle grain boundaries which can be increased in number through grain boundary engineering[16]. If the oxidation rate can be reduced through grain boundary engineering, this will allow for a fuel rods to have a longer in-reactor lifespan, leading to higher burn-ups, and potentially safer storage of spent fuel. Thus, by studying the initial oxide structures and growth mechanisms, there is great potential for improvements in material performance.

In this paper, we present a new method for studying the early onset of oxidation in Zircaloy-4. We compare our results to those obtained for the same alloy using an autoclave method, which is typically employed to study the long-term oxidation behavior of Zircaloy-4 and thus known to replicate the oxidation behavior seen in-reactor. Through the use of precession electron diffraction, selected area diffraction, and bright field transmission electron microscopy we will show that this new method can be used to replicate the oxidation process that occurs in an autoclave. Precession electron diffraction allows for determination of grain orientation and boundary angle, which when coupled with *in-situ* TEM that provides direct observation of the effect of these microstructural features on oxidation. In addition, this technique can be used to study the effect of alloy composition on oxidation behavior, including the effect of secondary phase particles. By controlling the environment, it is possible to achieve partial oxidation, allowing for the study of the initial oxide structures and texture effects during oxidation in addition to the *in-situ* observation of the sample.

2. Experimental Methods

2.1 Sample Preparation

Cross-sectional TEM lamellae were prepared from a pristine sheet of as-received, cold-rolled, stress-relieved alpha phase Zircaloy-4 (Zry-4) using a conventional focused-ion beam lift-out technique [40] in a FEI DB-235 and subsequently transferred to a Protochips environmental holder heating platform, known as a “E-chip”, using an ExpressLO *ex-situ* lift out system. Samples were then welded to the platform using e-beam tungsten or platinum deposition in the FIB to secure and enhance the heat transfer from the E-Chip heating element during oxidation experiment. Lift outs from bulk were made at random from the Zry-4 sheet, due to a combination of relatively small grain size, which ensured multiple grains within a sample and the difficulty of good EBSD in zirconium-based alloys[41] making targeting of specific boundaries difficult. By using precession diffraction, orientation information for the sample is readily available without the use of EBSD. During sample preparation, care was taken to minimize gallium damage to the sample by placing a protective top strap of either platinum or tungsten over the region on interest, and a final clean up step following thinning was conducted using 5 kV gallium. These samples were also made as thick as possible while remaining electron transparent, so as to help limit thin film effects on oxidation. In addition, *in-situ* samples were compared to autoclave oxidized bulk samples to confirm similar oxidation behavior to bulk. Finally, a SRIM calculation was done for a 30kV ion beam at 0°, which gave an ion range of 16.7 nm. Figure 1 illustrates the sample preparation route for in-situ FIB samples, the image on the left shows sample after standard FIB preparation cut free for *ex-situ* lift out, *ex-situ* lift out to an E-Chip in the center, and final sample preparation through FIB deposition on the right. For comparison, an autoclave-corroded sample of Zry-4 provided by Arthur Motta, which had been oxidized for 225 days at 360°C [31], was prepared using conventional FIB lift-out techniques.

Figure 1: Top images show *ex-situ* sample preparation; sample is made and loose in FIB trench, sample is placed on E-chip, then attached to E-chip with electron deposited Pt. Lower images show standard FIB preparation as used with the autoclaved samples.

2.2 Sample Characterization and Experimental Parameters

Samples were analyzed using a JEOL 2100 Lab6 TEM operated at 200 kV in conjunction with a Protochips environmental holder[42]. This holder is a gas cell of a sandwich type design[43–45], with two silicon chips with windows consisting of electron transparent amorphous silicon nitride for sample observation. Gases can be mixed in the holder manifold, then flowed into the cell for experiments, with experiments taking place either under static pressure or under flowing gas conditions with pressures up to 760 torr. Precession electron diffraction (PED)[46,47],

