EVOLUTION OF THE OXIDE MICROSTRUCTURE AND OXIDE GROWTH INDUCED RESIDUAL STRAINS DURING WATERSIDE CORROSION OF ZIRCONIUM ALLOYS

A Thesis in
Nuclear Engineering

by

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ABSTRACT

The oxide layer formed on Zircaloy-4 during high temperature waterside corrosion was characterized in an attempt to understand the mechanisms behind the corrosion process and the oxide transition. The samples examined were Zircaloy-4 and zirconium corroded with pure water at temperatures between 270 °C (520 °F) and 360 °C (680 °F) in an autoclave environment. The oxides were characterized using microbeam synchrotron x-ray diffraction and fluorescence, 3-D Laue x-ray microscopy, and scanning electron microscopy.

The crystal structure and chemical composition of the oxide as a function of position within the oxide layer were determined at the sub-micron scale using the x-ray microbeam at the 2-ID-D beamline at the Advanced Photon Source (APS) at Argonne National Laboratory (ANL). This facility is unique in that it combines high spatial resolution with high flux and allowed us to examine the oxide in an extremely detailed manner to produce new information on the oxide structure.

The oxide was found to be comprised primarily of monoclinic ZrO$_2$ with a small amount of tetragonal ZrO$_2$ as well. Well-defined periodic variations in the diffracted intensity from both phases as a function of distance from the oxide-metal interface were observed, with an average period of 1.9 µm corresponding to the oxide transition thickness. Strong in-phase relationships were observed between several of the main monoclinic and tetragonal diffraction peaks, and an out of phase relationship was seen in one monoclinic peak. The oxide grains were shown to grow with their monoclinic (200) planes parallel to the oxide-metal interface. A Zr$_3$O “suboxide” phase was observed in a small (1-2 µm) region of metal immediately adjacent to the oxide-
metal interface. This observation corresponds well to previous transmission electron microscopy studies which found a region of high oxygen content at this location. The measured tetragonal phase fraction was found to be highest at the oxide-metal interface, reducing over a range of approximately the oxide transition thickness to a constant bulk oxide value. Both the monoclinic and tetragonal grain sizes were observed to be smallest at the oxide-metal interface and grow in size to a maximum value with residence time in the oxide. The maximum tetragonal grain size was seen to be smaller than the monoclinic grain size. These studies helped us investigate the basic corrosion mechanisms through observation of the oxide structure which helped us answer questions on the role of each oxide phase during the corrosion process.

Strains in the metal substrate induced by volume expansion during oxide formation were investigated using the 3-D x-ray microscope at beamline 34-ID-E at the APS at ANL. This beamline has the capability to measure very small changes in d-spacing as a function of depth into a material, allowing us to measure changes in d-spacing (and thus calculate strain and stress) in metal grains immediately beneath the oxide layer. Since stresses in the oxide correspond to those in the metal, we were able to indirectly examine the oxide stress state and level as well as investigate the effect of oxide thickness and the oxide transition on accumulated stresses. Experiments were performed at room temperature and with the samples at the corrosion temperature to mitigate the effects of differential cooling between the metal and oxide.

The oxide grown on Zircaloy-4 was shown to induce some level of both plastic and elastic deformation in the underlying metal. Plastic deformation was visible in the streaking of the Laue x-ray spots. The degree and mode of plastic deformation were not calculated but were
qualitatively observed to vary with position between metal grains or even within different locations in a single metal grain. Bare metal Zircaloy-4 and crystal bar zirconium did not show evidence of plastic deformation in the metal. The level of stress in the oxide may be a result of the oxide thickness and oxide transition. Oxides just before transition were found to have a higher level of stress compared to oxides just after transition, and high stresses were again observed in oxides nearing their second transition thickness. The stress state in the metal was found to vary with position, as both tensile and compressive stresses were measured in different samples and grains in the same sample despite our expectations of an overall tensile stress in the metal. Temperature was shown to play a significant role in the measured strains in the metal. Stresses calculated from high temperature strains were lower than room temperature stresses, indicating that the stresses present during corrosion are lower than those measured at room temperature.
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Chapter 1: INTRODUCTION

1.1 Zirconium Alloys in the Nuclear Industry

Light water reactors comprise the entirety of the operating commercial nuclear power plants in the United States today. In this type of reactor pressurized water acting as both a coolant and a moderator is pumped through the reactor core where it can boil to create steam in the case of a boiling water reactor (BWR), or pick up heat that is transferred and used to create steam in a secondary water loop through a steam generator in the case of a pressurized water reactor (PWR). PWRs operate at a higher primary loop pressure (15 MPa) than BWRs (7 MPa) to ensure that bulk boiling does not occur. Typical coolant operating temperature for both designs ranges between 280 °C and 350 °C [1]. The reactor core consists of a lattice of fuel rods held in place by a framework of guide tubes and spacer grids as shown in Figure 1.1, with a slight variation in design depending on the reactor type. The individual nuclear fuel rods are made of a zirconium alloy tube called the fuel cladding that encapsulates cylindrical uranium dioxide fuel pellets stacked on top of one another. The fuel rods in a PWR are approximately 1 cm in diameter with a cladding wall thickness of 600-700 µm and a heated length of 3-4 meters. Reactor criticality is controlled during operation by control rods made of a strong neutron-absorbing material such as boron or cadmium, or by the addition of dissolved boric acid to the coolant (for a PWR only).
Zirconium alloys make excellent candidates for reactor core materials because of a combination of their low neutron absorption cross-section, good mechanical properties, and resistance to waterside corrosion. In a pressurized water reactor the primary components made of zirconium alloys are the cladding tubes, spacer grids, and guide tubes. The neutron transparency of core material is of critical importance to the operation of light water reactors. Current LWR designs utilize thermal neutrons to sustain the fission chain reaction. However thermal neutrons, which are simply neutrons that have been slowed down through interaction with the moderator to energies comparable with the reactor temperature, are significantly more likely to be absorbed by non-fuel core components than the fast neutrons created by fission. Since any unwanted neutron absorption negatively affects the neutron economy in the core, it is especially important that all core components be as neutron transparent as possible. This has led to the choice of zirconium alloys over stainless steel as the fuel cladding material.
Waterside corrosion is another significant challenge posed to any material used in the reactor core. The reactor coolant water is a thermally and chemically hostile place, with operating temperatures regularly above 300 °C and a chemical environment that can contain boric acid and lithium. Corrosion is one of the major factors that can limit the in-core lifetime of the fuel, especially when operated to high burnup. The current trend in the nuclear industry is to subject fuel to increasingly higher burnup in an effort to increase cycle length and capacity factor. In order to predict longer term behavior, it is important that we fully understand the mechanism for the degradation of the fuel cladding as the materials are pushed to progressively more severe duty conditions.
1.2 Alloy Microstructure and Corrosion Behavior

The standard cladding alloys that have been used for many years in light water reactors are Zircaloy-2 and Zircaloy-4. Boiling water reactors use Zircaloy-2, while pressurized water reactors favor Zircaloy-4. The separation comes primarily from the corrosion behavior of each alloy; with Zircaloy-2 better able to resist the nodular corrosion seen in BWRs and Zircaloy-4 giving better uniform corrosion resistance in PWRs [1]. A list of alloying element amounts for Zircaloy-2 and Zircaloy-4 can be found in Table 1.1, and a similar table showing the maximum impurity concentrations for each alloy can be found in Appendix A.

Table 1.1 – ASTM specifications for Zircaloy-2 and Zircaloy-4 [1].

<table>
<thead>
<tr>
<th>ASTM Ref.</th>
<th>R 60802</th>
<th>R 60804</th>
</tr>
</thead>
<tbody>
<tr>
<td>Common Name</td>
<td>Zircaloy-2</td>
<td>Zircaloy-4</td>
</tr>
<tr>
<td>Alloys (mass %)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sn</td>
<td>1.2 - 1.7</td>
<td>1.2 - 1.7</td>
</tr>
<tr>
<td>Fe</td>
<td>0.07 - 0.2</td>
<td>0.18 - 0.24</td>
</tr>
<tr>
<td>Cr</td>
<td>0.05 - 0.15</td>
<td>0.07 - 0.13</td>
</tr>
<tr>
<td>Ni</td>
<td>0.03 - 0.08</td>
<td>-</td>
</tr>
<tr>
<td>Nb</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>O</td>
<td>1000 - 1400 ppm</td>
<td></td>
</tr>
</tbody>
</table>

The microstructure of the Zircaloy alloys consists of a matrix of hexagonal close-packed $\alpha$-Zr and alloying elements in solid solution or in precipitates at all temperatures between ambient and normal reactor operation temperatures. A schematic of the hexagonal unit cell can be seen in Figure 1.2. While the microstructure is largely dependent on the heat treatment and chemistry of the alloy during fabrication, in general it consists of $\alpha$-phase grains with precipitated second phase particles. In pure Zr the $\alpha$-phase is the
equilibrium phase below 865 °C, where an allotropic transformation to a body centered cubic 
\( \beta \)-phase occurs [1]. Some physical properties of zirconium and Zircaloy-4 can be seen in

Table 1.2a and Table 1.2b. The primary alloying elements in Zircaloys are tin, iron, chromium, and oxygen. Tin and oxygen remain in solid solution and act to increase the corrosion resistance and yield strength respectively [1]. In Zircaloy-4 the iron and chromium are found in Zr-Cr-Fe second phase precipitates [2].

![Figure 1.2 – Hexagonal unit cell as found in \( \alpha \)-Zr and \( \alpha \)-Zry [2].](image)

<table>
<thead>
<tr>
<th>Table 1.2a – Major physical properties of zirconium at room temperature [1]</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Unit</strong></td>
</tr>
<tr>
<td>Density</td>
</tr>
<tr>
<td>Thermal Expansion</td>
</tr>
<tr>
<td>Young's Modulus</td>
</tr>
<tr>
<td>Lattice Parameter</td>
</tr>
<tr>
<td>Thermal Conductivity</td>
</tr>
</tbody>
</table>
Table 1.2b – Major physical properties of Zircaloy-4 at room temperature

<table>
<thead>
<tr>
<th>Property</th>
<th>Unit</th>
<th>Average</th>
<th>[1120] dir.</th>
<th>[0001] dir.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>g - cm(^{-3})</td>
<td>6.56</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Thermal Expansion</td>
<td>m/m - K(^{-1})</td>
<td>6.00 \times 10(^{-6})</td>
<td>4.95 \times 10(^{-6})</td>
<td>1.26 \times 10(^{-5})</td>
</tr>
<tr>
<td>Young's Modulus</td>
<td>GPa</td>
<td>92</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Lattice Parameter</td>
<td>nm</td>
<td>-</td>
<td>a(_0) = 0.3228</td>
<td>c(_0) = 0.5151</td>
</tr>
<tr>
<td>Thermal Conductivity</td>
<td>W - m(^{-1}) - K(^{-1})</td>
<td>21.5</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

1 Values given for the [1120] and [0001] directions were found in MATPRO Vol. 4 Rev. 2 in single-crystal correlations (4-27) and (4-28) [3]. The average CTE was provided by ATI Wah Chang.

2 Calculated using MATPRO Vol. 4 Rev. 2 equation (4-101) at 300 K [3].

3 These properties were derived from measurements by researchers at Bettis and Penn State, and will be valid only for the sample set described by this study.

Over the operational lifetime of an assembly in a nuclear reactor, the fuel cladding is exposed to a high temperature water environment for a period between three and five years. During this time a uniform oxide forms on the cladding that grows in thickness over time. The oxide can be characterized as a thin, protective layer that strongly adheres to the metal substrate and impedes further corrosion.

In all zirconium and zirconium-based alloys, the oxide phase formed is ZrO\(_2\) (zirconia). Zirconia has three natural allotropes that occur at different temperature ranges. A schematic of the unit cell for each phase can be seen in Figure 1.3. The high temperature (above 2100 °C) phase crystallizes in the cubic structure, with the zirconium atoms at the face centered cubic (FCC) lattice positions and the oxygen at the tetrahedral sites. The lattice parameter is 5.07 Å. Below 2100 °C cubic zirconia transforms into the tetragonal form by a displacive transformation, with the oxygen atoms moving upward or downward. The lattice parameters for the tetragonal phase are a=3.64 Å and c=5.27 Å. The monoclinic phase is stable below 1100 °C, and is a further distortion of the original cubic structure. The lattice parameters for the monoclinic phase are a=5.341 Å, b=5.232 Å, c=5.169 Å, \(\beta=99.218^\circ\),
α=γ=90°. The transformation from tetragonal to monoclinic is martensitic and thus diffusionless. Due to the speed of the reaction the tetragonal phase cannot be quenched, and is not stable at lower temperatures unless stabilized by other factors.

![Schematic drawings of cubic, tetragonal, and monoclinic ZrO₂](image)

Figure 1.3 – Schematic drawings of cubic, tetragonal, and monoclinic ZrO₂. In row (A) the Zr atom positions are located inside the red polyhedron and are not shown, while the O atoms are depicted as blue spheres on the corners. As an alternate representation Zr is shown as white dots and O as black dots in row (B) [4].

The oxide formed on Zr alloys at PWR operating temperatures exhibits a primarily monoclinic ZrO₂ crystal structure, with a small amount of tetragonal ZrO₂ [5-9]. Although the tetragonal phase is unstable at the oxide formation temperatures, it can be stabilized by several factors, such as high compressive stress [10], small grain size [5, 6], sub-stoichiometry [11], and alloying elements dissolved in the oxide [12]. Each of these conditions can be
found in Zircaloy oxides, especially near the oxide-metal interface. The amount of tetragonal phase found in the oxide is greatly dependent on the alloy. However, the tetragonal phase fraction has been consistently measured to be higher near the oxide-metal interface in keeping with the previously stated reasons [13].

The oxidation process occurs at the oxide-metal interface, with the reacting species diffusing through the oxide layer by various mechanisms [14]. A schematic showing the chemical reactions occurring during oxide formation is shown in Figure 1.4. While the oxide growth may be uniform in general, it is far from constant along the length of the cladding tubes. Because the coolant temperature is higher for increasing axial elevation, the oxide is generally thicker towards the top of the core. Additionally, the oxide thickness can be influenced by the presence of spacer grids and mixing vanes. These structures can cause a local decrease in the coolant temperature, resulting in a thinner oxide layer at spacer grid locations.
Figure 1.4 – Schematic of the oxidation process in zirconium alloys in the reactor core. Note that in an autoclave environment radiolysis would not occur.

The waterside corrosion kinetics of zirconium alloys can be described by two different regimes characterized by the oxidation rate [1, 15, 16]. The initial corrosion is called the pre-transition regime and shows an oxidation rate that is approximately described by \( \delta = K t^n \), with \( n \) between 0.2-0.5 [1, 14, 15, 17]. This regime is followed by the post-transition regime that can be identified by an increase in corrosion rate that shows approximately linear behavior with time. The departure from the pre-transition kinetics is called the oxide transition and entails an increase in corrosion rate related to a loss of oxide protectiveness. Following transition the pre-transition kinetics are reestablished and the process repeats. A general schematic of the pre-transition/post-transition oxidation behavior is shown in Figure 1.5. The oxide thickness at transition varies between alloys. The transition thickness is usually between 2 and 3 µm, with values closer to 2 µm reported for Zircaloy-4 [16, 18]. The oxide transition is observed in nearly all instances to be cyclic, with the initial pre- and post-transition regimes approximately repeated for a number of cycles beyond the initial
transition. An element of corrosion that is not common in Zircalloys but is often seen in pure zirconium is called breakaway corrosion, which is characterized by a complete loss of oxide protectiveness and a vastly increased corrosion rate. In the breakaway regime the oxide changes from a black, adherent film to a white, flaky one that easily spalls off the base metal, constantly exposing the substrate.

Figure 1.5 – Schematic of the Zircaloy corrosion regimes, showing the pre-transition, cyclic, and post-transition behavior. The dotted line indicates early models that did not recognize the cyclic pre-transition [19].

The change in the oxidation kinetics at transition can be explained by a brief loss of oxide protectiveness. It is believed that when stresses within the oxide reach a critical level, the oxide mechanically fails and loses its protective qualities. The amount of stress generated in the oxide and the critical stress are different for each alloy. The critical stress is controlled by the oxide microstructure and potentially by alloying elements that have become incorporated into the oxide.
There are three main sources of stress in the oxide layer. The first is related to the Pilling-Bedworth ratio, which is the ratio of the volume of ZrO$_2$ formed to the volume of the Zr metal consumed, and which has a value of approximately 1.56 for zirconia. A large fraction of the volume increase is accommodated perpendicular to the oxide-metal interface, which is a stress-free direction. However, some oxide growth occurs parallel to the oxide-metal interface. Growth in this direction is restricted by the metal substrate, which causes a compressive stress to be generated in the oxide and a corresponding tensile stress in the metal. The other two sources of stress are the oxidation of second phase particles, and the tetragonal to monoclinic transformation.

How the oxide loses protectiveness and why transition occurs is still not fully understood, and many studies have been undertaken in an attempt to explain the transition mechanism. In general there are two groups with an explanation for the transition mechanism.

The first group explains the transition as a result of lateral cracking at the oxide-metal interface originating from the stresses generated during oxide growth, called the “mechanical failure” hypothesis [7, 9, 20-22]. While lateral cracking in the oxide is frequently observed in scanning and transmission electron microscopy, it is unknown whether these cracks are created during oxidation or sample preparation. Bryner[16] showed that after careful sample preparation previously observed lateral cracking was no longer visible, indicating that the cracks were a result of insufficient support of the film during preparation. Additionally, it is not clear how lateral cracks can accelerate the oxidation without paths from the environment to the cracks.
The second group claims that the buildup of stresses leads to the formation of micro cracks and micro pores in the oxide, with the stresses being relaxed in the process. The theory is that when these small pores and cracks connect, they provide a pathway for the oxygen ions and water to migrate through the oxide to the oxide-metal interface. This is called the “formation of interconnected porosity” hypothesis [23-28]. While this hypothesis explains how connected pores and cracks could accelerate the corrosion rate, it is still unknown how the micro pores and micro cracks are generated and how they connect in a concerted manner in the first place.

While the mechanism of oxide growth is still not fully understood, some possibilities have been proposed based on experimental observation and are pending further testing. Several studies performed by Motta and Yilmazbayhan et al. [2, 13, 17, 18] have provided an experimental basis for one proposed mechanism that attempts to bridge the gap between the mechanical failures and interconnected porosity mechanisms, which is outlined in the following paragraph.

At the start of oxidation, small oxide grains begin to nucleate at the metal surface. This initial layer is comprised of both monoclinic and tetragonal phases, with a relatively large proportion of tetragonal grains that have been stabilized by high stress or oxide substoichiometry. A portion of the newly formed tetragonal grains will be properly oriented for growth (with their (110)$_T$ or (110)$_T$ planes parallel to the oxide-metal interface), and as such will self-select to grow. As the oxide grains grow they become columnar. At a critical column length the tetragonal grains will transform into the monoclinic phase while maintaining the same orientation. Improperly oriented tetragonal or monoclinic grains will remain as small
grains embedded in the oxide. The columnar monoclinic grains oriented with their $(200)_M$ plane parallel to the oxide-metal interface will proceed to grow into the metal. During the growth process, small mismatches in the orientation of the column with the preferred orientation and surrounding grains causes stress to accumulate. When the columnar grains reach an aspect ratio of roughly 4-5 the stress has built up to a level that causes the grain to stop growing. At this point re-nucleation of a new grain along the leading growth edge is required. When re-nucleation occurs, the newly created grains are small, equiaxed, and have a higher percentage of the tetragonal phase. The re-nucleated grains can then grow and form a new column of monoclinic oxide if properly oriented, or remain embedded in the oxide. On the scale of the entire oxide thickness, a buildup of bulk stresses will eventually cause the oxide to crack and undergo a global transition (at least on a lateral cm scale). This global transition causes a large scale re-nucleation of oxide grains through a similar mechanism as described before over a much wider area. At this point the entire process restarts, and the first step is repeated.

1.3 Goals of this Study

The objective of this thesis research is to further the fundamental understanding of the oxide transition mechanism and its influencing factors using advanced characterization techniques. It is currently not clear why the oxide transition occurs, but it has been hypothesized that stress accumulation as a result of the corrosion process is the cause. As such, a direct measurement of stress in oxide films and an understanding of its relation to
the oxide microstructure will help us understand the causes of oxide transition and loss of protectiveness.

In this study, the oxide microstructure has been characterized and oxide growth-induced stresses have been measured for a range of oxide thicknesses in Zircaloy-4 and pure zirconium. Conventional characterization techniques of optical and scanning electron microscopy have been used to characterize the oxides in cross-section. Advanced techniques have been employed using the Advanced Photon Source at Argonne National Lab to acquire microstructure and stress data. Microbeam x-ray diffraction and fluorescence at beamline 2-ID-D was used to characterize the oxide microstructure and 3-D x-ray structural microscopy was used at beamline 34-ID-E to measure oxide-induced stresses.

A number of specific questions regarding the oxide phases and stresses have been addressed during this work and are shown below.

1. How do oxide phases change with oxide thickness?
2. Is there a stress gradient in the oxide as a function of distance from the oxide-metal interface and does it vary with oxide thickness?
3. How is the stress related to the base metal texture?
4. How do stresses in oxide and the metal vary with oxide thickness?
5. Does this stress change with temperature?
6. How do these quantities change in crystal bar Zr?

Results pertaining to each of these questions will be shown in the following thesis. The alloys examined and characterization techniques will be discussed in greater detail in Chapter 2. Results and discussion of the data analysis are presented in Chapter 3. A summary of the conclusions outlined in Chapter 3 and recommendations for future work will be shown in Chapter 4.
Chapter 2: EXPERIMENTAL METHODS

2.1 Alloys and Samples Examined

The alloys examined during this study comprised both crystal-bar zirconium and Zircaloy-4. A full list of every sample analyzed is shown in Table 2.1. Oxidized samples were corroded between 680 °F (360 °C) and 520 °F (271 °C) in water using autoclaves at Bettis Atomic Power Laboratory. The Zircaloy-4 samples were cut from heats of α-annealed cold-worked and stress relieved material, and had alloying element and impurity compositions meeting ASTM B-350 requirements [16, 19]. Prior to corrosion the specimen dimensions were typically 25 mm x 25 mm x ~1 mm and were pickled using a solution of 39 vol.% HNO₃ plus 3.5 vol.% HF with the remainder water [19].

Two Zircaloy-4 samples designated as L1581 and N2511 will be specifically highlighted in chapter 3 with an extensive characterization of their oxide layer. These samples were corroded at 680 °F (360 °C) and 600 °F (316 °C) respectively. The corrosion kinetics curves for samples L1581 and N2511 are shown in Figure 2.1a and Figure 2.1b respectively. A total of four oxide transitions can be seen for L1581, followed by a final transition to a linear corrosion regime with no more periodic transitions detectable. N2511 shows four clear transitions in its kinetics curve as well.
Table 2.1 – Summary of sample designations, characteristics, and characterization techniques for all samples examined during this study

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Oxide Thickness (µm)</th>
<th>Corrosion Time</th>
<th>Corrosion Temp. (°F)</th>
<th>Material Type</th>
<th>Kearns Factor</th>
<th>Date and Beamline</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-3</td>
<td>0.15</td>
<td>40 min</td>
<td>680</td>
<td>Crystal Bar Zr</td>
<td>-</td>
<td>Dec-2011 34-ID-E</td>
</tr>
<tr>
<td>4-8</td>
<td>6.56</td>
<td>34 hr</td>
<td>680</td>
<td>Crystal Bar Zr</td>
<td>-</td>
<td>Oct-2010 34-ID-E</td>
</tr>
<tr>
<td>H1372J</td>
<td>3.25</td>
<td>140 days</td>
<td>680</td>
<td>Zircaloy-4</td>
<td>0.6</td>
<td></td>
</tr>
<tr>
<td>H1405J</td>
<td>0</td>
<td>-</td>
<td>680</td>
<td>Zircaloy-4</td>
<td>0.6</td>
<td>Aug-2010 2-ID-D</td>
</tr>
<tr>
<td>H1406J</td>
<td>2.09</td>
<td>120 days</td>
<td>680</td>
<td>Zircaloy-4</td>
<td>0.6</td>
<td></td>
</tr>
<tr>
<td>H1413J</td>
<td>2.63</td>
<td>140 days</td>
<td>680</td>
<td>Zircaloy-4</td>
<td>0.6</td>
<td></td>
</tr>
<tr>
<td>H1403J</td>
<td>0.29</td>
<td>40 min</td>
<td>680</td>
<td>Zircaloy-4</td>
<td>0.6</td>
<td></td>
</tr>
<tr>
<td>H1114R</td>
<td>0.99</td>
<td>34 hr</td>
<td>680</td>
<td>Zircaloy-4</td>
<td>0.33</td>
<td></td>
</tr>
<tr>
<td>H2287J</td>
<td>2.05</td>
<td>3003 days</td>
<td>520</td>
<td>Zircaloy-4</td>
<td>0.6</td>
<td></td>
</tr>
<tr>
<td>H1187R</td>
<td>2.51</td>
<td>120 days</td>
<td>680</td>
<td>Zircaloy-4</td>
<td>0.33</td>
<td></td>
</tr>
<tr>
<td>H1033J</td>
<td>101.4</td>
<td>2800 days</td>
<td>680</td>
<td>Zircaloy-4</td>
<td>0.6</td>
<td></td>
</tr>
<tr>
<td>H1190R</td>
<td>2.35</td>
<td>3003 days</td>
<td>520</td>
<td>Zircaloy-4</td>
<td>0.33</td>
<td></td>
</tr>
<tr>
<td>4-5B</td>
<td>9.28</td>
<td>20 days</td>
<td>680</td>
<td>Crystal Bar Zr</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>H1404J</td>
<td>0.65</td>
<td>34 hr</td>
<td>680</td>
<td>Zircaloy-4</td>
<td>0.6</td>
<td>Jul-2010 2-ID-D</td>
</tr>
<tr>
<td>H1405J</td>
<td>1.14</td>
<td>20 days</td>
<td>680</td>
<td>Zircaloy-4</td>
<td>0.6</td>
<td></td>
</tr>
<tr>
<td>H1406J</td>
<td>2.09</td>
<td>120 days</td>
<td>680</td>
<td>Zircaloy-4</td>
<td>0.6</td>
<td></td>
</tr>
<tr>
<td>H1405J</td>
<td>1.14</td>
<td>20 days</td>
<td>680</td>
<td>Zircaloy-4</td>
<td>0.6</td>
<td>Dec-2009 2-ID-D</td>
</tr>
<tr>
<td>N2511</td>
<td>12.0</td>
<td>3113 days</td>
<td>600</td>
<td>Zircaloy-4</td>
<td>0.6</td>
<td></td>
</tr>
<tr>
<td>L1581</td>
<td>39.5</td>
<td>1260 days</td>
<td>680</td>
<td>Zircaloy-4</td>
<td>0.6</td>
<td></td>
</tr>
<tr>
<td>H1033J</td>
<td>101.4</td>
<td>2800 days</td>
<td>680</td>
<td>Zircaloy-4</td>
<td>0.6</td>
<td></td>
</tr>
</tbody>
</table>

The Kearns factor shown refers to the normal Kearns Factor where \( f_v \) is the resolved fraction of basal poles aligned in the normal direction.

The total time at temperature for L1581 was 108.86 Ms (1260 days) which resulted in a final measured weight gain of 570 mg/dm\(^2\) and a corresponding average oxide thickness of 39.5 µm, following the data presented in [16]. Sample N2511 had a corrosion time of 3113
days at 600 °F (316 °C) leading to a final measured weight gain of 177 mg/dm² and an average oxide thickness of 12.0 µm.

Figure 2.1a – Weight gain for Zircaloy-4 sample L1581 corroded in 360 °C water after [16]. The sample shown in the second kinetics curve (L1607) has not been analyzed during this study and can be ignored.
2.2 Sample Preparation

Cross sectional oxide samples were prepared in order to study the oxide structure and phase distribution as a function of distance from the oxide-metal and oxide-water interfaces using microbeam synchrotron radiation at beamline 2-ID-D. Three different types of samples were used corresponding to the three different times in which the experiments took place. The samples used in the December 2009 experiment were prepared by researchers at Penn State while the samples used in July and August 2010 were prepared by the researchers at the Bettis Laboratory.
2.2.1 Cross Section Sample Type I Preparation

The process of obtaining the characterization-ready cross sectional samples from the provided corroded Zircaloy-4 coupons as prepared by the researchers at Penn State is described schematically in Figure 2.2. The coupons are cut using a diamond saw to obtain small rectangular strips of about 2 mm in width. This strip contains two oxide surfaces but one of the two was sacrificed as the strip is mechanically thinned in order to obtain a thickness of about 0.3 mm. The mechanical thinning is achieved by using crystal bond to protect the oxide layer studied, while the other side is mechanically polished using 400 grit silicon carbide paper. Once the strip is thin enough, it is placed inside the slot of the molybdenum rod, which is itself placed in a 3 mm diameter brass tube. Everything is then secured together using Epo-Tek® 353ND epoxy.
Figure 2.2 – Schematic of the process of mounting cross-sectional samples and a schematic of a cross sectional sample [29].

The molybdenum rod maintains mechanical stability of the sample and decreases the volume fraction of epoxy used. The molybdenum rod has a diameter of 2.26 mm and a length of about 40 mm. The slit in the rod is about 0.4-0.5 mm wide. The brass tubes have an external diameter of 3 mm and an internal diameter of 2.3 mm and about the same length as the molybdenum rods. The Epo-Tek® 353ND epoxy was cured on a hot plate at 60-80 °C for 10-15 minutes. Once the sample has been mounted in such a way, the rods are cut into small discs that are about 3 mm thick using a diamond saw.

The small cross sectional discs are then polished to a mirror finish. 180, 400, and 600 grit silicon carbide paper was used first on both sides in order to obtain two parallel surfaces. Then one side was polished further using Allied 8” 1200 grit silicon carbide adhesive discs
followed by 1 µm diamond paste and 0.05 µm colloidal silica solution. It was found that this technique did not result in good edge retention when applied to thin oxide samples, and will require some improvement for oxides thinner than 2-3 µm. The final form of the small cross sectional disk as prepared by Penn State is shown in Figure 2.3. The sample mounting directions as labeled (rolling direction parallel to the cross section surface normal direction) were verified for samples L1581 and N2511, and are correct for most samples examined using microbeam diffraction. The sample orientation can be verified by examining the relative intensities of the three α-Zr peaks visible in diffraction patterns taken from the metal. Samples mounted as noted in Figure 2.3 should have a low integrated intensity of the (002)$_{\text{HCP}}$ relative to the integrated intensity of the (100)$_{\text{HCP}}$ and (101)$_{\text{HCP}}$ peaks. A few samples were mounted with their rolling and transverse directions reversed relative to those shown in Figure 2.3, and will show a high integrated intensity for the (002)$_{\text{HCP}}$ peak.
2.2.2 Cross Section Sample Type II Preparation

The samples used in the July and August 2010 experiments were prepared by researchers at the Bettis Laboratory. The final cross sectional form is shown schematically in Figure 2.3. The 40-mil thick corrosion coupons are initially cut into a 1/8 inch by 1/4 inch rectangle with the oxide on both sides preserved. The cut coupon is then wrapped in thin foil (aluminum or copper), which is used to provide mechanical support for thin oxides during polishing. The copper foil was 1/4 inch wide copper tape used for scanning electron microscope applications with the sticky tape removed. A 40-mil notch 1/8 inch deep is then
cut into the end of a 1/4 inch long piece of stainless steel tubing with a 1/4 inch outer-
diameter. The wrapped specimen is then placed in the notch, and both are placed into a 
ferrule (9 mm diameter) from a stainless steel Swagelok fitting. The edge of the specimen to 
be examined should be at the wide end of the ferrule. The entire assembly is then hot-
mounted in Bakelite.

The samples were metallographically prepared using the following grinding schedule.

   I. 2 minutes on Struers MD (Magnetic Disc) ALLEGRO – 15 micron
   II. 2 minutes on Struers MD PLAN – 15 micron
   III. 5 minutes on Struers MD PAN – 6 micron
   IV. 5 minutes on Struers MD DAC – 3 micron
   V. 3 minutes on Struers OP Chem with OPS
       • Add drops of acid chem-polish during OPS polishing
       • Acid chem-polish composition:
          o 435 ml Water
          o 5 ml HF
          o 10 ml Nitric Acid
          o 50g Oxalic Acid

After polishing, the surface is covered with a piece of electrical tape for protection while 
breaking the sample from the mount. Next, the Bakelite mount is sliced to the desired 
thickness of the final specimen, or about 1/8 of an inch thick, using a high speed diamond 
cutoff wheel. Finally, the specimen can be broken out of the mount and the tape removed.

A final surface cleaning with methanol finishes the sample preparation.
2.2.3 Complications with Type II Cross Sectional Samples

There were several small issues with the Bettis-prepared cross sectional samples that became apparent during the experiments at the APS. The first issue was one of sample size. The samples are too large in diameter to allow the beam position to be properly calibrated, meaning that we could not fully determine where the microbeam was striking the sample. This was not a problem in samples with a continuous and uniform oxide layer, but there were complications with the small number of samples without uniform oxides. The foil wrap used to keep the oxide layer intact during polishing also caused a few issues. Although

Figure 2.4 - Schematic of the cross sectional disk sample as prepared by Bettis Atomic Power Laboratory for microbeam diffraction characterization at beamline 2-ID-D.
successful in improving oxide edge retention, the type of metal in the foil caused artifacts in the x-ray fluorescence spectra. The aluminum foil wrap caused a false nickel reading in the fluorescence data (we believe due to peak overlap with the Ni L-1 peak). The false nickel signature was actually somewhat useful for determining the sample surface location, and did not cause any problems with readings from other elements. The copper foil wrap introduced two problems. First, it prohibited the use of a large fluorescence detector aperture. The large aperture is capable of obtaining more counts from some of the lower fluorescing elements like tin or zirconium. However, the strong copper signal saturated the detector with the large aperture present, so it was necessary to use a smaller aperture and settle for less well defined zirconium and tin fluorescence data. Second, the copper generated a high x-ray background as well as a diffraction ring artifact in all of the diffraction patterns taken in August 2010. Figure 2.5 illustrates the location and appearance of the extra ring at various cross sectional locations in an oxidized Zircaloy-4 sample. The location of the ring in question is marked with a black arrow.
Figure 2.5 – Diffraction patterns taken at the outer oxide edge, inside the oxide, and inside the metal in sample H2287J illustrating the extra diffraction ring (marked with an arrow).

It is possible that polishing caused some smearing of the copper, causing the ring to be seen well into the oxide and metal as indicated in Figure 2.5. A simple Bragg’s Law calculation confirmed that the ring was a product of the (111) plane of FCC copper. While the copper diffraction ring is outside of the two-theta range containing the primary zirconia and zirconium reflections of interest, the extremely high background overwhelmed the intensity of the oxide reflections, complicating the data analysis of the copper wrapped samples.

### 2.2.4 Characteristics of Zircaloy-4 and Zirconium Coupon Samples

The samples examined using the 3-D x-ray microscope at beamline 34-ID-E were a combination of Zircaloy-4 and crystal bar zirconium as outlined in Table 2.1. No special sample preparation was performed before or during the experiment, since any change to the samples after corrosion could cause a change in the stress state of the oxide/metal system.
Optical micrographs of two crystal bar zirconium samples and a typical oxidized Zircaloy-4 sample are shown in Figure 2.6. In the crystal bar samples the grains are very large, with a grain size of 100-400 µm that are easily visible to the naked eye. Sample 4-3 has a very thin oxide layer (0.15 µm), and the visible colors are a result of optical interference contrast. Sample 4-8 has an average oxide thickness of 6.56 µm, however, the oxide thickness was variable on a grain-by-grain basis. While it is difficult to tell in the image, the sample has a “speckled” appearance, with some grains showing a white or spalled oxide and other grains maintaining a black or grey protective oxide. The Zircaloy-4 sample H1372J shows a typical black protective oxide with the base metal grains somewhat visible showing a grain size of 10-20 µm. The white line visible on the images of 4-8 and H1372J shows the position of the x-ray beam as it fluoresced with the sample surface. The fluorescence had not been previously observed and its origin was not determined.
Figure 2.6 – Optical micrographs of the top surface of the oxide for crystal bar zirconium samples (A) 4-3, (B) 4-8, and Zircaloy-4 sample (C) H1372J taken using the telescope at beamline 34-ID-E.
2.3 Advanced Photon Source X-Ray Diffraction Techniques

2.3.1 Characterization Technique I: Microbeam X-Ray Diffraction and Fluorescence at APS Beamline 2-ID-D

The 2-ID-D beamline is devoted to sub-micron high resolution X-ray studies. The X-rays are produced by the deceleration of the electrons present in the synchrotron as they pass through the insertion device of the beamline. This deceleration is accompanied by the emission of X-rays but since the deceleration occurs on the tangential coordinate of the acceleration vector of the electron, the X-rays are emitted in a straight line along a tangent to the storage ring. For the 2-ID-D beamline, the insertion device that is used to produce the X-rays is an undulator. Once the X-rays are emitted from the undulator, they go through a silicon double plate monochromator that allows the X-ray energy or wavelength to be varied in the range of 5 to 32 keV. The resulting monochromatic beam is then focused by using Fresnel zone plates. These zone plates contain concentric rings that are alternatively opaque and transparent. When the beam hits the plates, it diffracts around the opaque rings, and if the rings are properly spaced, the diffracted light will constructively interfere on the sample surface with the desired focus. The zone plate used at the 2-ID-D beamline has a diameter of 145 μm with an outermost zone width of 0.9 μm, a thickness of 900 nm and a focal length of 10 cm at 8 keV.

One of the major advantages of this beamline facility is the ability to simultaneously capture chemical and elemental data by X-ray fluorescence, and acquire microstructural and
phase information by X-ray diffraction. The experiment takes place by raster scanning the beam through the oxide layer in sub-micron increments. Through this process we simultaneously obtain both elemental and microstructural information as a function of the position in the oxide layer. A schematic of the experimental setup is shown in Figure 2.7, and a picture of a sample mounted in the beamline can be seen in Figure 2.8. A Newport Kappa diffractometer was used during the experiments and the diffraction data was collected by a CCD detector. The fluorescence data was recorded using a Ge(Li) Canberra solid state detector. In order to collect the fluorescence data, energy regions of interest (ROIs) corresponding to the K or L lines of the elements of interest were specified at the beginning of each experiment. The elements of interest are the elements that are expected to be present in the material. For this study, these elements were: zirconium (Zr), tin (Sn), chromium (Cr), iron (Fe), nickel (Ni), and copper (Cu). Depending on the distance between the CCD detector and the sample, the two-theta range of diffracting angles captured by the CCD varies. The closer the CCD is to the sample, the larger the two-theta range, and the larger the fraction of the diffraction ring captured. However, there is a decrease in the spatial resolution of the diffraction rings when placing the detector near the sample.
After having properly calibrated and aligned the sample and detectors, the beam was scanned through the oxide layer. The step size used in most cases was 0.2 μm, with larger step sizes employed occasionally. The focused size of the x-ray beam is 0.2 μm x 0.2 μm, but the incident angle to the sample caused the footprint of the beam to be about 0.2 μm x 1 μm (with the elongation parallel to the oxide-metal interface). The acquisition time for each step was usually 40 seconds with an x-ray fluorescence acquisition time of 10s. Longer or shorter diffraction and fluorescence acquisition times were used as need arose. The energy of the X-ray beam used was 17.79 keV (Dec. 2009) or 10.1 keV (Jul./Aug. 2010) which correspond to wavelengths of 0.696931 Å and 1.2277 Å respectively. The 2-D diffraction data is captured as a TIFF image and then has to be integrated in order to be analyzed.
2.3.2 Characterization Technique II: Residual Stress Determination using 3-D Laue X-Ray Diffraction at APS Beamline 34-ID-E

Beamline 34-ID-E at the Advanced Photon Source has been developed to perform spatially resolved studies of materials using a polychromatic x-ray beam. The beamline has a unique capability for three-dimensional spatially resolved measurements of phase, texture, strain, and deformation distributions in single and polycrystalline materials. Figure 2.9 shows the beamline setup and capabilities schematically. The advantage of using polychromatic radiation is that every grain illuminated by the x-rays generates a complete Laue pattern without sample rotation, in contrast to a monochromatic source that would require rotation to generate multiple reflections.

Figure 2.8 – Picture of a Bettis-prepared sample mounted in the hutch at beamline 2-ID-D. The CCD detector is located approximately below the camera position.
34-ID-E has the capability to depth-resolve the source of the detected Laue reflections. It does this using a differential scanning aperture which consists of a wire scanned 200 µm above the sample surface, which intercepts particular diffraction beams as it moves. Specialized data collection and analysis software allows the Laue patterns to be fit and indexed, with extraction of the crystal orientation and full strain tensors to $\sim 1 \times 10^{-4}$. Thus using a combination of polychromatic radiation, a differential scanning aperture, and specialized software it is possible to reconstruct the origin of the diffraction signal and obtain depth-resolved strain information rather than average values. Obtaining depth-resolved strain measurements was the function of this beamline for this study.
While the hardware and software used to obtain depth-resolved strain information is quite complex, the theory behind the measurements is reasonably simple. A strain-depth measurement (also referred to as an energy-wire scan) such as the ones obtained in this study is really a mating of two separate effects, x-ray diffraction based on the beam energy and depth resolution based on the differential scanning aperture.

Strain information is determined by the energy of the incident beam. Each reflection visible in a Laue pattern generated using a polychromatic beam is a product of a very small portion of the overall beam energy range that satisfies the Bragg diffraction condition for that plane. A change in the beam energy away from the ideal energy of the diffracted spot causes the diffracted intensity to decrease. A change in beam energy could however satisfy the diffraction condition for planes of a different d-spacing, such as those that might be displaced due to lattice strain. When performing an energy-wire scan, the beam is set as monochromatic, and scanned in small energy steps across a range of energies for a specific individual reflection. The beam is scanned in energy in steps as small as 1 eV, and the changes in d-spacing measured are extremely small, on the order of $10^{-4}$ Å. Scanning in energy allows for diffraction information on all strained and unstrained planes contributing to a single reflection to be acquired. Strain information can then be combined with depth information from the differential scanning aperture to create a strain-depth curve.

The differential scanning aperture consists of a very thin wire that is moved parallel to the sample surface in order to selectively block diffracted x-rays. This technique is how depth resolution is acquired, and remains the same whether the beam is monochromatic or
polychromatic. A schematic diagram of differential aperture depth resolution is shown in Figure 2.10, which will be used in the following explanation of the technique.