enabled by a NanoMEGAS™ system, was used to determine the phases present in each pristine sample prior to the *in-situ* experiment so as to confirm that no oxide was present prior to the *in-situ* experiment. In precession diffraction, a series of nanobeam diffraction patterns are collected as the beam is rastered over an area of the sample, similar to STEM. These patterns are then indexed via proprietary computer program to generate phase and orientation information, similar to EBSD. After initial characterization, a ~760 Torr gas mixture consisting of 50% oxygen/50% argon was introduced and the samples were heated at a rate of 5°C per second; one heating series was run from room temperature to 800°C and another from room temperature to 650°C. These conditions were selected to promote relatively rapid oxidation of the sample, such that oxidation could be observed in a reasonable time for *in-situ* TEM. In addition, the relatively aggressive gas mixture ensures uniformity between experiments as compared to room atmosphere, and allows for modulation of just temperature to get oxidation at the desired speed. Past work by a variety of authors in a variety of corrosive mediums has shown for zirconium based alloys, that while oxidation kinetics may be affected, overall oxide structure is not significantly changed[28,32]. The experimental conditions used resulted in the oxidation of the pristine lamellae; after completion of the *in-situ* experiments, nanobeam diffraction and precession diffraction were again used to identify and map the phases present in the samples. Samples were then analyzed post-oxidation in two separate ways: (1) *in-situ* oxidized lamellae were carefully removed from the E-Chip and placed on a standard TEM grid for high-resolution imaging, and (2) cross sections of the *in-situ* oxidized lamellae were prepared for additional precession diffraction in order to determine the structure, thickness and extent of the oxide grown during the experiment. Finally, the samples were compared with autoclaved oxidized materials. Autoclave oxidized samples are commonly used to study the oxidation behavior in zirconium based alloys. In order to compare the *in-situ* studies to a known standard, autoclave samples were analyzed using the same methods as the *in-situ* samples. Plan-view and cross-sectional methods described above were used to prepare these samples for imaging, diffraction and phase analysis.

3. Results and Discussion

3.1 *In-Situ* Characterization

The initial condition of the un-oxidized samples of Zry-4 showed a large amount of deformation in the microstructure, with a random distribution of grain boundaries. This was confirmed using precession diffraction, as seen in figure 2, which shows bright field TEM images of a pristine sample prior to the corrosion experiment along with the corresponding phase map and orientation map generated using precession diffraction. The phase map confirms that pure HCP zirconium is the dominant phase throughout the sample, as expected for pristine Zry-4.

Figure 2: Bright field TEM, orientation and phase maps from precession diffraction showing the initial sample condition.

Since FIB lift outs were taken at random from the bulk sample, the boundaries present in the Zircaloy-4 samples were of a random distribution, with the orientation map showing an example of the multiple boundaries present in a sample.

Figure 3: Snap shots from an oxidation experiment conducted at 650°C, showing (A) the start of the experiment, (B) midpoint of the oxidation with small oxide grains forming and a loss of contrast in the base metal microstructure, and (C) the final state of the sample showing small oxide grains obscuring the underlying microstructure.

During the oxidation experiment, it was seen that the sample becomes thicker as oxide forms, reducing contrast in the TEM image. Small grains formed during the experiment, with the microstructure of the underlying sample remaining stable, although difficult to discern due to decreased contrast. Figure 3 shows an in-situ oxidation experiment and illustrates the appearance of small oxide grains, as well as the decrease in contrast resulting from increased thickness. The initial sample condition is shown in (A), image (B) shows the midpoint of the experiment, with contrast starting to be reduced and small oxide grains beginning to dominate, and at the end of the experiment on the right (C) it can be seen that both contrast is reduced to almost nothing in thicker areas of the sample, and the underlying microstructure of the base metal is obscured by many smaller oxide grains formed on the sample surface. It is clear that the sample oxidized over the course of this experiment, as many smaller grains can be seen in the final image (C). This is to be expected during the oxidation process, based on the work of many past researchers who report small grain sizes in the oxide[26,27,48,49]. Figure 4 illustrates the oxidized sample after heating under presence of oxygen where clear changes in morphology can be observed. Following the oxidation experiment, precession diffraction was used to create a phase map of this region of the sample, as seen in figure 4. It was seen that the oxide formed as a mixture of monoclinic ZrO_2 (green), tetragonal ZrO_2 (blue), and some base metal of pristine HCP Zr (red) remaining.

Figure 4: Bright field TEM image on the left shows the region over which the phase map on right was generated. The phase map shows the sample to have mostly oxidized to form monoclinic ZrO_2 . This sample was oxidized at 650°C .

Past work done in both autoclave and reactor oxidized samples from a variety of authors confirms that the majority phase expected is monoclinic ZrO_2 , as this is the stable phase of ZrO_2 at room temperature, along with some tetragonal ZrO_2 [9,23,26,27,49]. However, past work utilizing both XPS[50] and synchrotron x-ray diffraction[24] indicate that the initial oxide layer may be composed of a majority phase of tetragonal ZrO_2 . As is seen in figure 4 (E), the in-situ experiment agrees well with these studies, showing what appears to be a relatively high concentration of tetragonal phase. Orientation maps created using precession diffraction, as shown in figure 4, indicate that there is some evidence of texture in the tetragonal ZrO_2 , however it appears that the monoclinic ZrO_2 does not show a strong texture. As for the HCP Zr base metal, most of the remaining base metal is of one orientation, indicating there may be orientation effects on the rate of oxidation, which is expected based on the work on Ploc[13]. In addition, samples oxidized *in-situ* were compared to autoclave oxidized samples to confirm the similarities in oxidation behavior and oxide structure.