![Schematic diagram of differential aperture depth resolution](image)

**Figure 2.10 – Schematic of the differential aperture scanning technique used to acquire depth information from diffracted beams using monochromatic or polychromatic x-rays.**

At fixed beam energy and with the wire at position A, a diffraction signal can be recorded at the noted pixel location on the detector. The diffraction angle is thus known since the pixel angular position on the detector is known. With the energy remaining fixed, the wire is moved to position B. The diffraction image recorded with the wire at point B is then subtracted from the image acquired when the wire was at point A to determine the intensity change on a per-pixel basis. When an intensity change in the pixel is noted, and since the pixel angle, incident beam position, and sample surface position are known, a ray
can be traced from the pixel back to the intersection point with the incident beam, giving the depth of origin inside the sample. The depth resolution is determined by the size of the wire step movement, which can be as small as 1 µm with the equipment currently available at the beamline. All diffraction information blocked within one wire step is considered as a single unit, and comparing the micron-level resolution of the wire with the sub-angstrom resolution of the beam energy it is clear that the wire step is the limiting resolution for the energy-wire scan technique.

2.3.3 Description of the Heating Stage Setup at Beamline 34-ID-E

A heating stage setup was used during the December 2011 experiment at 34-ID-E. The setup was used to heat corrosion coupon samples back to the corrosion temperature (360 °C/680 °F) in-situ such that strain-depth measurements could be taken while the sample was at temperature. Since the oxide layer was formed at high temperature, differential cooling between the oxide and the metal could introduce additional strains beyond those caused only by oxide growth. Thus if the sample is returned to the corrosion temperature these cooling strains will be removed and the only strain remaining should be a result of oxide growth. Several pictures of the heating setup in the beamline can be seen in Figure 2.11. The heating stage was made of machined aluminum with tolerances of $\pm \frac{1}{64}$”, and a detailed mechanical drawing with full dimensions can be found in Appendix B. Two Omega® CSS series $\frac{1}{8}$” diameter 15 watt cartridge heaters provided power to heat and hold the setup at temperature. An Omega® OS37-10-K model infrared thermocouple (IRTC) was used to
monitor and control the temperature of the sample. This particular model of IRTC was capable of being calibrated for varying sample emissivity and for accuracy over a variety of temperature ranges. Utilizing infrared temperature measurement and control proved advantageous since it allowed for direct sample average temperature measurement (via sample IR emission) at a standoff distance from the sample while not interfering with the x-ray equipment (beam/detector). The non-contact nature of the IRTC simplified the heating setup, as there was no need to attach and accommodate a contact thermocouple or probe to each sample. Controlling the whole setup was an Omega® CSi32-K model miniature benchtop controller. The controller moderated the sample temperature by receiving temperature data from the infrared thermocouple and then providing power to the cartridge heaters accordingly. A continuous feedback loop of temperature and power adjustments kept the sample at the desired temperature set on the controller. When set for an average temperature of 680 °F the controller was able to maintain temperature within ±20 °F.

Sample coupons were secured to the heating stage with high temperature silver paint, which helped establish good thermal contact and prevented the sample from moving during the experiment. The differential scanning aperture wire was switched from the usual 50 µm thick platinum wire to a 1 mm thick tungsten wire to accommodate for the radiative heat load from the sample at temperature.
In general, performing a strain-depth measurement consisted of two steps; determine a reflection of interest and establish a wire and energy range. The reflection of interest could be any individual Laue spot from any of the plane reflections visible on the detector. The energy range was determined for the selected reflection by setting the beam...
to monochromatic and scanning in energy around the energy that produced the maximum diffracted intensity to determine the maximum and minimum energy bounds where the reflection was still visible. The wire scan range was defined as the range the wire would need to traverse to completely block all intensity from the reflection of interest. The strain-depth measurement scans were arranged in two computational loops, one in energy and the other in wire position. The wire position was defined as the inner loop. The beam energy would be fixed and the wire scanned across its entire range in order to depth-resolve all reflections produced by that specific energy. After the wire scan was complete, the energy would be stepped by one increment and the process would be repeated. The energy step size used was between 1 and 3 eV, and the wire step size was 1 µm.

2.4 Scanning Electron Microscopy Examination of the Oxide Layer

The features of the cross-sectional oxide layers were examined using a scanning electron microscope (SEM). The oxide and its features are clearly visible in the SEM, and the oxide-metal interface can be clearly identified. The primary contrast mechanism between the oxide and the metal is the difference in average atomic weight between ZrO$_2$ and zirconium. Zircaloy-4 oxide has several distinct characteristics observable in the SEM that can be compared between samples of different oxide thickness. Figure 2.12 shows SEM images taken from several Zircaloy-4 samples and one crystal bar zirconium sample. The images were taken from mirror polished cross sectional samples of the types outlined in Section 2.2 using secondary electrons at an accelerating voltage of 5 kV.
The oxide layers formed on Zircaloy-4 show similarities even though the range of oxide thickness is very large. Periodic cracking is visible in the oxide layer. Each layer of cracking roughly corresponds to one oxide transition layer. When counted carefully the number of crack layers should roughly equal the number of oxide transitions, and when multiplied by an average transition thickness of ~2 µm should give the oxide thickness. In sample L1581 approximately 18-19 cracked layers are visible, H1033J shows 53-56 layers, and N2511 shows 5 distinct crack layers. The visible lateral crack length seems to be inconsistent between the oxides, but as this quality can be altered using different polishing techniques it should not be noted as dissimilarity between the oxides.
The oxide-metal interface appears to have a wavy nature, with periodic regions of thicker and thinner oxide. This characteristic is seen in nearly all oxides grown on zirconium alloys and is an indication that the oxide growth into the metal is uneven in the lateral direction. The variation in the oxide thickness caused by the uneven interface shape seems to increase with oxide thickness, with a maximum variation of 1 µm in N2511, 1.6 µm in L1581, and 8 µm in H1033J. The percent of the overall oxide thickness encompassed by the variations is small, with values of approximately 7% in N2511, 4% in L1581, and 7% in H1033J.

Veins of unbroken oxide are readily visible in the very thick oxide samples L1581 and H1033J. The veins can be seen as paths of unbroken oxide that contain no visible cracks, terminate existing cracks, and are continuous through the thickness of the oxide. The veins rarely take a straight path from the outer oxide to the oxide-metal interface, and usually take a more tortuous route. The points of minimum oxide thickness in the wavelike shape of the oxide-metal interface are the termination points for the veins, and are the point where the vein structure would continue to develop if the oxide were allowed to growth further. It has been hypothesized that the vein structures represent a network of high tetragonal phase oxide, with the growth and concentration of the tetragonal phase stabilized by high compressive stresses at the cusps of the scalloped oxide-metal interface [30]. An explanation for the secondary veins has been given as well [31], which postulates that the secondary veins are dragged behind small concavities in the non-uniform growth front and migrate laterally until they merge with a primary vein. It has also been proposed that the
second phase particles may play a role in the creation of secondary veins by causing small concavities in the oxide growth front [30].

The oxide layer formed on crystal bar zirconium as shown in Figure 2.12 (D) illustrates several of the key differences between corrosion in zirconium and Zircaloy and why pure zirconium is unsuitable as cladding material.

A large amount of broken oxide is visible in the upper portions of the image, indicating that the original oxide layer was much thicker and has either spalled off or been mechanically removed during polishing. Both outcomes showcase the mechanical weakness of the oxide grown on pure zirconium, which would readily spall and be removed by coolant flow in a reactor environment. This mechanical instability is one of the major differences between the corrosion behavior of zirconium and that of the Zircaloys. The oxide layer formed on Zircaloy is mechanically stable and adherent to the base metal, meaning it is not easily removed and does not spall off under normal reactor operating conditions.

The oxide layer close enough to the interface to remain intact contains a number of large lateral cracks formed as a stress relief mechanism during oxide growth. The cracks do not indicate the presence of oxide transitions as in Zircaloy-4, as pure zirconium enters a breakaway oxidation regime almost immediately after the start of corrosion. The high level of cracking may serve to facilitate further corrosion as the cracks form an easy path to the oxide-metal interface for corrosion species.

The oxide-metal interface is very irregular in pure zirconium. The interface shape appears to have no continuous or periodic features. While a somewhat wave-like shape can be seen in the interface, it occurs on a much greater scale than was observed in the Zircaloy-
4 oxides. Variations in the oxide thickness of up to 40 µm can be seen in certain locations. Note that the dark line bordering the interface may be a result of differential polishing between the metal and oxide creating an edge at the oxide-metal interface that resulted in a difference in contrast in the SEM, rather than a specific feature of the oxide. Dendritic growth behavior is commonly observed during corrosion in pure zirconium, with dendrites growing into the zirconium grain boundaries. This behavior may explain why large fingers of oxide are seen growing far into the metal ahead of the oxide growth front.
Chapter 3: EXPERIMENTAL RESULTS AND DISCUSSION

3.1 Synchrotron Microbeam X-Ray Diffraction and Fluorescence

As described in Section 2.3.1 two types of data are acquired simultaneously during experiments using the x-ray microbeam at beamline 2-ID-D. Diffraction patterns are acquired by a CCD camera while an x-ray fluorescence detector acquires information on alloy composition.

Elemental fluorescence information was used primarily to determine the location of the x-ray beam spot on the sample during the experiment. However, the information was also useful for identifying and confirming characteristics of the sample such as oxide thickness, oxide-metal interface location, and second-phase precipitate location. In addition if significant element redistribution was caused by the corrosion process, it should be possible to study this qualitatively with the fluorescence technique. Figure 3.1 shows a plot of typical fluorescence data gathered during a scan through the oxide in sample L1581. The oxide can be easily identified by the region of lower relative zirconium counts. The location of the oxide-metal interface in the overall scan can be roughly identified by the sharp increase in zirconium counts. The oxide thickness can be estimated from the fluorescence data, in this case confirming an oxide thickness of approximately 40 µm which is in agreement with prior SEM observations and weight gain calculations for this sample. The tin, which is fully in solid solution in the unoxidized metal, can be seen to remain homogeneously distributed in the oxide, apparently undisturbed by the corrosion process.
While not shown in Figure 3.1, the presence and rough location of iron-chrome second phase precipitates can be identified using fluorescence information. The precipitates produce a localized spike in the iron and chrome fluorescence counts over a region of a few scan steps, usually one micron or less. While the precipitates themselves are very small, the beam has a certain interaction volume with the sample which can cause the precipitates to appear larger than they actually are.

![Plot of the fluorescence counts for zirconium and tin at each point during a scan of the oxide and metal in sample L1581.](image)

**Figure 3.1** – Plot of the fluorescence counts for zirconium and tin at each point during a scan of the oxide and metal in sample L1581.

In order to quantify the microdiffraction data acquired at beamline 2-ID-D it is necessary to perform an integration of the diffracted intensities recorded in the diffraction patterns. The integration process is illustrated in **Figure 3.2a**. Each diffraction pattern is integrated around the circumference to create a plot of diffracted intensity versus two theta angle. The integration is accomplished using a computer program called *CCD Sum Sdiapp*.
that has been created by scientists at beamline 2-ID-D specifically for this purpose. After integration the values obtained of diffracted intensity vs. two-theta are corrected for Lorenz polarization before they are analyzed.

![Integration to create an intensity versus 2θ plot from the diffraction patterns acquired at beamline 2-ID-D.](image)

Figure 3.2a – Integration to create an intensity versus 2θ plot from the diffraction patterns acquired at beamline 2-ID-D.

Depending on the location of the diffraction maxima along the chi angle on the CCD image it was necessary in some circumstances to vary the size and location of the integration slice (the area inside the red lines in Figure 3.2a). While the example integration area shown in Figure 3.2a is useful because it covers a large two-theta range, it can miss a significant amount of intensity from low two-theta peaks (see green arrows in fig. 3.2a). This error can
be corrected by lowering the two-theta range of the integration slice so that the chi-angle range can be increased, or integrating over the entire square diffraction image. An illustration of the normal (red outline) and two alternate methods (blue and green outlines) of integration is shown in Figure 3.2b. Both solutions have their own shortcomings however. Using a smaller two-theta range (green) means that less oxide peaks can be fully characterized. Integrating over the entire diffraction image (blue) means that various chi-angle ranges are used for diffraction rings found in the normal integration slice (proportionally more of the ring is shown on the CCD image for a low two-theta reflection than a high two-theta reflection). As such, a correction factor must be applied to the integrated data so that the integrated intensities for each diffraction ring remain proportionally the same to one another. The correction was applied as a direct modification to the integrated intensity for each peak. The correction factors were calculated using the ratio between peak center two-theta locations (since the center locations are related to the diffraction ring circumference), using the (002)M peak as a baseline. This means that peaks at a lower two-theta than the (002)M will have their overall intensity uniformly reduced and peaks at a higher two-theta will have their intensity uniformly increased. The diffraction data presented in the following sections was integrated using the blue integration wedge with intensity correction factors applied, giving the best possible picture of the peak shapes while introducing only a small error in the relative peak intensities.
Figure 3.2b – Illustration of the different two-theta and chi ranges used to integrate diffraction data. The normal range is outline in red, a low chi high two-theta range in green, and the whole-pattern range in blue.

Once each diffraction pattern has been integrated, it is necessary to deconvolute the diffraction peaks to obtain phase information from them. Peak deconvolution was accomplished using a program created by AISN Software Inc. called PeakFit [32]. PeakFit takes the integrated diffraction data in the form of a Microsoft Excel or text file, plots it based on user specified axes (intensity versus 2θ in this case) and then allows the user to attempt to reproduce the overall diffracted intensity by inserting peaks where necessary. The user is required to modify the shape, size, location, and number of peaks to fit the intensity spectrum as closely as possible.

The basic fitting process was as follows: first the background was removed using a visual estimate and the PeakFit background removal tool. The background was determined using a best fit model (meaning that whichever model fit best, exponential, quadratic, logarithmic, etc., was used) with 0.5% tolerance and a 2\(^{nd}\) derivative zero algorithm. The
background removal was largely a visual fit by the user rather than an automatic fit. The minima in the spectrum were user-identified as zero-points for the background removal curve and were inserted or removed as necessary to ensure that none of the actual peak intensity was removed along with the background. A PeakFit spectrum showing the background removal step is shown in Figure 3.3a.

The background itself is a product of a number of different factors associated with the integration process and the data acquisition method. One notable feature of the spectrum shown in Figure 3.3a is that the background is higher at high two-theta values than it is at low two-theta. This originates from the integration process and the “zero” count value associated with the CCD detector. The CCD by default will have some non-zero “dark field” value for all of its pixels that results from electrical bias within the detector. Since diffraction rings at high two-theta trace a longer arc than those at lower two-theta, a larger number of pixels will be included in the integration of high two-theta rings. This means that a larger background will be recorded at high two-theta simply because the dark field value for more pixels has been summed up.
Figure 3.3a – PeakFit spectrum from the oxide layer in N2511 before background removal. The red line indicates the new zero after the background is removed.

Following this step, peaks of the appropriate height and width were inserted. The experimental spectrum was fitted such that the minimum number of peaks was initially used (for example, preference was to fit an experimental peak with one larger peak rather than multiple small ones whenever possible). Following the initial fit an iterative process was used by comparing the PDF for the peaks of all possible phases to those fit already and then modifying the shape and number of peaks as necessary. Peaks from a number of different phases were possible, including Zr (pdf# 05-0665), monoclinic ZrO$_2$ (pdf# 37-1484) tetragonal ZrO$_2$ (pdf# 42-1164), orthorhombic Zr$_3$O (pdf # 22-1025) and Zr delta hydride (pdf# 34-0649) in the two-theta range studied. Pearson VII peak shape (a model of peak shape that can vary between Lorentzian and Gaussian depending on the peak parameters) was used, which
allows the user to alter the overall intensity as well as the full width at half maximum and the full width at tenth maximum [33]. After the appropriate peaks had been inserted and sized correctly, the $R^2$ values (measurement of the fit accuracy to the experimental spectrum) found were typically above 99%. The peak residuals, or the difference between the experimental and user-fit spectrum at any given point were usually 1-1.5% (or 1000 out of 100,000) and no systematic errors (consistently high or low residuals) were present. Once the spectrum is fitted, a summary of the fit characteristics is recorded. An example of a fitted spectrum and the accompanying residuals is shown below in Figure 3.3b.

Figure 3.3b is an example of a “good” fit with acceptable residuals. The top portion of the figure is an overlay of the experimental and user-fit spectra, and as expected with any good fit they overlap nearly perfectly and are difficult to tell apart at this scale. The $R^2$ value for the fit shown is 0.999248, meaning that the user fit accounts for 99.92% of the intensity of the experimental spectrum which is above our defined limit for an acceptable fit. The user-inserted peaks are shown in red, and correspond largely to either monoclinic or tetragonal ZrO$_2$ with the exception of one peak. The peak inserted at $2\theta = 12.846$ as residual intensity on the right shoulder of the (-111)$_M$ peak has been seen in previous studies but has not yet been identified to be associated with any oxide phases. The fit residuals, which are a measure of the deviation of the user fit from the experimental spectrum, are shown in the lower portion of the figure. Two characteristics indicate an acceptable level of residuals in this fit; the scale of the residual peaks and the lack of systematic errors. The color scheme shows low residuals in blue, mid-level in green and high residuals in red. We can see that the residuals are roughly 2% or less of the peak intensity at any given point, which signals that
the fit is good and there is not a large misfit between the spectra at any point. We can also see a general lack of systematic errors (consistently unbalanced high or low residuals) in the residuals, with the exception of one or two areas between major peaks. It can be difficult to remove the background completely from these areas as they contain intensity from the tails of some of the major monoclinic peaks, and as such consistently show a higher residual than the areas of the fit with better background removal.
Figure 3.3b – A typical PeakFit plot review shown for sample L1581 taken within the bulk oxide. The upper plot shows the experimental spectrum with the peaks used to fit it overlaid, and the lower plot shows the residuals that exist in the fit.
A number of checks are performed during the fitting process to ensure that the fit is physical. As mentioned previously the peaks are indexed to known peaks so that the phases are identified. In most cases all peaks could be indexed to known phases. Occasionally it was not possible to identify a peak by comparing it to the expected phases. As mentioned earlier one such peak was found systematically on the high two-theta side of the (-111) peak. This particular peak has been observed in previous studies [2] and has not yet been identified with any possible Zircaloy-4 phase. A number of small artifact peaks usually appeared throughout each oxide scan which could not be identified, but none were systematic and were normally so narrow that they did not interfere with the fitting of the regular oxide peaks. The 2θ location of a particular peak of a given phase is checked from scan to scan to ensure that it does not un-physically drift to artificially account for variation of the fitting of the diffracted intensities. In principle the peak breadths for a given phase should be similar. Then, the full width at half maximum (FWHM) and full width at tenth maximum (FWTM) are also checked to ensure that their ratio is not excessively small (a result of an extremely broad peak which often appear to compensate for missing background intensity) and that peaks of the same phase have similar values.

An example of the comparison of the observed peak locations to their predicted PDF peak locations is shown in Table 3.1 taken from representative locations 12 µm into the bulk oxide past the oxide-metal interface and 1.4 µm ahead of the oxide-metal interface in the metal. In this case the difference in peak location between the observed and indexed peaks is well below 1%, with the exception of the (101) tetragonal ZrO₂ peak, which is systematically observed at a higher 2θ than the powder diffraction value. The systematic
shift of the (101) tetragonal ZrO$_2$ peak has been observed in previous studies [13, 34]. The good agreement observed here has been seen systematically in the oxide layers studied.

Table 3.1 – A comparison of the experimental and PDF 2θ peak locations along with probable phase and plane in sample L1581 taken from two representative locations: The monoclinic and tetragonal peaks from the bulk oxide at 12 µm into the oxide from the oxide-metal interface, and the metal, hydride, and suboxide peaks from a location 1.4 µm into the metal before the oxide-metal interface.

<table>
<thead>
<tr>
<th>Phase</th>
<th>(h k l)</th>
<th>d-spacing (Å)</th>
<th>Calculated 2θ</th>
<th>Observed 2θ</th>
<th>% ∆</th>
</tr>
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<td>Monoclinic ZrO$_2$</td>
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<tr>
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<td>10.9900</td>
<td>10.9982</td>
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</tr>
<tr>
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<td>3.1650</td>
<td>12.6421</td>
<td>12.6642</td>
<td>0.175</td>
</tr>
<tr>
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<td>13.3629</td>
<td>13.5620</td>
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</tr>
<tr>
<td>Monoclinic ZrO$_2$</td>
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<td>14.2115</td>
<td>14.2102</td>
<td>0.009</td>
</tr>
<tr>
<td>α-Zr</td>
<td>(1 0 0)</td>
<td>2.7980</td>
<td>14.3085</td>
<td>14.3005</td>
<td>0.056</td>
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<tr>
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<td>15.4036</td>
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<tr>
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</table>

1 The observed values shown are from a representative single location. The observed center location can shift slightly, with standard deviations for the three phases of $\sigma_{M2r02} = 0.0047^2$, $\sigma_{T2r02} = 0.0103$, and $\sigma_f = 0.0022$ (all in degrees two-theta).

2 A single standard deviation for the monoclinic phase center locations was calculated by averaging the $\sigma$ value at each point as calculated by PeakFit over the entire oxide, then averaging all of the monoclinic peaks together. The tetragonal and hcp Zr $\sigma$ values were averaged over one or two peaks.

After generating text files with a summary of the fit for each scan location using PeakFit it was necessary to collate the important quantities from the numerous data files.
A Microsoft Excel program written by Dr. Randy Lott of Westinghouse called Diffscan4 was employed to this end. Diffscan4 is a macro within the Excel program that is designed to read and extract data directly from the PeakFit output summaries. The data is extracted based on the peak 2θ center locations, with a lower and upper limit specified by the user to define a bin for each peak and compensate for any slight drift in the peak center location. Once all the peaks have been properly accounted for, Diffscan4 will extract information from the text files on the peak center location, integrated peak area, FWHM, and the standard deviation for these quantities for each PeakFit output summary each of which corresponds to a single location in the oxide layer. The extracted data can then be plotted and analyzed further. **Figure 3.4** shows a plot of the peak center locations for the peaks indexed in sample L1581 at each scan point (one unique diffraction pattern per point), as extracted by Diffscan4 from the PeakFit output summary from each point. Only a small amount of drift is visible in the peak center locations as a function of distance in the oxide but no significant variations can be observed. This is a further check that the fitting/integration/collation process has been done properly.
Figure 3.4 – Peak center location for each scan point in sample L1581 as compiled by Diffscan4 from the PeakFit output summaries. Positive values on the distance axis indicate a position within the oxide.

Identification of the oxide phases present as a function of position within the oxide is a powerful ability of the microbeam diffraction technique at beamline 2-ID-D. The integrated diffraction data itself can be used to examine overall trends in the oxide phase development through the creation of surface and contour plots of the overall diffracted intensity, as shown in Section 3.1.1. The data compiled after the integrated diffraction spectra have been fit can be used for a detailed analysis and comparison of the oxide phases and for the calculation of quantities such as the tetragonal fraction.
3.1.1 Phase Analysis using Diffracted Intensity Surface and Contour Maps

Surface and contour plots of the integrated diffraction data created using Matlab and used to obtain an overall picture of the distribution of diffracted intensity and for following the development of the individual peaks for each phase as the oxide forms. Figure 3.5 shows a contour and surface plot generated using Lorenz polarization-corrected integrated data from a scan of the oxide layer formed on sample N2511 (13 µm oxide, corroded for 3113 days at 600 °F). The plot is composed of a layering of diffraction patterns such as shown in Figure 3.2a so that the diffracted intensity is plotted versus 2θ and for various locations and in the oxide layer. The position “0” indicates the oxide-metal interface, beyond which is the metal (negative positions) and the 13 µm thick oxide layer (positive positions).

On examination of Figure 3.5 for sample N2511, a number of oxide and metal peaks can be identified which correspond to the monoclinic and tetragonal oxides phases as well as the hexagonal close-packed (HCP) metal. Peaks associated with the monoclinic ZrO$_2$ phase are the primary peaks visible within the oxide layer, with only one tetragonal ZrO$_2$ peak clearly visible (the (101)$_T$). The base metal shows peaks corresponding to the HCP structure, with two major peaks visible within the 2θ range studied which corresponds to the texture of the metal studied. A delta ZrH$_2$ hydride peak (111)$_δ$ can also be seen alongside the metal peaks in certain locations (since the hydrides are thin platelets in cross-section they are not expected to appear continuously). The phases inferred for the metal and oxide peaks observed are consistent with those seen in previous studies of Zr alloy oxides [2]. Additionally, there are some peaks in Figure 3.5 that cannot be clearly observed at first
glance using this analysis technique (such as the (002)$_h$) and require a more detailed
deconvolution of the intensity versus two-theta plots that will be described in Section 3.1.2.

The thickness of the oxide layer can be measured using the points where the oxide
peaks are observed to appear and disappear. A marked periodicity in the peak intensity can
also be observed in several of the oxide peaks. The periodic variations correspond
approximately to the distance between oxide transitions. The distance between the periods
in N2511 is 1.9 µm on average, which is in good agreement with the transition thickness of
Zircaloy-4 (1.8 µm) observed in previous studies [16-18].

Some elements of the oxide and metal texture can be noted by observing the relative
intensity of the peaks found in each layer. The oxide shows strong (111)$_M$ and (-111)$_M$ peaks
as expected, along with a number of less intense monoclinic peaks. Notably missing is the
(200)$_M$ peak, indicating that the oxide grains are oriented in such a way that the (200)$_M$ plane
is parallel to the x-ray beam during our experiments. Based on our experimental geometry
this means that the oxide grains develop with their (200)$_M$ planes parallel to the oxide-metal
interface. Three strong peaks can be seen in the metal region, two from HCP zirconium and
one from a delta-hydride. The (0002) basal plane peak is barely visible when it is visible at
all. This observation confirms that we examined the sample in the rolling direction: as based
on the texture of rolled sheet Zircaloy-4 we expect the basal poles to be primarily oriented in
the transverse direction.

Another notable feature is the consistency in the diffracted intensity of the oxide
peaks between oxide transitions. Each oxide peak appears to return roughly to the same
level of intensity after each oxide transition. This suggests that the oxide is developing with
an identical structure and texture between every transition, and that a repetitive mechanism is taking place in oxide formation.

Figure 3.5 – Integrated x-ray diffracted intensity versus 2θ angle scans for sample N2511 from the oxide-water interface through the oxide and into the base metal.
Sample L1581 (39.5 µm oxide, corroded for 1260 days at 680 °F) was analyzed using a surface and contour plot as well, shown in Figure 3.6. In this case, a much larger oxide layer is seen, which makes the details less visible. Monoclinic and tetragonal oxide peaks are visible as well as metal and hydride peaks. The oxide and metal peaks indicated in the figure are the same as those labeled in Figure 3.5 with the exception of peaks at high two-theta values that are not shown. Some spreading of the (10\(\overline{1}0\)) Zr peak can be seen near the oxide-metal interface, which may be a result of some saturation of the detector instead of a physical feature. Periodicity to the same degree as seen in N2511 is not visible, even though four clear oxide transitions are visible in the corrosion kinetics curve for this sample shown in Figure 2.1.
In this section we examined some characteristics of the oxide and metal using surface and contour maps constructed from a layering of integrated intensity versus two-theta plots. We observed diffraction peaks corresponding to both monoclinic and tetragonal ZrO$_2$ in the...
oxide, as well as peaks corresponding to HCP zirconium and delta ZrH$_2$ hydrides in the metal.

Regular periodic intensity variations were visible in several of the main monoclinic and tetragonal oxide peaks, with the distance between the periods corresponding to the oxide transition thickness for Zircaloy-4. In the next section we examine each individual peak in greater detail using the integrated peak intensity.

3.1.2 Phase Analysis using Individual Peak Integrated Intensities

By plotting the integrated peak intensities against distance in the oxide layer it is possible to study development of each oxide phase as the oxide grows. Figure 3.7 is a plot of oxide phase peak intensity (plotted directly from the integrated diffraction data) versus distance from the oxide-metal interface for samples N2511 and L1581. Positive distance values indicate a position within the oxide and negative values indicate a position within the metal.
Figure 3.7 – Integrated peak intensity as a function of distance from the oxide-metal interface for samples (A) N2511 and (B) L1581.

A number of observations can be made from the examination of Figure 3.7(A) and Figure 3.7(B) about the oxide grown on samples N2511 and L1581.
3.1.2.1 Oxide Periodicity

Both N2511 and L1581 show strong periodic variations in the intensity of the oxide peaks as noted earlier in Figure 3.5 and Figure 3.6, most noticeably in the $011_M$, $111_M$, $002_M$, and $020_M$ peaks. N2511 shows strong periodicity in many peaks throughout the oxide thickness, while L1581 shows clear periodicity in the first four oxide transitions, i.e., the first oxide to form, and hence the furthest from the oxide-metal interface in Figure 3.7. The four visible periods in L1581 agree well with the four oxide transitions that can be observed in the corrosion kinetics for this sample shown in Figure 2.1. The distance between the periods is about $1.8 - 1.9 \mu m$ for both samples shown, which agrees with previous measurements of Zircaloy-4 period thickness taken during corrosion at this temperature [13, 18].

A relationship can be observed between the periodicity of several of the oxide peaks for sample N2511 in Figure 3.7(A). The major oxide monoclinic and tetragonal peaks ($011_M$, $101_T$, $111_M$, $020_M$, $002_M$) appear to be in-phase with one another. This observation conflicts with some previous findings which showed that the variations between the $020_M$ and $101_T$ peaks were out of phase with each other [18]. Strong in-phase periodicity could indicate that the periodic variations in diffracted intensity are not a result of changes in the oxide phase content but rather a result of cracking or some geometric variation that periodically reduces the overall diffracted intensity. However, peaks such as the (-111)$_M$ and (102)$_M$ show little periodic variation. Furthermore, a slight out of phase relationship can be observed in the first two periods of the (012)$_M$ peak. This may indicate that the in-phase relationships are not a product of geometric features and may be a result of the corrosion process instead.
In sample L1581, Figure 3.7(B) shows that periodic intensity variation can again be observed in several of the oxide peaks. The \((011)_M\), \((020)_M\), and \((002)_M\) show an in-phase relationship with one another. Most notable is the periodicity of the \((011)_M\) peak which is very well defined and regular. The regular periodicity of the \((011)_M\) is similar to that seen previously in sample N2511, but occurs in fewer peaks and for fewer transitions in L1581. N2511 had periodicity corresponding to the oxide transition thickness through the entire 12 \(\mu\)m oxide. However in L1581 the \((011)_M\) shows periodicity in only the first four transitions corresponding to the first 8-10 microns of oxide formed.

The loss of periodicity could be due to the oxide growth front entering a different grain with a different orientation than the grain first consumed. Without knowing the orientation of the base metal grains at this location before corrosion we cannot say specifically which orientations affect the oxide periodicity. However, this data does suggest that the orientation of the base metal grains may have an effect on oxide texture.

Also of interest in L1581 is the very strong periodicity visible in the \((012)_M\) peak. The intensity of the \((012)_M\) is nearly perfectly out of phase with the \((011)_M\) intensity. Due to the close orientation of the two planes (18.17° of separation), this finding suggests that a twisting of the grain about its growth axis (the \((200)_M\) plane normal) may be occurring.

**Figure 3.8** shows two diffraction patterns taken (A) at a location of high \((011)_M\) and low \((012)_M\) intensity, and (B) at a location of low \((011)_M\) intensity. The change in orientation could come about as a result of grain growth accommodation with the surrounding oxide grains. We can see that while the \((011)_M\) intensity is largely dependent on a single spot, the \((012)_M\) intensity is much more diffuse over the chi angle range. One possible explanation is
that immediately following the oxide transition and nucleation of new oxide grains, a greater portion of small monoclinic grains do not share a texture, and only develop a more uniform texture as the grains grow and accommodate one-another. This texture evolution could lead to the decrease in intensity of the diffuse $(012)_M$ reflection and cause the increase of the coherent $(011)_M$ spot visible in the diffraction patterns.

![Diffraction patterns](image)

**Figure 3.8** – Diffraction patterns taken from the oxide layer in sample L1581 showing locations of (A) maximum $(011)_M$ and minimum $(012)_M$ intensity, and (B) minimum $(011)_M$ and maximum $(012)_M$ intensity. The diffraction patterns correspond to locations (A) 35 µm and (B) 33.8 µm into the oxide past the oxide-metal interface.

The general trend of in-phase periodicity between the primary monoclinic peaks as observed in both N2511 and L1581 conflicts with observations made during some previous studies [13, 18] of Zr alloys that showed an out-of-phase periodic relationship between the $(101)_T$ and $(020)_M$ peaks. The prior work supported the proposed oxide growth mechanism described in Section 1.2 by showing that additional tetragonal phase was formed (through an increase in $(101)_T$ diffracted intensity) during periods of low monoclinic phase diffracted intensity. This The observations made during this work do not support the same
conclusion, as the in-phase relationship between the monoclinic and tetragonal peaks implies that there could be another oxide growth mechanism at work.

3.1.2.2 Oxide Texture

In the 200\textsubscript{M} family of planes the (200)\textsubscript{M} intensity is seen to be very low or non-existent in both N2511 and L1581. However the (020)\textsubscript{M} and (002)\textsubscript{M} are clearly visible. Based on the orientation of the sample during investigation this indicates that the oxide grows in an orientation with the (200)\textsubscript{M} plane parallel to the oxide-metal interface. Previous studies have shown that oxides grown on other Zr alloys maintain a similar grain orientation [18].

As was observed earlier in the surface map for sample N2511, the uniformity of peak intensity between transitions can be seen again in Figure 3.7 (A). Many of the primary monoclinic peaks show similar maximum and minimum intensity values during each oxide transition and throughout the oxide thickness. This indicates that the oxide grains are forming regularly with nearly the same orientation before and during each transition. This feature is not seen to the same extent in L1581, where we can observe a decreasing intensity with successive oxide transitions in the peaks that show regular periodicity.
Another method of quantifying the relationship between the monoclinic and tetragonal phases is through the use of the well-known Garvie-Nicholson formula [35] to calculate the tetragonal fraction $f_T$.

$$f_T = \frac{I_{101}^T}{I_{111}^M + I_{101}^T + I_{111}^M} \quad \text{(Eq. 3.1a)}$$

where $I_{101}^T$ is the integrated intensity under the (101) tetragonal peak and $I_{111}^M$ and $I_{111}^M$ correspond to the integrated intensities of the (111) and (-111) monoclinic peaks respectively. Note that the tetragonal fraction as presented here is uncorrected for texture.

The standard Garvie-Nicholson formula is most appropriate for powders or other random texture materials. Given a pole figure for each sample, intensity correction factors can be calculated for each peak intensity based on individualized texture as done in [13]. Since we do not have detailed texture data for the samples shown here, we are unable to calculate texture correction factors. However, if we assume that our samples have a similar texture to those examined in [13] (a reasonable assumption for Zircaloy-4) we can apply those previously calculated texture correction factors. The calculation of each texture correction factor is shown in detail by Yilmazbayhan et al. in [2, 13]. The final corrected Garvie-Nicholson formula is shown below in equation 3.1b.
\[ f_T = \frac{\gamma_{101}^T(90)I_{101}^T}{\gamma_{111}^M(90)I_{111}^M + \gamma_{101}^T(90)I_{101}^T + \gamma_{111}^M(90)I_{111}^M} \]  
(Eq. 3.1b)

where \( \gamma_{111}^M(90) \), \( \gamma_{101}^T(90) \), and \( \gamma_{111}^M(90) \) correspond to the texture correction factors of the (-111)\(_M\), (101)\(_T\), and (111)\(_M\) peaks respectively. The gamma values used were \( \gamma_{111}^M(90) = 25 \), \( \gamma_{101}^T(90) = 2.2 \), and \( \gamma_{111}^M(90) = 0.88 \). Texture correction does not appear to drastically change the shape and features of the tetragonal fraction curve, and instead simply scales the entire curve uniformly up or down [13]. Figure 3.9 shows the calculated uncorrected and corrected tetragonal fraction versus distance from the oxide-metal interface for samples N2511 and L1581 based on the peak intensities shown in Figure 3.7.

In Figure 3.9 (A) the tetragonal fraction for sample N2511 can be seen. The highest tetragonal fraction is observed at the oxide-metal interface with a value of about 15\% (uncorrected). This value then steadily decreases over a distance of approximately 2 \( \mu \)m to an average of 5-6\% (uncorrected) within the bulk oxide. Correcting for texture reduces the \( f_T \) maximum seen at the oxide-metal interface to approximately 4\% and the bulk value to 1.6\% but does not appear to change the shape of the curve, which follows the periodicity seen in the integrated peak areas for the peaks utilized.

Figure 3.9 (B) shows the tetragonal fraction calculated for sample L1581. Again the highest \( f_T \) value is found adjacent to the oxide-metal interface, with a value of about 9\% (uncorrected) followed by a steady decrease over roughly a 2 \( \mu \)m distance to an average of about 3\% (uncorrected) in the bulk oxide. Texture correction again reduces the \( f_T \) maximum at the oxide-metal interface to 3.5\% and the bulk oxide value to approximately 1\%. No
consistent trends can be observed in the shape of the curve as the peak intensity periodicity observed in this sample was much less marked than that seen in N2511.

The uncorrected tetragonal fraction observed in both samples agrees well with the results found in previous studies [13, 34], which found that for Zircaloy-4 the tetragonal fraction was systematically highest at the oxide-metal interface at a value of 10-15%, decreasing to less than 10% at distances farther than 3 µm from the oxide-metal interface. In addition to the (101) the (002) peak was also observed in both N2511 and L1581 throughout the oxide thickness. This peak had been previously observed near the oxide-metal interface in Zircaloy-4, ZIRLO, and model Zr alloys [17], and was postulated as an indicator for a precursor phase of monoclinic ZrO₂. However a consistent shoulder on the (020) peak was observed throughout the oxide layer in both samples examined at a 2θ position that indicates the presence of an (002) peak. As can be seen in Figure 3.7 the (002) peak intensity does not appear to show any periodic trends or relationships with other monoclinic or tetragonal peaks, and instead shows its presence throughout the oxide. The lack of any periodic features or relationships to other peaks does not support the idea of the (002) indicating a monoclinic phase precursor. The (002) peak also does not show an intensity increase near the oxide-metal interface as seen in the (101) peak, indicating that the intensity increase may be due to a stronger alignment of the tetragonal grains near the interface in addition to the larger portion of tetragonal phase along the oxide formation front.
Figure 3.9 – Tetragonal fraction $f_T$ calculated using the Garvie-Nicholson formula and shown as a function of distance from the oxide-metal interface for sample (A) N2511 and (B) L1581.
3.1.2.4 Identification of the Suboxide Phase

A zirconium suboxide phase was identified in both samples N2511 and L1581 in the metal region close to the oxide-metal interface. The suboxide was identified as Zr$_3$O by its peak center two-theta location using two peaks seen on the shoulders of the (111)$_M$ and (020)$_M$ peaks. The peaks associated with this phase were found in a small region within 1-2 µm of the oxide-metal interface. In previous studies the Zr$_3$O phase has been identified in a number of zirconium alloys including Zircaloy-4 [18]. Figure 3.10 shows a representative PeakFit spectrum taken from a location 1.4 µm past the oxide-metal interface (into the metal) in sample L1581. Each peak has been identified and labeled using the specified colored arrows. The locations of the peaks identified as Zr$_3$O matched their PDF peak locations within our tolerances such that we can confidently identify them as such. Since a ZrO suboxide phase has been reported as well [36], the potential peak locations of the ZrO phase have been marked. We can see that no apparent peaks exist that would identify the presence of ZrO at this location. The lack of any observable ZrO peaks is consistent within the region where Zr$_3$O is observed in both samples N2511 and L1581. However, the ZrO layer seen by the previous studies is very thin (0.1-0.2 µm), so it could be easily missed.
Figure 3.10 – PeakFit intensity vs. two-theta spectrum taken 1.4 µm past the oxide-metal interface into the metal in sample L1581 showing the presence of the Zr₃O suboxide phase and the absence of a ZrO suboxide phase.

3.1.3 Grain Size Determination

The FWHM was extracted from the fitted peak summaries for each peak along with the integrated peak areas. The FWHM for the main oxide and tetragonal peaks are shown for samples N2511 and L1581 in Figure 3.11. The average FWHM for the monoclinic peaks is about 0.2 degrees two-theta and the average for the (101)₄ peak is approximately 0.38 degrees two-theta. The monoclinic peaks appear to maintain a relatively constant FWHM through the thickness of the oxide. However, a general increase in the FWHM can be seen for all of the monoclinic peaks starting at a distance of 2-3 µm from the oxide-metal interface.
and reaching a maximum at the interface. Most notable is the (020)\textsubscript{M} peak in sample N2511 which shows a much more significant FWHM increase than the other monoclinic peaks in that sample. It should be noted, that while error bars have not been included in Figure 3.11, significant variation in the determination of FWHM is possible on a point-by-point basis. The average standard deviation (σ) in the FWHM determined for the monoclinic peaks is 0.01 degrees 2θ or less, while the average σ for the FWHM of (101)\textsubscript{T} is much higher at 0.028 degrees 2θ. Imprecision in the manual fitting can help account for the erratic nature of the FWHM curves, especially the curve for (101)\textsubscript{T}. Manual deconvolution of the peaks can be difficult, and while every attempt is made to maintain a uniform fit, perfection is simply not attainable. Thus the most reliable information to be obtained for the study of FWHM are the overall trends and average values of FWHM. The many small erratic variations should be discounted as errors inherent in the fit and fitting technique.
Figure 3.11 – Peak FWHM shown for the primary monoclinic and tetragonal phase peaks in sample (A) N2511 and (B) L1581.
3.1.3.1 Williamson-Hall Deconvolution of Size and Strain Broadening

The peak broadening near the oxide-metal interface can be attributed to two main causes: strain broadening and small grain size. Strain broadening causes the diffraction peaks to broaden due to diffraction from non-uniformly distributed strained planes of slightly different d-spacing from the unstrained planes [37]. Smaller oxide grains result in a greater amount of incoherent x-ray scattering than larger grains, which causes the diffraction peak to broaden [37]. A Williamson-Hall analysis [38] can be used to deconvolute the effects of size and strain broadening to determine which effect is the cause of the variation in grain size near the oxide-metal interface. Size broadening and strain broadening can be expressed according to the following proportions:

$$FWHM_{\text{sample}} \propto \varepsilon_{\text{lattice}} \frac{\sin \theta}{\cos \theta}$$ \hspace{1cm} \text{Strain broadening}$$

$$FWHM_{\text{sample}} \propto \frac{0.9\lambda}{t \cos \theta}$$ \hspace{1cm} \text{Size broadening}$$

where $FWHM_{\text{sample}}$ is the measured FWHM minus the instrumental broadening (in radians $2\theta$), $\theta$ is the Bragg angle (in radians), $\varepsilon_{\text{lattice}}$ is the lattice strain, $\lambda$ is the x-ray beam wavelength (in nm), and $t$ is the sample particle size (in nm). A Williamson-Hall plot can be used to deconvolute size from strain broadening in the manner shown in Figure 3.12. In this figure we plot $(FWHM_{\text{sample}} \times \cos \theta)$ against $(\sin \theta)$ using data from the major monoclinic oxide peaks at various $2\theta$ locations. Under these conditions the slope of the curves plotted is proportional to the strain broadening and the y-intercept is proportional to the size broadening. A perfectly horizontal curve will indicate size broadening only, a sloped curve with a zero y-intercept indicates pure strain broadening, and a combination of the two
indicates the presence of both effects. Note that we have not differentiated between plastic and elastic strains in this analysis, as localized elastic strain, some level of plastic strain, or the presence of dislocations may all play a role in peak broadening.