3.2 Comparison of *in-situ* and autoclave samples

Autoclave oxidized samples were studied using the same methods as the *in-situ* samples to provide a direct comparison. As such, Figure 5 shows a phase map (B) and corresponding bright field image (A) for the *ex-situ* oxidized sample (autoclave-corroded) to compare to the *in-situ* samples.

Figure 5: Analysis of an autoclave-oxidized sample at the oxide-metal interface. (A) Bright field TEM image showing the precession diffraction area. (B) Phase showing phases present in the precession area. (C) Nanobeam diffraction pattern taken from the autoclave sample showing the presence of monoclinic ZrO₂. (D) Orientation map for HCP Zr (E) Orientation map for monoclinic ZrO₂ (F) Orientation map for tetragonal ZrO₂ all from the precession area in (A).

The phases present in the autoclave corroded sample correspond well to the results from the *in-situ* samples, showing a distribution of the two oxide phases, monoclinic ZrO₂ with areas of tetragonal ZrO₂. Small columnar grains of ZrO₂ are visible growing from the base metal, which again shows good agreement with what was seen for the *in-situ* experiments. This shows that the oxidation process being observed in the TEM is similar to the oxidation process that has been well studied in long term autoclave and in-reactor tests by a variety of authors[1,23,26,27,49]. The orientations seen in the *in-situ* sample also mimic the orientations present in the autoclave sample, with some texture present in the tetragonal ZrO₂ (figure 5F), and little to no texture present in the monoclinic ZrO₂ (figure 5E). In figure 5D, the underlying base metal shows only one orientation; this is most likely due to a small scan size.

3.3 Cross-sections of *in-situ* samples

When a cross section of an *in-situ* TEM sample oxidized at 800°C was made, it was seen that the sample had oxidized through the complete sample thickness (figure 6A-E). The phases present in the oxide were found to be a mixture of tetragonal and monoclinic ZrO₂, as seen in figure 6B.

The structure formed during the oxidation appears very similar to the oxide structure seen in the *ex-situ* sample (figure 5). Samples that are oxidized through thickness also show the distinct cracking behavior parallel to what would be the oxide-metal interface expected in this system, and also show the appearance of columnar type grains, as is shown supplemental figures 3 and 4. Using the same technique, a cross section sample was made from the lamella oxidized at 650°C (figure 6F-J) and this sample appears to have been mostly oxidized, but small regions of pure unoxidized HCP zirconium remain within the sample in some regions. It should be noted that when characterized via precession diffraction in plan view (figure 4), this sample shows mostly

oxides as the phases present, due to the stronger diffraction from the oxide as compared to the remaining base metal. In the standard plan view *in-situ* experiment geometry, the TEM beam passes through the sample. In the case of an oxidized sample, this results in diffraction information being collected from three distinct layers in the sample: the top oxide surface, the base metal, and the lower oxide surface. Supplemental 2 shows a schematic of the beam path and resulting diffraction patterns. During precession diffraction analysis, the strongest diffraction pattern is the matched or “chosen” for a given acquisition spot; in a typical oxidized sample, the oxide diffraction patterns are stronger and brighter than that of the base metal diffraction patterns, and thus the diffraction analysis- both phase and orientation- is a reliable method to obtain a qualitative view of total oxide formed on the sample. When cross-sectioned (figure 6 F-J), it is possible to observe the remaining base metal in the sample and the overall distribution of oxide relative to the base metal. Strain relaxation during cross sectioning can occur, and is discussed in detail later in this section.

Figure 6: Cross sections from FIB lift outs oxidized *in-situ* at 800°C (A-E) and 650°C (F-J) and the corresponding phase and orientation maps for the bright field TEM images. (C) and (H) Orientation maps for HCP Zr. (D) and (I) Orientation maps for monoclinic ZrO₂. (E) and (J) Orientation maps for tetragonal ZrO₂.