The components of size and strain broadening can be calculated using a Williamson-Hall plot as shown in Figure 3.12. The strain component can be obtained from the slope of the line (Cε), where C is some constant and ε is the strain. The size component is obtained from the y-intercept at sinθ=0 (Kλ/D), where K is the Scherrer constant (usually assumed as K=0.9), λ is the radiation wavelength, and D is the grain size.

![Figure 3.12](image)

Figure 3.12 – Schematic of how a Williamson-Hall plot can be used to deconvolute size broadening from strain broadening and how the components of size and strain can be obtained.

**Figure 3.13** shows the results of a Williamson-Hall analysis for samples N2511 and L1581 at various locations in the bulk oxide and near the oxide-metal interface. The peaks
used to create the plots are the \((110)_M, (011)_M, (-111)_M, (111)_M, (020)_M, (002)_M, (102)_M, \) and \((012)_M\). Data taken from three distinct locations are shown; one at the oxide-metal interface (green curve), another within one transition distance into the oxide and corresponding to the distance where the FWHM increase is observed from the oxide-metal interface (blue curve), and the last within the bulk oxide (red curve) beyond one transition distance. In both samples we can see that the slope of the trend lines remains approximately constant at each oxide location. This indicates that some degree of strain is present and that it remains approximately constant with distance from the oxide-metal interface. However the fact that the y-intercept of the fitted lines increases with proximity to the oxide-metal interface indicates that size broadening is occurring and that the grain size is smaller near the oxide-metal interface. This result shows that size broadening is the dominant cause in the change of the peak FWHM, and that the oxide grains grow with residence time in the oxide layer until they reach a maximum size. This result is logical and agrees with our current understanding of oxide growth where small grains are nucleated at the oxide-metal interface and subsequently grow. The effect of strain broadening appears to be relatively constant throughout the oxide layer. This seems somewhat illogical, as the region near the oxide-metal interface is highly stressed and is thus expected to show more strain broadening than the more relaxed oxide far from the interface. The calculated standard deviation for the peak centers and FWHM of 0.01 degrees 2θ or less is not large enough to cause a significant change on the Williamson-Hall plot.
Figure 3.13 – Williamson-Hall plot for samples (A) N2511 and (B) L1581 showing the effects of size and strain broadening on the oxide grains at various distances in the oxide from the oxide-metal interface.

The grain size at each oxide location noted in Figure 3.13 can be calculated using the size component of the Williamson-Hall plot given as \((K\lambda/D)\) in Figure 3.12. This approach allows the grain size to be approximated using the diffraction peak FWHM while excluding the effects of peak strain broadening. By extending the fit on the W-H plot to zero on the x-axis, the y-intercept can be taken as the size broadening component and set equal to \((K\lambda/D)\) to solve for the grain size ‘D’. The y-intercept values for both N2511 and L1581 for the bulk
oxide and oxide-metal interface are shown in Table 3.2, along with their associated grain size. The grain sizes were calculated using using $K=0.9$ and $\lambda=0.06969$ nm. The grain sizes shown are applicable to the monoclinic phase only, as no tetragonal phase peaks were used to create the W-H plot. Additionally, given that the monoclinic grains are not equiaxed but are elongated in the [200] direction [39], the grain size calculated using this technique represents an overall average grain size since peaks from several difference facets of the monoclinic unit cell were used to construct the fit.

Table 3.2 – Calculated grain sizes using the size component of the Williamson-Hall plot for samples N2511 and L1581 for locations at the oxide-metal interface and within the bulk oxide further than one transition distance from the interface.

<table>
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<th>O/M Interface Y-Intercept</th>
<th>Bulk Oxide Grain Size (nm)</th>
<th>O/M Interface Grain Size (nm)</th>
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<tbody>
<tr>
<td>N2511</td>
<td>0.0006</td>
<td>0.0012</td>
<td>104.54</td>
<td>52.27</td>
</tr>
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<td>L1581</td>
<td>0.0008</td>
<td>0.0014</td>
<td>78.40</td>
<td>44.80</td>
</tr>
</tbody>
</table>

The grain size calculations show a much smaller monoclinic grain size at the oxide-metal interface than in the bulk oxide, as expected from our previous examination of the FWHM and W-H plots. In both samples the grain size appears to approximately double in the 2-3 µm between the interface and the beginning of the bulk oxide. The bulk oxide grain size values of 104 nm for N2511 and 78 nm for L1581 are significantly larger than those found in previous TEM and microbeam diffraction studies which found monoclinic grain sizes of approximately 20 nm [17, 18, 39]. However, the prior microbeam diffraction studies performed grain size calculations using the peak FWHM and the Debye-Scherrer formula rather than a Williamson-Hall analysis.
Unlike a W-H plot, the Debye-Scherrer formula does not take into account the individual effects of size and strain broadening. If the entire peak broadening is assumed to be size broadening this could lead to the calculation of a smaller grain size than is real if any amount of strain broadening is present. The results of the Williamson-Hall analysis show that a significant amount of strain broadening is present (by the non-zero slope of the fit line) in the monoclinic peaks. As such it may be necessary to subtract some level of strain broadening from the FWHM to accurately calculate the grain size using the Debye-Scherrer formula. However, for direct comparison with previous work the results of Debye-Scherrer grain size calculations for sample N2511 and L1581 based on the FWHM values from Figure 3.11 will be presented in the following section.

### 3.1.3.2 Grain Size Determination using the Debye-Scherrer Equation

The FWHM can be used for calculating the oxide grain size using the Debye-Scherrer equation. The particle size $d$ is given by the equation as:

$$
\frac{d}{B_{\theta \cos \theta}} = \frac{0.9 \lambda}{B_{\theta}}
$$

(Eq. 3.2)

where $B_{\theta} = (B^2 - B_i^2)^{1/2}$ is the particle size broadening for a given peak, $B$ is the measured peak FWHM in radians $\theta$, $B_i$ is the instrumental broadening measured using a standard, $\theta$ is the diffraction angle (half the measured 2$\theta$), and $\lambda$ is the wavelength of the incident radiation (0.0693 nm in this instance). The instrumental broadening was not measured specifically for this experiment, but a value of 0.051 degrees two-theta found during previous work using the same instrument and a NIST 660a LaB$_6$ powder standard was used instead [13]. The
Debye-Scherrer formula is valid for particles up to ~100 nm, which means that although the size of metal grains cannot be calculated, the FWHM can be used to find the size of the oxide grains. The ideal application of this technique is towards randomly oriented equiaxed (spherical) particles. Neither of these conditions are met by the oxide grains. Since it is known that the grains in the oxide film are mostly large columnar or small and equiaxed [39], and given the geometry of the experimental setup, the diffracted beams were primarily from planes oriented perpendicular to the long axis of the columnar grains. This means that for the monoclinic phase the ‘grain size’ given is representative of the column width rather than an equiaxed grain size. A schematic of this effect is shown in Figure 3.14 for the representative \((020)_M\) and \((002)_M\) planes. For simplicity the term ‘grain size’ will be used to describe the results presented. For the tetragonal grains the equiaxed assumption can be considered valid.

Note again that any component affecting the peak broadening is assumed to be size broadening by this analysis. As previously explained any effects of strain or deformation on the peak width will be included in the size broadening and may result in an inaccurate grain size if significant strain broadening is present. The results presented here are for direct comparison with previous Debye-Scherrer grain size calculations which may contain the same errors.
Figure 3.1 – Schematic of the grain dimensions that can be calculated using different diffracting planes in a columnar monoclinic grain. The dimension of the long face of the monoclinic grain cannot be calculated as no diffraction information was recorded from the (200)\textsubscript{M} plane.

Figure 3.15 shows the grain size calculated using equation 3.2 and the (101)\textsubscript{T}, (111)\textsubscript{M}, and (020)\textsubscript{M} FWHMs as a function of distance from the oxide-metal interface for samples N2511 and L1581. For sample N2511 the monoclinic grain size is 15-20 nm, with an average grain size of 18.6 nm calculated from the average over all the monoclinic peaks shown. The overall average is calculated by individually averaging each monoclinic peak over the bulk oxide thickness (the region where the FWHM remains relatively constant), and then averaging all of the individual average values together. The tetragonal phase grain size calculated using the (101)\textsubscript{T} peak gives an average grain size of 9.3 nm over the entire oxide layer.
Similar results are shown for sample L1581. Averaging the monoclinic peaks yields an overall average grain size of 22.7 nm. The FWHM of the (101)$_T$ peak yields an average grain size of 9.5 nm. The average grain sizes are consistent with those found for Zircaloy-4 monoclinic and tetragonal phases in previous work and are consistent with TEM observations as well [13, 17].
Figure 3.15 – Grain size for the monoclinic and tetragonal oxide phases calculated using the Debye-Scherrer equation as a function of distance from the oxide-metal interface for samples (A) N2511 and (B) L1581.

In both samples smaller monoclinic oxide grain sizes are seen near (2-3 µm) the oxide-metal interface. A decrease in grain size of approximately 5 nm is visible in both the
(111)\textsubscript{M} and (020)\textsubscript{M} peaks. The tetragonal phase does not appear to change size with proximity to the oxide-metal interface in L1581, and only very slightly in N2511. The width of the monoclinic peaks shows a broadening with proximity to the oxide-metal interface, which corresponds to a decrease in grain size. This observation is consistent with oxide grains being constantly nucleated near the oxide-metal interface.

There is a notable spread in the apparent grain size indicated by the various monoclinic peaks examined in both samples. In general it seems that the (020)\textsubscript{M} indicates the smallest grain size and either the (011)\textsubscript{M} or the (111)\textsubscript{M} the largest, with a difference between the two of roughly 4-5 nm. This is consistent with our FWHM results that show a similar spread, with the peaks that show a larger grain size having a smaller FWHM than those that show a smaller grain size. We can also observe a difference of 2-3 nm in the grain sizes calculated using the FWHM of the (020)\textsubscript{M} and (002)\textsubscript{M} peaks. This observation seems to indicate that there is a difference in the monoclinic column width in two different directions. While a slight difference between the two directions does exist in the monoclinic unit cell, we would not expect such a large difference in grain size based on this alone. Our observations may be a result of strain causing non-uniform broadening between the (020)\textsubscript{M} and (002)\textsubscript{M} peaks that has been incidentally accounted for as size broadening as explained previously.

A significant difference is observed in the calculated monoclinic grain size between samples N2511 and L1581. Table 3.3 shows a comparison between the average grain size calculated from each peak and phase shown in Figure 3.15. We can see that the monoclinic oxide grains in sample L1581 are in all cases larger than those in sample N2511. The
The difference in size is roughly 4-5 nm, or 15-25% difference depending on the plane used to make the calculation. Since both samples were Zircaloy-4 of similar composition and fabrication, the most likely reason for the difference in grain size is the corrosion conditions. Sample N2511 was corroded at 600 °F for roughly 3100 days, while sample L1581 was corroded at 680 °F for roughly 1200 days. The higher temperature may have caused L1581 to develop larger oxide grains while the lower temperature and much longer exposure time could have allowed a finer oxide structure to develop on N2511. Interestingly the tetragonal grain size is similar in both samples at approximately 9 nm, perhaps indicating that the tetragonal grains are stabilized only to a certain maximum size at which point they will cease to grow or will transform into the monoclinic phase [17].

Table 3.3 – Comparison of the monoclinic and tetragonal grain size averaged over the bulk oxide (excluding the region near the oxide-metal interface) calculated using the Debye-Scherrer formula for samples N2511 and L1581.

<table>
<thead>
<tr>
<th>Oxide Peak</th>
<th>Grain Size (nm)</th>
<th>Difference (nm)</th>
<th>% Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>N2511</td>
<td>L1581</td>
<td></td>
</tr>
<tr>
<td>(011) M</td>
<td>20.7</td>
<td>25.1</td>
<td>4.5</td>
</tr>
<tr>
<td>(-111) M</td>
<td>17.9</td>
<td>21.6</td>
<td>3.7</td>
</tr>
<tr>
<td>(101) T</td>
<td>9.3</td>
<td>9.5</td>
<td>0.2</td>
</tr>
<tr>
<td>(111) M</td>
<td>20.3</td>
<td>24.1</td>
<td>3.8</td>
</tr>
<tr>
<td>(020) M</td>
<td>15.5</td>
<td>19.8</td>
<td>4.3</td>
</tr>
</tbody>
</table>
3.2 Residual Stress Determination using 3-D Laue X-Ray Diffraction

The 3-D x-ray microscope at beamline 34-ID-E was used to measure elastic strains induced in the metal by oxide growth in Zircaloy-4 and crystal bar zirconium samples and to make qualitative observations on the nature of plastic strain in the metal substrate caused by oxide growth or other means.

3.2.1 Origins of Stress Accumulation

The oxide grown on zirconium and Zr alloys occupies a larger volume than the metal it consumes. The Pilling-Bedworth ratio of ZrO$_2$ (defined as $V_{\text{oxide}}/V_{\text{metal}}$) is 1.56, meaning that the volume of the oxide is 56% greater than the volume of the metal consumed to create it. As stated previously, since the oxide remains adherent to the metal substrate the volume change must be accommodated in some way. Most of the volume change occurs in the oxide growth direction (perpendicular to the metal surface); however a small fraction of this volume expansion occurs in the in-plane direction. The lateral oxide expansion is constrained by the metal substrate which induces a stress in the oxide layer. Since the oxide expansion is restricted by the metal the oxide layer is put into compression, and the metal substrate into tension. It is important to assess the stress accumulation in the oxide during growth, as the oxide transition has been associated with stress accumulation [13, 27, 30].
3.2.2 Zirconium Alloy Laue Patterns

A sample Laue pattern from a bare metal Zircaloy-4 sample is shown in Figure 3.16(A). The indexing of this Laue pattern is shown in Figure 3.16(B). The pattern illustrates the six prism planes along with the single basal reflection. Other reflections are also visible on the Laue pattern, which may originate from other grains beneath the surface layer. The basal reflection (labeled as 002 in 3.16(B)) is just slightly off-center in the diffraction pattern, which means that the grain is oriented in such a way that its basal plane normal direction is nearly aligned with the sample surface normal.

Figure 3.16a – Laue pattern taken from a bare metal Zircaloy-4 sample showing the raw Laue reflections.
Figure 3.16b – Indexing of the Laue pattern shown in Figure 3.16a illustrating the basal, prism, and pyramidal planes in the hcp Zr base metal structure.

Using such diffraction patterns and the procedures described in Section 2.3.2, it was possible to determine elastic strain and stress in the metal substrate and relate it to the stress in the oxide layer.
3.2.3 Determination of Oxide-Growth Induced Elastic Strain and Stress

Elastic strains in the metal substrate were measured using the technique previously described in Chapter 2. Since this technique requires large grains it was not possible to measure strains directly from the oxide due to the extremely small size of the oxide grains. However since the elastic energy stored in the metal should match that stored in the oxide, the technique allowed us to indirectly determine the oxide stress. There were some difficulties in separating the strains induced by oxide growth from other strain-inducing effects such as residual manufacturing stresses and differential thermal expansion after cooling from corrosion temperatures. Our efforts to account for these extra effects will be detailed in later sections.

The strain is measured through a change in the d-spacing of a particular plane, as compared to the unstrained value. Because of the geometry of corrosion, the ideal planes to measure a change in d-spacing would be those oriented perpendicular to the induced stress direction. However we were limited in this instance, by sample and experimental setup geometry to studying planes whose normal vectors were oriented within 15 degrees of the sample surface normal direction. As a result, the strains measured by the technique result from Poisson’s effect. As illustrated in Figure 3.17 an in-plane stress (such as the type caused by restricted lateral oxide expansion) applied to a metal grain with normally oriented basal planes will affect the (0002) d-spacing. A tensile stress will result in a smaller (0002) d-spacing, since the prism planes being pulled apart will cause a contraction of the grain in the (0002) direction by Poisson’s effect, as illustrated. A compressive stress would have the opposite effect, causing an elongation in the (0002) direction and a larger (0002) d-spacing.
The same d-spacing change can also be seen in normally oriented prism planes, although correctly oriented prism planes are less common due to texture. We chose to use the (0002) basal plane of the HCP zirconium as the primary reflection for measurements in our experiments. The basal reflections are easy to identify on the Laue patterns and due to the texture of the Zircaloy-4 and zirconium samples there were an ample number of grains with the proper orientation for examination.

Figure 3.17 – Schematic representation of the effect of oxide growth on generalized stress in the oxide and metal layers and of the change in the d-spacing of normally oriented basal planes when subjected to an in-plane tensile stress, through Poisson’s effect.
3.2.4 Elastic Stress Determination as a Function of Sample Depth

Using 3-D reconstruction software at beamline 34-ID-E and a special Igor® software package created for this specific purpose by beamline scientists we were able to determine d-spacing (correlated with elastic strain) as a function of depth into the metal. The raw data from the experiment is initially plotted as a value denoted as Q (nm⁻¹), which is inversely related to the d-spacing according to:

\[ d = \frac{2\pi}{Q} \quad \text{(Eq. 3.3)} \]

All of the data shown in the following sections has been converted from Q to d-spacing during post-experiment data analysis. The strain can be calculated from the difference in measured d-spacing, compared to an unstressed baseline value \( d_0 \).

\[ \varepsilon = \frac{d - d_0}{d_0} \quad \text{(Eq. 3.4)} \]

Out-of-plane strains can be connected to in-plane strains through Poisson’s ratio. If the out-of-plane strain is noted as \( \varepsilon_{OP} \), the in-plane strain as \( \varepsilon_{IP} \), and Poisson’s ratio as \( \nu \), the relationship between the two strains is;

\[ \nu \varepsilon_{OP} = -\varepsilon_{IP} \quad \text{(Eq. 3.5)} \]

The strain can then be used to calculate the stress via Hooke’s Law, \( \sigma = E \varepsilon \), where \( \sigma \) is the stress, \( E \) is Young’s modulus, and \( \varepsilon \) is the strain.

Acquiring a reliable standard for the unstrained value of the lattice parameters and planar d-spacing values (\( d_0 \)) is critically important to this method of stress/strain...
determination. While the lattice parameters for zirconium metal are well documented, those for Zircaloy-4 are not and can even change between manufacturing heats. The alloying elements in Zircaloy-4 create changes in the zirconium lattice dimensions that are large enough to cause a significant difference in the calculated strains when pure zirconium lattice parameters are substituted instead. Measurements taken from a single sample of Zircaloy-4 used in this study gave a calculated c-direction lattice parameter and basal plane (0001) d-spacing of 5.151 Å as compared to a basal plane d-spacing of 5.148 Å for pure zirconium. The equipment currently available at the beamline is capable of measuring changes in d-spacing on the order of $10^{-3}$ Å, so even the small difference between zirconium and Zircaloy-4 is measurable and noticeable in the data and must be accounted for. The same is true for planes of any other orientation, although we did not make lattice parameter or d-spacing measurements in Zircaloy-4 for any planes beyond the basal. Note that the grain size of the Zircaloy-4 studied was on the order of 20 microns, suggesting that the entire grain diameter was captured in the depth scans.

3.2.4.1 Bare Metal Zircaloy-4 Elastic Strains

Bare metal Zircaloy-4 was examined to establish a baseline for any potential residual strains in the matrix that would be present before corrosion. Normally we would expect there to be no strain in the bare metal grains since these grains were prior stress relieved at high temperature after fabrication (if no internal stresses remain) and no oxide layer is present yet.
**Figure 3.18** shows a d-spacing versus depth plot (also referred to as an energy-wire scan or a strain-depth plot) for bare metal Zircaloy-4 sample H1393J. In this figure the sample surface is indicated, and information can be obtained to 25 µm depth and beyond, as shown. The horizontal dotted line indicates the unstrained d-spacing for the (0002) plane in Zircaloy-4 (a measured (0001) d-spacing of 5.151 Å yields an (0002) d-spacing of 2.5755 Å). The curve aligns well with the calculated unstrained d-spacing, suggesting little residual stress. The curve is relatively flat throughout the entire depth probed, meaning that the grain examined remains unstrained to a depth of 25 µm below the sample surface.

Strain-depth analyses were repeated in multiple grains within the same bare metal sample, all with similar results: every curve aligns well with the calculated unstrained d-spacing value and the curves remain flat with depth. This is illustrated in **Figure 3.19**, which shows the results of strain-depth measurements from four different grains in bare metal Zircaloy-4. The horizontal dotted line again indicates the calculated unstrained (0002) d-spacing.

A baseline stress of a few MPa can be calculated from the bare metal strain d-spacing-depth measurements using equations 3.4 and 3.5. Prior studies have measured residual strains in both Zircaloy-2 and Zircaloy-4 of up to 100 MPa [40, 41]. As such we expect there to be some residual strains present as a result of the manufacturing process.
Figure 3.18 – D-spacing versus depth as measured using the (0002) plane in unoxidized bare metal Zircaloy-4. The horizontal dotted line indicates the calculated unstrained d-spacing of 2.5755 Å.

Figure 3.19 – D-spacing versus depth in four separate grains in bare metal Zircaloy-4 measured using the (0002) plane. The horizontal dotted line indicates the calculated unstrained d-spacing of 2.5755 Å.
Note that the zero mark on the depth axis is arbitrary*, and does not correspond to the location of the sample surface (*the zero mark is actually based on the wire scan range so it is not entirely arbitrary, but can be considered arbitrary with respect to the d-spacing measurement). Since multiple reflections were usually visible in the Laue patterns it was important that we verified that the reflection we selected was indeed from a crystallite located at the sample surface. Measuring any strains from a grain not at the surface would not reflect the influence of the oxide layer and thus would not be valid for our analysis. A wire scan of the reflection intensity as a function of depth using polychromatic radiation was performed to determine the location of the sample surface. This procedure was performed for each reflection analyzed, and all strain-depth results reported in the previous and following sections have been verified to be from grains at the sample surface, regardless of their starting value on the depth axis.

3.2.4.2 Oxidized Zircaloy-4 Elastic Strain at Room Temperature

The elastic strains induced by oxide growth were measured in Zircaloy-4 at room temperature using the previously described technique of differential scanning aperture 3-D x-ray microscopy. Four different Zircaloy-4 samples with varying oxide thickness were examined in this fashion. The oxidized Zircaloy-4 samples examined were labeled H1405J, H1406J, H1413J, and H1372J and their characteristics are listed in Table 2.1. A composite of the complete d-spacing-depth measurement data for these samples is shown in Figure 3.20. Note that, while most of the measurements are for separate grains in the same sample, the
two shown for H1372J are from different points within the same grain. Again the basal plane was used to measure the change in d-spacing with depth through the (0002) or (000 10) planes as marked. The unstrained d-spacing value has been marked with a horizontal dotted black line. As noted earlier all of the grains shown were confirmed to be at the sample surface and are thus considered to reflect the stress/strain in the oxide.

Figure 3.20 has been arranged using a new parameter created for this study designated as $\gamma$ (gamma) that is presented as a measure of how close the oxide layer is to transition (also referred to as the oxide transition parameter in later sections). It is calculated by dividing the difference between the current oxide thickness and the previous transition oxide thickness by the average transition thickness for Zircaloy-4. A gamma value near zero indicates the oxide has just undergone transition, and a gamma value approaching 1 indicates that the oxide is nearing its next transition. A sample calculation of the gamma value for sample H1372J (3.25 µm oxide) is shown below assuming a transition thickness of 1.8 µm.

$$\gamma_{H1372J} = \frac{(3.25 \mu m - 1.8 \mu m)}{1.8 \mu m} = 0.81$$
Figure 3.20 – D-spacing-depth measurements taken in Zircaloy-4 at room temperature. The curves correspond to data from the following samples: (A-B) H1406J grains 1-2, (C-D) H1413J grains 1-2, (E-F) H1405J grains 1-2, (G) H1372J grain 1 spot 1, (H) H1372J grain 1 spot 2. The unstrained d-spacing \( d_0 \) is marked on each curve by a dotted black line.

The effect of oxide growth on the elastic strain state in the metal can be clearly seen in Figure 3.20. A perturbation in the d-spacing profile is visible in each of the curves to some degree at or near the sample surface. The degree of perturbation varies significantly, both between grains in a single sample and between samples of different oxide thickness. One
common feature that appears in five of the eight curves shown is an initial low in the d-spacing that is followed by an increase over a distance of 3-5 µm where the d-spacing approximately reaches the unstrained value. This feature is illustrated in Figure 3.20 (A,C,F,G,H) and highlighted specifically in **Figure 3.21**.

![D-spacing--depth plot](image)

Figure 3.21 – D-spacing--depth plot taken from a basal oriented grain in Zircaloy-4 sample H1372J showcasing the effect of the oxide layer on the d-spacing profile with depth.

The feature highlighted in Figure 3.21 shows approximately the stress/strain state that would be expected to be caused by the growth of an oxide layer in compression, thus putting the metal layer in tension. The initial d-spacing is below the unstrained value, indicating that the basal plane d-spacing was reduced by some mechanism. Since there is no force applied directly normal to the basal planes, this movement must be due to Poisson’s effect through a response to strain of the prism planes in the lateral direction. This was a common repeating feature seen in the majority of our measurements. As such, we can infer that a lateral tensile stress in the metal is present, with a possibility for variation depending on local conditions.
Some features visible in Figure 3.20 are not consistent from grain to grain and do not align with our expected outcomes. A slight compressive stress in the metal appears to be indicated by the curve in Figure 3.20 (E). This plot shows a higher d-spacing than the unstrained value measured in the unoxidized condition, suggesting that the basal planes parallel to the sample surface have been stretched apart through Poisson’s effect in response to compression of the prism planes. This effect seems to be nearly the exact opposite of the one in Figure 3.20 (F) from a different grain in the same sample which shows the expected tensile stress state in the metal. The curves shown in Figure 3.20 (B,D) do not appear to show the oxide perturbation seen in several other measurements. While some level of strain is indicated, it appears to affect the entire depth of the grain instead of just the surface.

The variation in strain within an individual or sample or grain may be due to local effects of the oxide-metal interaction rather than the result of a far-field stress. In an effort to explain the scalloped shape of the oxide-metal interface, Hutchinson et al. [30] proposed a mechanism whereby the metal adjacent to the protruding regions of oxide is in a state of high localized tension while the metal at the cusps is in a high state of compression. If this mechanism is correct we could measure a tensile stress at one location in the metal and a compressive stress at another. Based on our SEM observations, the diameter of the cusped and scalloped regions is approximately 2-3 µm (for Zry-4 in oxides of similar thickness to those shown here). This means that if the shape of the oxide-metal interface can influence the local stress state at the oxide-metal interface, we could easily measure two different stress states, given the small size of the x-ray beam. However, the level of compressive
stress in the metal at the cusps may simply lower the local tensile stress rather than counteract and override it depending on the exact stress value.

Anisotropy in the zirconium matrix may also play a part in local variations in stress levels. Figure 3.22 shows an orientation grain map from a 200 µm x 200 µm area in Zircaloy-4 sample H1372J and its associated (0001) pole figure. Note that the colors in the pole figure correspond to those in the grain orientation map (for example, the blue grain highlighted in the figure). The orientation map was created by recording a polychromatic beam Laue pattern at 2 µm increments in a grid, and then indexing the Laue spots for orientation as described and shown in Section 3.2.2. Although a broad range of grain orientations are shown, the majority of grains are aligned within 15-30 degrees of the (0001) pole, as expected for this sample texture. However this variety of grain orientations, coupled with the anisotropic properties of the HCP Zr matrix could lead to neighboring grains reacting very differently to laterally applied stress. Further study on the strain tensors of the individual grains shown in Figure 3.22 is necessary before we can make a definitive conclusion on the potential effects of neighboring grains.
Figure 3.22 – Grain orientation map and its associated (0001) pole figure for a 200 µm x 200 µm region in Zircaloy-4 sample H1372J.

There are other features in Figure 3.20 that may not be associated with oxide growth effects. In Figure 3.20 (B,G) we see a sizable gap midway through the d-spacing profile associated with a sharp decrease in the d-spacing followed by a sharp jump to approximately the unstrained value. This feature may be associated with a grain boundary, although the fact that the d-spacing profile continues for another 10 micron or more in depth means that the underlying grain would have to have nearly the same orientation as the surface grain (which seems unlikely). There may be dislocations present at the depth of the gap, as missing or stretched planes would cause a similar effect on the measured d-spacing as stress-induced strain effects.

The curve in Figure 3.20 (C) appears to show a compressive stress through a higher d-spacing at the sample surface, followed by a tensile stress slightly deeper into the metal. We
currently have no clear explanation for how the two stresses could be present in the same grain at similar depths in the metal.

### 3.2.4.3 Determination of Stress in Oxidized Zircaloy-4 at Room Temperature

The stress in the metal can be calculated by using equations 3.4 and 3.5. The maximum deviation from the unstrained value in each strain-depth curve was manually extracted in order to calculate the stress. An example of the point where the d-spacing was extracted from is shown in Figure 3.23.

![Figure 3.23](image.png)

**Figure 3.23** – Plot of d-spacing versus depth for Zircaloy-4 sample H1405J showing the location of the minimum d-spacing used to calculate the stress in the metal.

**Table 3.4** shows the calculated strain and stress in the metal for bare metal and oxidized Zircaloy-4, using the d-spacing taken from each curve, as shown in Figure 3.19 and Figure 3.20. Negative values denote a compressive stress and positive values a tensile stress.
The out-of-plane stresses were calculated directly from the strain, while the in-plane stresses were calculated using the out-of-plane stresses modified by Poisson’s ratio (ν=0.3) following equation 3.5. The oxide transition parameter γ (as detailed in Section 3.2.4.2) indicating how close the oxide on each sample is to transition is also shown.

Table 3.4 – Calculated strains and stresses in the metal substrate for bare and oxidized Zircaloy-4 at room temperature.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Oxide Thickness (µm)</th>
<th>Out-of-plane Strain</th>
<th>Out-of-plane Stress (MPa)</th>
<th>In-plane Stress (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H1393Jγ0</td>
<td>0.00</td>
<td>2.72E-04</td>
<td>-34</td>
<td>-10</td>
</tr>
<tr>
<td></td>
<td>0.00</td>
<td>1.16E-04</td>
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<td>0.00</td>
<td>2.33E-04</td>
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</tbody>
</table>

The most noticeable effect in Table 3.4 is the large difference seen in the stress accumulation for the last sample H1372J as compared to the other samples. Assuming a model in which stress accumulates before transition and is released on transition, one would expect a large value of the oxide transition parameter γ to be associated with a larger stress.

As was evident from the d-spacing-depth curves, a mixture of compressive and tensile stress states can be seen. Additionally, some variation of stress in oxidized samples could be due to local stress relief mechanisms such as cracking. Our expectations were that
the stress would increase until reaching a maximum value just before the oxide transition, at which point it would be relieved and begin to accumulate again [7, 8, 20, 42].

We observe in-plane stresses in the metal of roughly 40 MPa in a pre-transition oxide just over 1 micron thick, and then stresses as low as 9 MPa in a post-transition 2 micron oxide. However the stress does not appear to increase significantly between 2 and 2.63 micron, with stresses of approximately 20 MPa calculated in the thicker oxide. In contrast, high in-plane tensile stresses of approximately 120 MPa were calculated in the 3.25 micron oxide sample H1372J. Assuming a 1.8 µm transition thickness, this sample should be near a second transition. These observations seem to support our expectations of stresses given a certain thickness of oxide; however these conclusions should be considered carefully because of the paucity of data. Additional measurements in individual samples may be necessary to discern a clearer picture of stress accumulation as a function of oxide thickness.

Figure 3.24 shows the calculated in-plane stresses as presented in Table 3.4 plotted as a function of oxide thickness. Positive stress values indicate tension while negative values indicate compression, and the vertical red line indicates the Zircaloy-4 oxide transition thickness.
Figure 3.24 – Calculated in-plane stresses in the metal at the oxide-metal interface in oxidized Zircaloy-4 as a function of oxide thickness. The red line indicates the oxide transition thickness for Zircaloy-4.

As stated previously, our expectations are that the level of accumulated stress will depend on how near the oxide layer is to its next transition, rather than the overall oxide thickness. As such, instead of plotting the calculated stress against the oxide thickness, we can plot it against the oxide transition parameter $\gamma$ to better view the stress accumulation as a function of proximity to the next oxide transition. **Figure 3.25** shows the same calculated in-plane stresses as presented in Table 3.4 and Figure 3.24, but plotted against the oxide transition parameter $\gamma$, which is a measure of how near the current oxide layer is in thickness to its next transition (for example, an oxide with $\gamma=0.5$ is halfway between its last transition and its next, and will need to grow an additional 50% of the transition thickness before it undergoes the next oxide transition).
Figure 3.25 shows that the accumulated stress increases as the oxide approaches transition. The stress does not appear to change substantially from the residual bare metal stresses until the oxide exceeds half of the transition thickness. A significant increase in the stress can then be observed, with a maximum stress in the oxide nearest to transition.

Figure 3.25 – Calculated in-plane stresses in the metal at the oxide-metal interface in oxidized Zircaloy-4 as a function of the proximity of the current oxide layer thickness to its next transition. Gamma values near zero indicate the oxide has just undergone transition and values approaching 1 indicate the oxide is nearing its next transition.

Knowing the stress in the metal allows us to calculate the stress in the oxide through a simple energy balance calculation. Per unit volume, the energy content (N-m) of the volume of oxide should equal that of the affected metal. The oxide stress can be calculated through the following formulation:

\[
(\sigma \times V)_{oxide} = (\sigma \times V)_{metal} \quad \text{(Eq. 3.6)}
\]
If we assume an area of 1 cm$^2$ for both volumes we can expand the formula and solve for the oxide stress:

$$1 \, cm^2 \times \delta \times \sigma_{oxide} = \sigma_{metal} \times 1 \, cm^2 \times depth \quad (Eq. \, 3.7)$$

Where $\delta$ is the oxide thickness and depth is the depth of the metal affected. Eliminating the areas and solving for oxide stress we obtain a simple formulation for the oxide stress based on the ratio of the oxide thickness to metal thickness.

$$\sigma_{oxide} = \frac{depth}{\delta} \sigma_{metal} \quad (Eq. \, 3.8)$$

The ratio of depth of investigation to oxide thickness for each oxidized Zircaloy-4 sample is shown in Table 3.5. The depth of interaction in the metal is a variable that could significantly alter the calculation if not accounted for properly. Based on the results of our d-spacing-depth measurements, we assumed that the interaction depth was the depth range in which we observed the oxide perturbation. This range covered approximately 4 µm for each sample examined. We did not use the entire depth probed by each measurement since the d-spacing-depth data indicated very little stress was present in the metal past the several micron near the surface.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Oxide Thickness (µm)</th>
<th>Depth (µm)</th>
<th>Depth Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>H1406J</td>
<td>2.09</td>
<td>4.5</td>
<td>2.15</td>
</tr>
<tr>
<td>H1413J</td>
<td>2.63</td>
<td>3.5</td>
<td>1.33</td>
</tr>
<tr>
<td>H1405J</td>
<td>1.14</td>
<td>4</td>
<td>3.51</td>
</tr>
<tr>
<td>H1372J</td>
<td>3.25</td>
<td>4.5</td>
<td>1.38</td>
</tr>
</tbody>
</table>
The calculated oxide stresses are shown in Table 3.6. We can see that the in-plane stress in the oxide layer is on the order of a few hundred MPa or less. These values agree with previously studies which measured average oxide stresses of 0.2-2 GPa, and up to 5 GPa in some very thin films [42-44]. In thick films such as the ones used during this study, Kim et al. predicted compressive stresses of approximately 2 GPa, which increase with proximity to the oxide-metal interface [42]. Despite the mixture of compression and tension seen in individual metal grains, the oxide stress state should be compressive, as it has been well established in the literature [16, 20, 42, 43]. Our own observations show a majority of measurements indicating a tensile stress in the metal as well, leading to a compressive stress in the oxide.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Oxide (µm)</th>
<th>Metal Strain</th>
<th>OP Metal Stress (MPa)</th>
<th>OP Oxide Stress (MPa)</th>
<th>IP Metal Stress (MPa)</th>
<th>IP Oxide Stress (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H1406J</td>
<td>2.06</td>
<td>-8.54E-04</td>
<td>107</td>
<td>-230</td>
<td>32</td>
<td>-69</td>
</tr>
<tr>
<td></td>
<td>2.06</td>
<td>2.33E-04</td>
<td>-29</td>
<td>63</td>
<td>-9</td>
<td>19</td>
</tr>
<tr>
<td>H1413J</td>
<td>2.63</td>
<td>-7.77E-04</td>
<td>97</td>
<td>-129</td>
<td>29</td>
<td>-39</td>
</tr>
<tr>
<td></td>
<td>2.63</td>
<td>7.77E-04</td>
<td>-97</td>
<td>129</td>
<td>-29</td>
<td>39</td>
</tr>
<tr>
<td>H1405J</td>
<td>1.14</td>
<td>1.51E-03</td>
<td>-189</td>
<td>664</td>
<td>-57</td>
<td>199</td>
</tr>
<tr>
<td></td>
<td>1.14</td>
<td>-1.28E-03</td>
<td>160</td>
<td>-562</td>
<td>48</td>
<td>-169</td>
</tr>
<tr>
<td>H1372J</td>
<td>3.25</td>
<td>-3.40E-03</td>
<td>425</td>
<td>-588</td>
<td>127</td>
<td>-176</td>
</tr>
<tr>
<td></td>
<td>3.25</td>
<td>-3.18E-03</td>
<td>398</td>
<td>-551</td>
<td>119</td>
<td>-165</td>
</tr>
</tbody>
</table>
3.2.4.4 Effect of Temperature on Stress Accumulation

Differential thermal contraction between the oxide and the metal may have a significant effect on the stress states of the oxide and metal at room temperature. Every sample examined during this study was corroded at temperatures above 300 °C (with the natural exception of uncorroded material). Since the corrosion process occurs at a spatially uniform high temperature, we can assume that the oxide is formed in a thermally unstressed state. Once the autoclave is turned off and the sample is allowed to cool, differential cooling between the metal and oxide could induce thermal stresses in the sample that were not present during corrosion. The average thermal expansion coefficient of the oxide layer is higher than that of the matrix ($\alpha_{mZrO_2} = 7.8 \times 10^{-6} \ K^{-1}$ for the monoclinic phase and $\alpha_{Zr} = 6.0 \times 10^{-6} \ K^{-1}$ [3]). Based on these average values we expect the oxide to contract more than the metal on cooling. However the thermal expansion of the HCP Zr matrix is very different between the basal and prism directions, with $\alpha_c = 12.6 \times 10^{-6} \ K^{-1}$ and $\alpha_a = 4.95 \times 10^{-6} \ K^{-1}$ [3]. The oxide layer also contains a small percentage of the tetragonal phase, which has a significantly higher thermal expansion coefficient with $\alpha_{tZrO_2} = 13.02 \times 10^{-6} \ K^{-1}$ [3].

Even though the average thermal expansion coefficient of the Zr matrix is quite different from that of the $a$ and $c$ directions, the average value should be sufficient for our analysis. The texture of the metal is such that the majority of grains have their basal poles aligned within 30° of the sample surface normal, meaning that most of the basal contraction will be accommodated vertically, and the majority of the lateral contraction will follow the prism plane thermal behavior, which is closer to the average value than the $c$-direction
values. In the oxide, the tetragonal ZrO$_2$ properties can be ignored as well, since the tetragonal fraction constitutes on average only a few percent of the oxide layer and the grain size is much smaller than that of the monoclinic phase.

With these assumptions, and using the average values of the thermal expansion coefficient for the metal and oxide, the oxide should be expected to contract more than the metal substrate. Any contraction in the lateral direction would be in direct opposition of the attempted growth expansion of the oxide. This effect could alter the overall stress state and must be accounted for in some manner. Our attempts to measure strains at high temperature to negate any potential thermal effects will be discussed in more detail in a coming section.

### 3.2.4.5 Oxidized Zircaloy-4 Elastic Strain and Stress at High Temperature

In an attempt to address the potential effects of stresses induced by thermal contraction mismatch during cooling from corrosion temperatures, d-spacing-depth measurements were performed on Zircaloy-4 samples while heated in-situ back to the corrosion temperature where the oxides were formed. High temperature measurements were taken at identical locations as room temperature measurements in sample H1372J (3.25 µm oxide). Two different locations within the same grain in H1372J were compared between room and high temperature. In this section, high temperature (HT) refers to the corrosion temperature of 680 °F (360 °C) and room temperature (RT) refers to ambient temperature of approximately 73 °F (23 °C).
The results of d-spacing-depth measurements taken at high temperature are shown in Figure 3.26 and compared to the curves taken at the same locations at room temperature. At this temperature the average metal lattice spacing has increased to roughly 5.16 Å following the Zircaloy-4 thermal expansion coefficient. The effects of the oxide layer are still clearly visible at high temperature at both locations in sample H1372J. The perturbation from the oxide layer appears largely in the same fashion as at room temperature. Comparing Figure 3.26 (A) and (B) we can see that although the high temperature curve retains the oxide perturbation, it actually appears smoother than the room temperature curve. The large gap in the curve is now replaced by a smooth transition from a low d-spacing to a constant higher value just under the calculated unstrained d-spacing at this temperature. This may be an effect of some relaxation of strains present at room temperature. The curves in Figure 3.26 (C) and (D) very closely resemble one-another. A large oxide perturbation is visible in both, beginning with a low d-spacing and increasing to nearly the same shape to just below the unstrained value.
Figure 3.26 – Comparison between D-spacing-depth measurements taken in Zircaloy-4 sample H1372J at room temperature and high temperature. Room temperature plots (A,C) correspond to their high temperature counterparts (B,D) to the right.