The vast majority of the oxide consisting of monoclinic ZrO_2 with small localized areas of tetragonal ZrO_2 corresponds well with previous studies done in bulk oxidized sample[24,26,27]. In addition, the phases and orientations that are identified in the cross sectioned sample also correspond well with those found in the autoclave-oxidized samples. Figure 7 shows a phase and orientation maps for an autoclave-oxidized sample in a region far from the metal-oxide interface. When compared to the cross-sectioned *in-situ* sample in figure 6, it is easy to see the presence of similar oxide structure as well as orientations. In the case of the plan view sample shown in figure 4, it is thought that the higher amount of tetragonal ZrO_2 is the result of this being the initial oxide layer forming, which is expected based on past studies using XPS and synchrotron XRD[24,50]. As seen in figure 5, near the oxide metal interface, there is a higher incidence of tetragonal ZrO_2 as compared to far from the interface as is seen in figure 7. The use of phase mapping via precession electron diffraction to identify tetragonal and monoclinic ZrO_2 was recently shown by Garner et al. to be reliable, and showed minor amounts of tetragonal ZrO_2 within the oxide layer of a autoclave oxidized sample[27]. The presence of a minor amount of tetragonal ZrO_2 may be the result of the thin TEM foil not allowing for sufficient stress to accumulate, in turn stabilizing this phase. Platt et al, have showed this behavior in recent work via finite element modeling that among other factors, relaxation in the oxide promoted the transformation of tetragonal ZrO_2 to monoclinic ZrO_2 [51]. We have seen a similar behavior when the phase maps between the plan view of the *in-situ* sample and the cross section of the *in-situ* sample are compared. The cross section sample is thinned in such a manner that the sample can relax, resulting in a lower fraction of the stress-stabilized tetragonal phase as compared to the plan view of the same sample.

Figure 7: (A) Conventional TEM image of an autoclave oxidized sample far from the oxide metal interface showing the region over which precession diffraction was taken. (B) Phase map showing a majority phase of monoclinic ZrO₂. (C) Orientation map for HCP Zr. (D) Orientation map for monoclinic ZrO₂. (E) Orientation map for tetragonal ZrO₂.

This stress stabilization of the tetragonal phase has also been shown by XRD and synchrotron studies, with the tetragonal phase fraction being reduced when relaxation occurs[52]. Other studies have shown that small amounts of tetragonal ZrO₂ will remain after preparation of a TEM foil[24,27], but it is difficult to determine the amount of stress required to stabilize this phase.

The partial oxidation that occurred in the sample oxidized at 650°C reveals a possible dependence of oxidation on crystallographic orientation, as expected based upon previous work done on bulk alloys and thin film zirconium samples[13,22,35,53], and future work will focus on better elucidating these effects. Ploc, using an agglomeration of data from various authors, showed that when oxide thickness is shown versus Zr orientation certain directions show a preference for thicker oxides, however this work was focused on the epitaxial relationship of the oxide to the base metal[13]. Both Ploc and Glavicic revealed orientation relationships between the oxide and the base metal, and more recently, Garner et al found that oxidation rate may be partially controlled by oxide structure[13,22,27]. Additionally, the crystallographic texture of the initial oxide formed on the surface of the base metal can also be determined using the cross section technique presented above, which may offer insight into whether an oxide is protective or non-protective. At this point there appears to be a texture to oxide, as the orientations seen in figure 6 show, which is expected based on the work of Li et al. Gong et al. and Garner et. al. [27,35,39]. In particular, the monoclinic oxide appears to show a (010) type texture. Further work needs to be done to examine the texture in the oxide grown using the *in-situ* method and its effect on oxide growth. Pole figures resulting from the precession diffraction data for figures 4-6 are available in the supplemental information.

While *in-situ* TEM provides a good method for studying initial oxide formation, there are some limitations to this technique. It is limited to early stage oxidation because of sample size, particularly sample thickness. In addition, when using *in-situ* TEM, the environment that can be used is limited by the TEM holder capabilities, such that pressures of only up to one atmosphere of pressure can be reached, and hot liquid environments are not currently viable, although experiments in high humidity environments are starting. Autoclave oxidized samples are much better for the study of long-term oxidation behavior and of the associated kinetics of oxidation. However, this technique provides a good method for study of the first stages of the oxidation process because of its high spatial and temporal resolution.

4. Conclusions

Through the use of environmental TEM combined with precession diffraction techniques, it was shown that the bulk scale corrosion of Zry-4 in an autoclave can be successfully replicated on the nanoscale inside the TEM. It was seen that Zry-4 forms both monoclinic and tetragonal ZrO₂ structures that appear similar to the structures seen in autoclave samples. This structure compares well with the oxide structure seen in literature, and the initial phase also corresponds to the initial oxide layer seen on autoclave-corroded samples. Thus, *in-situ* TEM can replicate the corrosion behavior of this alloy and elucidate the effects of texture, grain, and grain boundary orientation on the corrosion performance of this alloy. Moreover, the environmental cell design used for this experiment offers great flexibility, and can be used to study a variety of materials

under extreme environments at the TEM scale. This design allows for studies in oxidation of thin films, hydride formation, catalyst studies, and boundary effects on corrosion processes.

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