The effects of thermal expansion can be seen in both high temperature measurements. The measured d-spacing deep in the metal corresponds to the calculated unstrained value at temperature to approximately the same degree as room temperature measurements indicate. However the exact value of the unstrained d-spacing at high temperature is uncertain. Due to texture variations, the thermal response of zirconium and its alloys can be variable. The Department of Energy (DoE) database MATPRO [3] offers thermal expansion correlations for single-crystal Zircaloy-4 that cover a wide range of temperatures. We found that the thermal expansion coefficients given there did not match well with our data, greatly over-predicting the basal plane thermal response. Since temperature-specific data is not widely available for Zircaloy-4, and correlations in the literature [45] showed the average thermal expansion coefficient of Zircaloy-4 to be similar to that of pure zirconium, we chose to use the thermal expansion coefficient of pure Zr in the
c-direction to calculate the unstrained Zircaloy-4 d-spacing at high temperature. Godlak et al. [46] provided a value of $\alpha_c = 9.97 \times 10^{-6} K^{-1}$ at 600 K for pure zirconium, which was used in conjunction with (0001) d-spacing values of $d = 5.151 \text{ Å}$ for Zircaloy-4 and $d = 5.148 \text{ Å}$ for zirconium to calculate the unstrained d-spacing at high temperature. These values are summarized in Table 3.7.

Table 3.7 – Room temperature and high temperature (0001) basal plane d-spacing values for zirconium and Zircaloy-4. The thermal expansion coefficient is given for a temperature of 600 K.

<table>
<thead>
<tr>
<th></th>
<th>$\alpha_c (K^{-1})$</th>
<th>Room temp. d-spacing (Å)</th>
<th>High temp. d-spacing (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zirconium</td>
<td>$9.97 \times 10^{-6}$</td>
<td>5.148</td>
<td>5.161</td>
</tr>
<tr>
<td>Zircaloy-4</td>
<td>$9.97 \times 10^{-6}$</td>
<td>5.151</td>
<td>5.1681</td>
</tr>
</tbody>
</table>

Stresses in the metal at high temperature can be calculated using a similar procedure as used to find stress at room temperature. The minimum d-spacing in the high temperature curves in Figure 3.26 was recorded and used to calculate strain, which was then used with Hooke’s Law to calculate the stress. The calculated in-plane stresses at high temperature in Zircaloy-4 sample H1372J are shown in Figure 3.27 alongside the room temperature results presented earlier. Three different locations were examined (two with room temperature counterparts, one without). We can see that the stresses at high temperature are less than those at room temperature at all three locations. A comparison of the room temperature and high temperature stresses along with their associated oxide stresses (as calculated by volumetric energy balance described earlier) in H1372J is shown for out-of-plane stresses in Table 3.8, and in-plane stresses in Table 3.9. An in-plane stress relaxation of almost 75 MPa
can be seen at one location, and a 30 MPa relaxation at the second. Without a room temperature counterpart we cannot see any stress relaxation in the third spot, however the in-plane stress calculated is the lowest of the three at 36 MPa.

![Figure 3.27 – Calculated in-plane stresses in the metal at the oxide-metal interface at room temperature and high temperature as a function of oxide thickness.](image)

Table 3.8 – Comparison of out-of-plane stresses at room temperature and high temperature at each HT location examined in Zircaloy-4 sample H1372J. Location 3 does not have a room temperature counterpart.

<table>
<thead>
<tr>
<th>Location</th>
<th>Metal RT Stress (MPa)</th>
<th>Metal HT Stress (MPa)</th>
<th>Δσ</th>
<th>Oxide RT Stress (MPa)</th>
<th>Oxide HT Stress (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>425</td>
<td>178</td>
<td>-247</td>
<td>588</td>
<td>247</td>
</tr>
<tr>
<td>2</td>
<td>398</td>
<td>289</td>
<td>-109</td>
<td>551</td>
<td>400</td>
</tr>
<tr>
<td>3</td>
<td>-</td>
<td>121</td>
<td>-</td>
<td>-</td>
<td>167</td>
</tr>
</tbody>
</table>
Table 3.9 – Comparison of in-plane stresses at room temperature and high temperature at each HT location examined in Zircaloy-4 sample H1372J. Location 3 does not have a room temperature counterpart.

<table>
<thead>
<tr>
<th>Location</th>
<th>Metal RT Stress (MPa)</th>
<th>Metal HT Stress (MPa)</th>
<th>$\Delta \sigma$</th>
<th>Oxide RT Stress (MPa)</th>
<th>Oxide HT Stress (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>127</td>
<td>54</td>
<td>-73</td>
<td>176</td>
<td>74</td>
</tr>
<tr>
<td>2</td>
<td>119</td>
<td>87</td>
<td>-32</td>
<td>165</td>
<td>120</td>
</tr>
<tr>
<td>3</td>
<td>-</td>
<td>36</td>
<td>-</td>
<td>-</td>
<td>50</td>
</tr>
</tbody>
</table>

As an estimate of how much stress we might expect to relax due to thermal expansion mismatch we can perform a calculation for the elastic mismatch in a symmetric bilayer as outlined by Cai et al. [47]. Our samples can be considered a symmetric bilayer as the oxide is grown uniformly on both sides of the corrosion coupon in an isothermal environment. As given by Cai et al. the formula for the biaxial elastic stress in a symmetric laminate is as follows:

$$\sigma_1 = \left(\frac{1}{1+mn_e}\right)\left(\frac{E_1}{1-\nu_1}\right)\Delta \varepsilon \quad \text{(Eq. 3.9)}$$

where $\Delta \varepsilon = (\varepsilon_2 - \varepsilon_1)$ is the elastic strain mismatch, $E_1$ and $\nu_1$ are the elastic modulus and Poisson’s ratio of layer 1, and $m$ and $n_e$ are the layer thickness ratio and the layer modulus ratio given by;

$$m = \frac{h_1}{h_2} \quad \text{(Eq. 3.10)}$$

and

$$n_e = \left(\frac{E_1}{1-\nu_1}\right)\left(\frac{1-\nu_2}{E_2}\right) \quad \text{(Eq. 3.11)}$$

For our case the zirconium metal is defined as ‘layer 1’ and the oxide as ‘layer 2’. Using a metal thickness of 800 µm and oxide thickness of 3.25 µm we find $m = 246.15$. The elastic
modulus of the metal and oxide were found in MATPRO as \( E_{\text{metal}} = 92.4 \, \text{GPa} \) and
\( E_{\text{oxide}} = 152.4 \, \text{GPa} \), with a Poisson’s ratio of \( \nu = 0.3 \) for both materials [3]. Using these properties we calculated a value of \( n_e = 0.6063 \). The elastic strain mismatch was calculated as \( \Delta \varepsilon = (\varepsilon_2 - \varepsilon_1) = (\alpha_2 - \alpha_1)(T_2 - T_1) \) and using the thermal expansion coefficients for the oxide and metal listed earlier we found a value of \( \Delta \varepsilon = 5.99 \times 10^{-4} \).

Substituting all the relevant quantities into Equation 3.9 we calculated an overall stress in the metal of \( \sigma_1 = 0.16 \, \text{MPa} \). However this will be the far-field stress felt over the entire thickness of the metal. If we assume that the primary effects of the mismatch will be felt in the metal region immediately adjacent to the oxide and reduce the interaction thickness to approximately 20 \( \mu \text{m} \), the stress can be recalculated to a new value of \( \sigma_1 = 14.95 \, \text{MPa} \). This value is below the in-plane stress relaxation calculated using the d-spacing but is still within the same order of magnitude, and given a 20 MPa standard deviation associated with the calculated stresses could be considered an accurate estimate of the stress relaxation.

The difference in Young’s modulus between room temperature and high temperature can be illustrated by plotting the out-of-plane stresses on a stress-strain curve. Figure 3.28 plots the room temperature and high temperature results and shows that the Young’s modulus is lower at high temperature than at room temperature. The value of \( E=74 \, \text{GPa} \) shown was calculated using a MATPRO correlation for Zircaloy-4 at 630 K [3].
The results of our high temperature studies appear to indicate a significant influence of temperature on the stress in the metal and oxide. The stresses calculated at high temperature were significantly lower in Zircaloy-4 than those found at room temperature, indicating that some stress relaxation may have occurred. It may be possible to establish a single stress value that can simply be subtracted from room temperature measurements, but more high temperature measurements are necessary to explore this possibility.
3.2.4.6 Elastic Strain and Stress in Crystal Bar Zirconium

D-spacing-depth measurements were taken from grains in oxidized crystal bar zirconium for comparison to results found in Zircaloy-4. Figure 3.29 shows optical micrographs of samples 4-3 (0.15 µm oxide) and 4-8 (6.56 µm oxide) identifying the points in the grains where strain-depth measurements were taken. Two locations in the same grain were examined in sample 4-3 as shown in Figure 3.29 (A). The interference colors indicate areas of slightly different oxide thickness. Figure 3.29 (B,C) show the locations in two separate grains examined in sample 4-8. There are several features visible that resemble twinning, slip lines, or even simple scratches on the oxide surface in sample 4-8 that may or may not be present in the underlying metal (highlighted by white arrows in Figure 3.29 (B,C). Note that all of the micrographs are taken from the top of the oxide layer and do not directly show the metal grain but, rather, the surface outline of the oxide growing on top of the grain.
The elastic strains in crystal bar zirconium appear to resemble those seen in bare metal rather than oxidized Zircaloy-4. Figure 3.30 shows the d-spacing-depth curves taken from the locations indicated in Figure 3.29. A major feature in all of the curves is their flatness and proximity to the unstrained d-spacing value over the entire depth, with Figure 3.30 (C) looking nearly identical to bare metal Zircaloy-4. Figure 3.30 (D) does show a similar perturbation as those seen in oxidized Zircaloy-4 with the d-spacing initially low and then increasing with depth to the unstrained d-spacing. However, this feature is not seen at all in
any other measurements taken in crystal bar Zr. The locations examined in sample 4-3 shown in Figure 3.30 (A,B) have different thicknesses of oxide at two points in the same sample. It is believed that the point labeled ‘spot 1’ in Figure 3.30 (A) has a thinner oxide than the point labeled ‘spot 2’ in the same figure, because heat tinting coloration progresses from yellow (for the thinnest oxides) to blue (thicker oxides) [48]. Spot 1 and spot 2 correspond to Figure 3.30 (A) and Figure 3.30 (B) respectively. The region of thicker oxide appears to have a more significant effect on the shape of the strain-depth curve than the thinner oxide. The overall features for both curves are similar, although those in Figure 3.30 (A) are more pronounced. The curve in Figure 3.30 (A) also contains another gap similar to the ones noted earlier in several Zircaloy-4 measurements. There does not appear to be an increase or decrease in the d-spacing on either side of the gap, so a grain boundary or other intergranular feature as the cause seems unlikely. Any gap in these curves is a result of a lack of x-ray reflections that are traceable to that particular depth range. As such, a gap will be a result of some feature that causes the incident x-rays to diffract at a very different angle from the initial Laue spot or not diffract at all, such as potentially an annealing twin.
The stresses were calculated in crystal bar zirconium using the same technique as those for Zircaloy-4. The maximum out-of-plane stress measured was roughly 80 MPa at one point, which corresponded to an in-plane stress of less than 25 MPa. The remainder of the out-of-plane stresses were calculated to be 40 MPa or less, placing them at nearly the same level as the stresses calculated for bare metal Zircaloy-4. This comes as expected since the d-spacing-depth curves show good agreement with the unstrained d-spacing value.

In addition, one measurement was taken in crystal bar zirconium sample 4-8 at high temperature. A comparison between the room temperature and high temperature d-spacing-depth measurement is shown in Figure 3.31. Although the d-spacing increases following thermal expansion, it still resembles the room temperature curve, does not vary...
with depth, and agrees with the unstrained d-spacing value at high temperature. The out-of-plane stress calculated at high temperature in this sample was tensile at 51 MPa, which is practically the same as the 44 MPa tensile stress that was calculated at room temperature for this location. This finding would appear to suggest that temperature had little to no effect on the stresses in crystal bar zirconium.

![Figure 3.31 – D-spacing-depth measurement taken at the same location in sample 4-8 at room temperature (A) and high temperature (B).](image)

Overall very little elastic stress can be observed in crystal-bar zirconium. This may result from two possible different effects. First is that the metal itself is rather soft compared to Zircaloy-4, and as such it may be able to deform plastically to accommodate oxide-growth induced stresses. Second, the oxide layer grown on crystal bar Zr may not be as adherent as the Zircaloy-4 oxide layer, which would result in smaller stresses applied to the metal.

More measurements in crystal bar zirconium are necessary to draw meaningful conclusions on the effect of temperature, as our single high temperature measurement
indicated no change in the stress from room temperature. This seems unlikely, given the still-intact nature of the oxide on the sample examined.

3.2.5 Examination of Oxide-Growth Induced Plastic Strain

When comparing the Laue patterns taken from bare metal and oxidized samples, evidence of the oxide growth affecting the metal substrate is apparent from the distortion of the Laue spots. Figure 3.32 shows a comparison of the basal reflections taken from a bare metal Zircaloy-4 sample and one with a 2.63 µm oxide layer. The Laue spot in the oxidized sample corresponding to the (0002) reflection is distorted as compared to the circular and undistorted reflection seen in the bare metal sample. The degree of distortion in the reflections from oxidized samples varies greatly from grain to grain, at grain boundaries, and even within a single grain. Similar work by other researchers has associated the distortion of the Laue reflection with plastic strain in the metal [49, 50]. The shape and degree of distortion can be correlated to the plastic deformation mechanisms operating on the sample. Work is in progress to quantify the degree of plastic strain or the mode of deformation based on the shape of the reflection. No plastic deformation is visible in the bare metal reflection; the spot is round and symmetrical indicating that only the effects of beam spreading and possible elastic strain (as a result of peak shift) are present.
Figure 3.32 – Comparison of the (0002) basal plane Laue reflections from (A) bare metal Zircaloy-4, and (B) oxidized Zircaloy-4 with a 2.63 µm oxide.

In the following sections we classify and illustrate the degree of distortion seen in the (0002) basal plane reflections for bare metal and oxidized Zircaloy-4, as well as oxidized crystal bar zirconium.

3.2.5.1 Plastic Strains in Zircaloy-4

Figure 3.33 shows (0002) Laue reflections taken from oxidized Zircaloy-4 samples H1405J, H1406J, H1413J, and H1372J which were corroded at 680 °F (360 °C) and have average oxide thicknesses of 1.14 µm, 2.09 µm, 2.63 µm, and 3.25 µm respectively (previously studied for elastic strain/stress in Section 3.2.4.2). Plastic deformation is readily visible in the Laue reflections. As stated above, shape changes in the Laue reflection from a symmetrical spot are an indicator of some level of plastic deformation in the interrogated region [50]. The (0002) basal reflections from four Zircaloy-4 samples with different oxide
thicknesses are shown in Figure 3.33. Varying degrees of distortion of the Laue spots can be observed in each sample. The oxide thickness does not appear to have a systematic influence on the severity of the spot deformation. Location within the grain and proximity to physical features such as grain boundaries appear to play a much more significant role in the visible spot distortion and thus plastic deformation, as will be illustrated later.

Figure 3.33 – Basal spot (0002) Laue reflections for Zircaloy-4 samples with oxide thicknesses of (A) H1405J-1.14 µm, (B) H1406J-2.09 µm, (C) H1413J-2.63 µm, and (D) H1372J-3.25 µm.

An analysis of the variation in visible plastic deformation as a function of position within a single grain was performed on Zircaloy-4 sample H1372J (3.25 µm oxide). A series of eight Laue patterns were taken beginning in the center of the grain and progressing in a line towards the grain boundary at 1 µm intervals, with the final Laue pattern recorded roughly
at the grain boundary, as shown in Figure 3.34. The grain was an (0002) basal oriented grain that was also used for strain-depth analysis. Figure 3.35 shows the basal reflection for each of the eight Laue patterns beginning with 3.35 (A) in the middle of the grain and progressing to 3.35 (H) at the grain boundary. A significant evolution in the Laue spot deformation can be seen between each step as well as between the center and edge of the grain. The level of plastic deformation appears to lessen slightly in the first three microns, since the region of highest intensity in the Laue spot appears to become more coherent. However as we approach the grain boundary the Laue spot becomes progressively more distorted, and is appears to be the most distorted (the main high intensity reflection appears the most broken up) at the grain boundary. The direction and degree of streaking of the Laue spot changes continually with position, meaning that the mode of deformation is either different, as seen between Figure 3.35 (A) and (C), or is present to a different degree as is the case between Figure 3.35 (C) and (D). It is difficult to say if the grain boundary has a direct effect on the plastic deformation visible in the Laue patterns. While the Laue spot in Figure 3.35 (H) at the grain boundary is very distorted, so is the one in from the center of the grain in Figure 3.35 (A). From these pictures however it is clear that the oxide-growth induced strains can vary widely with position, even within a single grain. It may be more revealing to study the effects of grain boundaries on the Laue spots in a bare metal sample that does not show the effect of oxide growth in addition to strains already present.
Figure 3.34 – Optical image of the top of the oxide layer on sample H1372J. The outline of the metal grain examined has been highlighted in green along with the approximate locations of each Laue pattern shown below in Figure 3.35.

Figure 3.35 – Basal plane Laue reflections taken from eight separate locations separated by 1 µm between the grain center and boundary for a single grain in sample H1372J. The reflection from the grain center is shown in (A) and progresses at 1 µm steps to the grain boundary shown in (H).
**Figure 3.36** shows a comparison between the basal Laue reflections at room and high temperature at the two locations in H1372J. The overall shape of the Laue spots does not appear to change, with the slight exception of the second location in H1372J. We should not expect a drastic change in the spot shape as temperature will have little influence on the plastic deformation causing the spot smearing. The more significant difference between Figure 3.36 (C) and (D) may be due to the beam being placed at a very slightly different location on the sample at high temperature. Thermal expansion of the entire heating setup caused the coordinates of the room temperature measurement points to change, and as such we had to manually locate the points using optical telescope images. As shown earlier in Figure 3.35, the Laue spot shape can vary greatly over small distances, which may be the case here if the beam was improperly positioned. The beam appears to have been accurately positioned at the first location in H1372J, as the shapes of the Laue spot are similar between room and high temperature. This is particularly true for spot 1 in Figure 3.36.
Figure 3.36 – Laue reflections of the (0002) basal plane taken at room temperature and high temperature in Zircaloy-4 sample H1372J. The images correspond as follows: (A-B) room-high temp. H1372J spot 1, (C-D) room-high temp. H1372J spot 2.

3.2.5.2 Plastic Strains in Crystal Bar Zirconium

An examination of the Laue patterns taken from oxidized crystal bar zirconium was also performed for comparison with the features seen in Zircaloy-4. Two Zr samples were used, one with a very thin oxide (0.15 µm) labeled sample 4-3 and another with an average oxide thickness of 6.56 µm labeled 4-8. These samples are described in greater detail in
Section 2 and optical micrographs are shown in Figure 2.6. The grains examined in both samples were (0002) basal oriented grains as previously described.

Images of the basal reflections from each sample are shown in Figure 3.37. In contrast to the basal reflections seen in Zircaloy-4 those from crystal bar Zr show virtually no evidence of plastic deformation. The Laue spots are clean and symmetrical and very much resemble reflections from bare metal Zircaloy-4.

The presence of an oxygen diffusion layer is one possible explanation for the lack of visible plastic deformation in the thick oxide Zr. In pure Zr corrosion an oxygen-rich layer has been observed in the metal ahead of the oxide corrosion front [51]. Oxygen acts as a solution strengthener in zirconium, with small additions increasing the yield strength by a great deal (150 MPa for every 1000 ppm oxygen added) [1]. It is possible that the oxygen ingress into the metal that occurs during corrosion has hardened the underlying metal to a point where it does not plastically deform. Without knowing the exact oxygen concentration in our sample it is difficult to calculate the potential degree of hardening. However even if we assume a small amount of oxygen comprises the oxygen layer, the potential yield increase can be very large. For example, a 5 at.% addition (which is well below the solubility limit of 29 at.%) converts to over 9000 wt. ppm oxygen locally. Oxygen layer content values of greater than 20 at.% have been reported for Zircaloy-4, which has a much more protective oxide and a much thinner layer [39]. In crystal bar sample 4-3, the oxide layer may simply be too thin to have induced enough stress to cause plastic deformation, since the very short corrosion time would not have allowed for a meaningful oxygen layer to build.
A comparison of the Laue spots from sample 4-8 at room temperature and high temperature is shown in Figure 3.38. Virtually no change can be observed as a result of the temperature difference. We would not expect thermal expansion to affect the plastic strain state so this observation comes as expected. We would instead expect a change in the lattice spacing proportional to the thermal expansion coefficient (consistent with the change shown in Figure 3.31), which would manifest in the Laue pattern as a slight shift in the position of the basal spot as compared to the room temperature position. This can be observed in Figure 3.38, as the high temperature spot appears to have shifted by several pixels in the positive x-direction as compared to its room temperature position.
Figure 3.38 – Laue reflections of the (0002) basal plane taken at room temperature and high temperature in crystal bar zirconium sample 4-8. Images (A-B) correspond to room temperature and high temperature respectively.

Overall little can be seen in the (0002) basal plane Laue reflections from crystal bar zirconium. The Laue spots show no signs of plastic deformation in the metal at room temperature or high temperature, regardless of oxide thickness. We can also connect this observation to the elastic strains measured using these same Laue spots. As detailed in Section 3.2.4.6, the elastic strains in oxidized crystal bar zirconium were found to be very low, with the d-spacing-depth profiles closely matching those from bare metal Zircaloy-4. Two possible explanations for the lack of elastic strain were given, one that plastic deformation of the metal was relaxing oxide-induced strains, and the other that the oxide was weakly adherent to the metal and did not induce strain in the first place. Since we do not observe any plastic deformation (through Laue spot distortion) in crystal bar zirconium, our data supports the idea that the oxide induces very little strain in the metal during growth because it is not strongly adherent and will instead mechanically fail first. Oxides grown on pure zirconium are well known to spall heavily, so this is a sensible explanation.
Chapter 4: CONCLUSIONS AND FUTURE WORK

4.1 Conclusions

A study of the oxide phase content and oxide growth-induced stresses in oxide layers formed on Zircaloy-4 and crystal bar zirconium in high temperature water was performed using synchrotron x-ray diffraction at the Advanced Photon Source at Argonne National Laboratory. Oxidized samples were examined in cross section using x-ray microdiffraction at beamline 2-ID-D and unaltered oxidized corrosion coupons were examined using the 3-D x-ray microscope at beamline 34-ID-E. X-ray microdiffraction allowed us to determine the oxide phase content as a function of position in the oxide and make a number of observations on other physical oxide features. The 3-D x-ray microscope was used to measure strains in the metal substrate induced by oxide growth. Conclusions based on the results of each technique will be summarized in the following sections.

4.1.1 Conclusions on Microbeam Synchrotron Diffraction and Fluorescence

Oxide layers grown on Zircaloy-4 samples were characterized in cross section using this technique to determine the oxide phase content as a function of position in the oxide as well as a number of other qualities such as tetragonal fraction, grain size, and phase orientation relationships. The main conclusions of this study are:
The oxide was found to be primarily composed of monoclinic and tetragonal phase ZrO$_2$. The relative amounts of each phase were variable through the oxide thickness.

Well-defined periodic variations in the oxide phase content as a function of distance from the oxide-metal interface were observed. The average distance between periods was measured to be 1.9 µm, which corresponded well with oxide transition thickness for this material.

Strong periodic relationships were observed between a number of the primary monoclinic and tetragonal oxide diffraction peaks. These peaks (011$_M$, 101$_T$, 111$_M$, 020$_M$, 002$_M$) were in-phase with one-another throughout the oxide thickness. The observed periodicity disagrees with our current theorized oxide growth mechanism and indicates our observations may result from geometric variations reducing the overall diffracted intensity. However the (012)$_M$ peak was observed to be out of phase with the other monoclinic peaks suggesting that the in-phase relationships may indeed be a result of the corrosion process.

Intensity from the (200)$_M$ diffraction peak was not observed while the (020)$_M$ and (002)$_M$ were clearly visible. This indicates the oxide growth occurs with the (200)$_M$ plane parallel to the oxide-metal interface.

A Zr$_3$O "suboxide" phase was observed in a small (1-2 µm) region of metal immediately adjacent to the oxide-metal interface. This observation corresponds well to previous transmission electron microscopy studies which found a region of high oxygen content at this location.
• The tetragonal phase fraction as determined by the Garvie-Nicolson Formula was found as a function of distance from the oxide-metal interface. This value was observed to be highest at the oxide-metal interface and decrease over a range of approximately 2 µm to a stable value in the bulk oxide. Without correcting for texture, tetragonal fraction values of 15% and 9% were found at the oxide metal interface in two Zry-4 samples, with respective bulk oxide values of 5% and 3%.

• The oxide diffraction peaks were observed to broaden in the oxide region within 2-3 µm of the oxide-metal interface, and reach a maximum width at the interface.

• The oxide peak broadening was deconvoluted using a Williamson-Hall analysis, where it was determined that size broadening (due to smaller grain size) was the dominant cause of the increase in peak FWHM seen near the oxide-metal interface.

• The monoclinic ZrO$_2$ grain size was calculated using the diffraction peak size broadening component as determined using a Williamson-Hall deconvolution of the size and strain broadening. A bulk oxide grain size of 80-100 nm, and a grain size of the 45-50 nm was calculated using this technique.

• The grain size for monoclinic and tetragonal oxide phases was calculated using the Debye-Schererrer equation for a number of oxide diffraction peaks. The average monoclinic grain size was found to be approximately 15-20 nm, and the average tetragonal grain size somewhat smaller at 9 nm.

• The monoclinic grain size was observed to be smallest at the oxide-metal interface, growing to reach a stable bulk oxide size over a range of 2-3 µm beyond the interface. The tetragonal grain size was constant throughout the oxide thickness.
4.1.2 Conclusions on Residual Stress Determination using 3-D Laue Diffraction

Oxide corrosion coupons were characterized using Laue diffraction techniques to determine the strains induced by oxide growth in Zircaloy-4 and crystal bar zirconium samples. These strains were related to stresses in the metal and the oxide in an attempt to relate growth induced stress to the oxide transition. The main conclusions of this study are as follows:

- Bare metal Zircaloy-4 shows small residual strains. Calculated stresses in bare metal samples were on the order of a few tens of MPa which are within the range of residual stresses due to cooling after annealing reported in previous literature.
- Oxide growth had a variable effect on the elastic strains in the metal grains. Both tensile and compressive stresses were observed in the metal, which goes against our expectations of a purely tensile state in the metal. However, the majority of measurements showed repeating features indicating that oxide growth had in general induced a tensile stress in the metal.
- The stress in the metal was observed to increase as the oxide layer approached transition. Samples with oxide layers nearing transition showed the highest stresses in the metal. Samples with oxide layers that had just undergone or were not near transition showed significantly lower stresses.
- The level of stress in the metal ranged from a few MPa in bare metal Zry-4 to several hundred MPa in Zry-4 with an oxide approaching transition. The maximum stress calculated through movement of the (0002) basal plane was 425 MPa in tension (corresponding to a 127 MPa stress in the lateral direction).
- Elastic stresses within the oxide layer were calculated to be on the order of several hundred MPa, which is in agreement with values found for oxides of this thickness in previous literature.

- Oxide growth on crystal bar zirconium did not appear to have a large effect on the elastic or plastic strains in the metal. The calculated elastic stresses were on the same order as those found in bare metal Zircaloy-4. Laue spots taken from multiple crystal bar samples showed no distortion indicative of plastic strain.

- Temperature may play a large role in the magnitude of the elastic strains measured in Zircaloy-4. Stresses calculated from (0002) basal plane strain measurements at high temperature were significantly lower than those measured at the same location at room temperature. The measured stress was found to relax by approximately 100 MPa and 250 MPa between room and high temperature at two separate locations in Zircaloy-4.

- Crystal bar zirconium showed almost no change in the calculated stress between room temperature and high temperature.

- The oxide grown on Zircaloy-4 induces some level of plastic strain in the underlying metal. Laue patterns taken from oxidized Zircaloy-4 show distortion in the Laue spots ranging from slight to severe, which indicates varying levels of plastic deformation. Laue patterns from bare metal Zircaloy-4 show no deformation in their Laue spots.

- The degree and mode of plastic deformation in oxidized Zircaloy-4 was observed to vary significantly with position over even a small range. Laue patterns taken at small
intervals showed a large change in the distortion of the Laue spot at each point, indicating a change in the plastic deformation.

- Plastic strains were not visible in the Laue patterns taken from crystal bar zirconium. The Laue spots showed no distortion and closely resembled the Laue spots from bare metal Zircaloy-4. The oxide layer grown on crystal bar zirconium may be weaker than the one grown on Zircaloy-4, and could mechanically fail before reaching stress levels that would induce plastic strain in the metal.
4.2 Recommendations for Future Work

4.2.1 Future Work on Microbeam Synchrotron Diffraction and Fluorescence

The application of material markers to the oxide cross section would be useful to help link microbeam diffraction studies to oxide characterization using optical and scanning electron microscopy. The markers would allow for features observed in the x-ray data to be correlated directly with visible features in the oxide or metal.

Samples with a relatively thick oxide layer (5-10 µm) should be used with this technique. Over the course of our study we found thin oxide samples to be difficult to work with in a number of ways, including polishing, microscopy, and data analysis. Even with the extremely small size of the focused beam at 2-ID-D, very few measurements can be taken from a 1-2 µm oxide, leaving little room to see phase development or other oxide trends that are easily visible in a thicker oxide.

Irradiated samples could be used in a similar study as this one where the oxide phases as a function of position are characterized and compared to oxides formed in an autoclave environment.
4.2.2 Future Work on Residual Stress Determination using 3-D Laue Diffraction

More measurements in Zircaloy-4 samples at room temperature using a finer separation of oxide thicknesses are needed. In order to observe exactly how the oxide thickness affects the elastic stress, a fine separation of oxide thicknesses (such as 1 µm, 1.2 µm, 1.4 µm, etc.) is needed to conclusively establish that any trends in the stress are present, and if the oxide transition does indeed accompany a stress relaxation. Multiple measurements will be necessary in each sample as well to establish a good statistical basis, as a large number of outliers and unexpected results were obtained over the course of our study that muddled our picture rather than making things clearer.

Work at high temperature needs to be explored further. Only a limited number of measurements have been taken, and more are necessary to validate our initial results.

The in-situ evolution of strain could be explored by corroding a bare metal Zircaloy-4 sample in air and taking continual measurements of the strain. While the time scales involved would not allow the sample to be corroded to transition, this experiment would help us understand how the strain develops during the corrosion process.

A long term experiment could also be performed involving measuring an oxidized sample just before transition, corroding it beyond transition, then examining it again immediately after. This could help establish the effect of the oxide transition on the elastic or plastic strains and perhaps allow the possible stress relaxation at transition to be observed directly.
REFERENCES


Appendix A: Zirconium Alloy Composition and Impurities

Table A.1 – Composition of the Zircaloy-2, Zircaloy-4, and Zr-Nb alloys [1].

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Appendix B: Heating Stage Schematics
Material: Aluminum  
Center Hole Thread: 8-32  
Tolerances: 1/64”

The central depression will need to have fillets cut in the corners to accommodate the milling bit. This should not pose a problem as long as the bit is small and the fillet does not exceed half the wall thickness.

This heating stage needs to be thermally insulted from its mounting apparatus, preferably by using ceramic washers on the mounting screw but metal washers are acceptable as well. Two 15W cartridge heaters are capable of maintaining sample temperatures in excess of 700 °F with good stage thermal isolation and no forced convection cooling.
Appendix C: Powder Diffraction Files for Zirconium and Zirconium Oxides

The two-theta angles presented in the appendix were calculated using a beam energy of \( E=17.79 \text{ KeV} \), corresponding to an x-ray wavelength \( \lambda=0.696931 \text{ Å} \).

Table C.1 – PDF for \( \alpha \)-zirconium (\( a=3.232 \text{ Å}, \ c=5.147 \text{ Å} \))

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Table C.2 – PDF for monoclinic ZrO\(_2\) (\( a=5.3129 \text{ Å}, \ b=5.2125, \ c=5.1471, \ \beta=99.218^\circ \))

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### Table C.3 – PDF for tetragonal ZrO$_2$ (a=3.64 Å, c=5.27 Å)

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### Table C.4 – PDF for tetragonal ZrO$_2$ 2 (a=5.12 Å, c=5.25 Å)

<table>
<thead>
<tr>
<th>d-spacing (Å)</th>
<th>Intensity</th>
<th>(hkl)</th>
<th>Two-Theta (degrees)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.960</td>
<td>100</td>
<td>(1 1 1)</td>
<td>13.522</td>
</tr>
<tr>
<td>2.600</td>
<td>18</td>
<td>(0 0 2)</td>
<td>15.405</td>
</tr>
<tr>
<td>2.540</td>
<td>25</td>
<td>(2 0 0)</td>
<td>15.771</td>
</tr>
<tr>
<td>2.120</td>
<td>6</td>
<td>(1 1 2)</td>
<td>18.921</td>
</tr>
<tr>
<td>1.830</td>
<td>65</td>
<td>(2 0 2)</td>
<td>21.954</td>
</tr>
</tbody>
</table>

### Table C.5 – PDF for tetragonal ZrO$_2$ 3 (a=3.8984 Å, c=5.152 Å)

<table>
<thead>
<tr>
<th>d-spacing (Å)</th>
<th>Intensity</th>
<th>(hkl)</th>
<th>Two-Theta (degrees)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.95</td>
<td>100</td>
<td>(0 1 1)</td>
<td>13.56767679</td>
</tr>
<tr>
<td>2.575</td>
<td>8</td>
<td>(0 0 2)</td>
<td>15.55498663</td>
</tr>
<tr>
<td>2.544</td>
<td>12</td>
<td>(1 1 0)</td>
<td>15.74572707</td>
</tr>
<tr>
<td>2.095</td>
<td>1</td>
<td>(0 1 2)</td>
<td>19.14923749</td>
</tr>
</tbody>
</table>
### Table C.6 – PDF for hexagonal Zr₃O (a=5.563 Å, c=31.185 Å)

**Hexagonal Zr₃O**

PDF No 22-1025

<table>
<thead>
<tr>
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<th>Intensity</th>
<th>(hkl)</th>
<th>Two-Theta (degrees)</th>
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<tbody>
<tr>
<td>4.660</td>
<td>50</td>
<td>(0 1 2)</td>
<td>8.577</td>
</tr>
<tr>
<td>3.840</td>
<td>50</td>
<td>(0 1 5)</td>
<td>10.413</td>
</tr>
<tr>
<td>3.290</td>
<td>20</td>
<td>(1 0 7)</td>
<td>12.160</td>
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<tr>
<td>2.817</td>
<td>80</td>
<td>(1 1 0)</td>
<td>14.211</td>
</tr>
<tr>
<td>2.601</td>
<td>80</td>
<td>(0 0 12)</td>
<td>15.399</td>
</tr>
<tr>
<td>2.477</td>
<td>100</td>
<td>(1 1 6)</td>
<td>16.174</td>
</tr>
<tr>
<td>2.273</td>
<td>5</td>
<td>(2 0 5)</td>
<td>17.637</td>
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<tr>
<td>2.140</td>
<td>50</td>
<td>(0 2 7)</td>
<td>18.743</td>
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<tr>
<td>2.081</td>
<td>5</td>
<td>(0 0 15)</td>
<td>19.279</td>
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<tr>
<td>1.911</td>
<td>80</td>
<td>(1 1 12)</td>
<td>21.013</td>
</tr>
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</table>

### Table C.7 – PDF for hexagonal Zr₃O₁₋ₓ (a=5.63 Å, c=15.59 Å)

**Hexagonal Zr₃O₁₋ₓ**

PDF No 21-1498

<table>
<thead>
<tr>
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<th>(hkl)</th>
<th>Two-Theta (degrees)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.130</td>
<td>70</td>
<td>(1 0 2)</td>
<td>9.680</td>
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<tr>
<td>3.040</td>
<td>10</td>
<td>(1 0 4)</td>
<td>13.164</td>
</tr>
<tr>
<td>2.815</td>
<td>80</td>
<td>(1 1 0)</td>
<td>14.222</td>
</tr>
<tr>
<td>2.599</td>
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<td>(0 0 6)</td>
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<td>2.475</td>
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<td>(1 1 3)</td>
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</tr>
<tr>
<td>1.909</td>
<td>80</td>
<td>(1 1 6)</td>
<td>21.035</td>
</tr>
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</table>

### Table C.8 – PDF for cubic ZrO (a=4.6258 Å)

**Cubic ZrO**

PDF No 51-1149

<table>
<thead>
<tr>
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<th>Intensity</th>
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<th>Two-Theta (degrees)</th>
</tr>
</thead>
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<td>14.995</td>
</tr>
<tr>
<td>2.313</td>
<td>91</td>
<td>(2 0 0)</td>
<td>17.329</td>
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</tbody>
</table>
Table C.9 – PDF for cubic ZrH$_{1.66}$ (a=4.781 Å)

<table>
<thead>
<tr>
<th>Cubic δ-ZrH$_{1.66}$</th>
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<td><strong>PDF No 34-0649</strong></td>
<td></td>
</tr>
<tr>
<td>d-spacing (Å)</td>
<td>Intensity</td>
</tr>
<tr>
<td>2.760</td>
<td>100</td>
</tr>
<tr>
<td>2.391</td>
<td>47</td>
</tr>
</tbody>
</table>

Table C.10 – PDF for hexagonal ZrFe$_{1.5}$Cr$_{0.5}$ (a=5.0069 Å, c=8.193 Å)

<table>
<thead>
<tr>
<th>Hexagonal ZrFe$<em>{1.5}$Cr$</em>{0.5}$</th>
<th></th>
</tr>
</thead>
<tbody>
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</tr>
<tr>
<td>d-spacing (Å)</td>
<td>Intensity</td>
</tr>
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<td>3</td>
</tr>
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<td>2.504</td>
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<td>2.168</td>
<td>13</td>
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<tr>
<td>2.138</td>
<td>100</td>
</tr>
<tr>
<td>2.096</td>
<td>76</td>
</tr>
<tr>
<td>2.049</td>
<td>15</td>
</tr>
<tr>
<td>1.916</td>
<td>10</td>
</tr>
<tr>
<td>1.853</td>
<td>9</td>
</tr>
</tbody>
</table>
Appendix D: Orientation Grain Maps and Pole Figures

Figure D.1 – Grain orientation maps and their associated pole figures for the indicated samples.
Appendix E: 2-ID-D Beam Alignment and Data Acquisition Procedure

1. Once you decide to change sample, move sample X to zero, move kphi to zero.

2. Go into the hutch and change the sample. Load the sample with the face aligned with (parallel to) the beam at the center of the pin hole.

3. Close the hutch and open the shutter.

4. Move OSA_X to 6.1. (note that there is a hole in the shield to allow the beam through after OSA is moved)

5. Look at the TV monitor for the sample shadow. If you see nothing (all black), move sample in +y increments until you see the sample edge. When you find the sample, use sample x to find the middle height of the sample.

6. Set kphi manually to roughly align kphi to zero (use steps of 0.25 micron). Set the aligned value of phi to zero. (note that the point where kphi adjustments stop causing the sample to shift to –y will be the zero point)

7. Move sample surface to the middle of the zone plate using sample y. Set that value to Y to zero, then move sample Y to +300 to move the sample out of the way. Also move OSA_X back to zero.

8. Set up OSA_Y scan (use middle mouse wheel button to drag motor to scan(m7.val)).
   a. Clear detector trigger 4 in scan window which often has “CLBK” instruction
   b. Width = 0.05 mm
   c. 26 steps
   d. Change acquisition time to live 1s, real 2s, and count time in both windows to 1s.
   e. Begin a scan, reading detector 4 (D04, Upstream ion chamber)
   f. The scan should have a maximum center plateau. Move to the center of the plateau and remember to accept the change. Set that OSA_Y position as zero.

9. Repeat step 8 for OSA_X (m2.val)

10. Move sample Y back to zero. Change kphi to a value equal to negative half the diffraction angle at mid ccd (kphi = -Nu/2). (e.g. -13.5 degrees for a Nu of 27 degrees)
11. Perform a sample z (m37.val) scan to place the beam in the middle of the sample. Use a millimeter scale (ex. 3500 for a 3mm diameter sample). The appropriate fluorescence detectors must be used for all remaining scans (D04 may be disabled).

12. Perform a sample x (m38.val) scan to find the middle of the sample as well as the oxide on the top or bottom edge. A millimeter scale may again be used (ex. 1000 for a ~1mm sample)

13. Several more sample x scans may now be performed to narrow down the scan range until a final scan range is found.

Setup for the Acquisition of Diffraction Patterns

1. Create a new file in the folder of your choice if the sample is new.

2. Go to the CCD Image Grabber program.
   
   a. Go to Setup – File System
      i. Click browse to select or create a folder for images to be saved into.
      ii. Change the file index to 1
      iii. Change the filename template
   b. Go to Setup – Acquisition and set the acquisition time to 60s, or your choice.
   c. In the ROI tab, make sure the save ROI to file box is checked.

3. Close XIA shutter if you have not already.

4. Change the preset live/real time in the mca window (1/3 of CCD time). (ex. 10/40s for 40s acquisition time, and 10/30s for a 30s acquisition in this case) The count time can be set equal to or approximately the real time (35/25s for 40/30s acquisition).

5. In the #4 trigger detector type: 2idd:ccd.AcquireCLBK (note: case sensitive)

6. Do not leave until at least the first file is produced and saved (~8Mb tiff image)

Additional Notes

Triggers
2. 2idd:mca1EraseStart
3. 2iddf:scaler1.CNT
4. 2idd:ccd.AcquireCLBK – only this one should be modified

*When kphi is changed, the entire sample assembly rotates.
Any changes to sample z occur in the plane of the current kphi, not the beam.
*Written August 2010
Appendix F: Energy-Wire Scan Setup at Beamline 34-ID-E

Wire Range Determination and Scan Setup

- Select and grain and a Laue spot of interest.
- Select the appropriate wire range using the polychromatic beam.
  - The wire range should encompass the distance where the leading edge of the wire is just before the point where it begins to block the reflection to the point where the reflection is completely blocked by the wire.
  - Select an appropriate wire step size, usually 1-1.5 µm.
- Select an appropriate beam energy.
  - Change the beam to monochromatic and select the energy appropriate for the chose reflection
  - Energy harmonics can be used if the fundamental peak energy does not fall within the beamline limits of 7-32 KeV.
  - Select an appropriate energy step size, usually 1-3 eV.
- Define a small region of interest (ROI) around the chose Laue spot using the polychromatic beam.

Energy Range Determination

- Using a monochromatic beam set near the appropriate energy for the Laue spot, decrease the energy until the spot disappears or leaves a constant residual. The energy where this occurs is $E_{MIN}$.
- Increase the energy until the spot reaches an intensity peak. The energy at the intensity peak will be $E_{MAX}$.
- The energy range will be the difference between the maximum and minimum energies.

Additional Information

- Selecting the appropriate beam energy is initially dependent on the indexation of the chosen spot
- The spot chosen can be based off a white-beam wire scan (used to determine the depth origin of the spot)
- If multiple grains are present, use the aforementioned white-beam wire scan to determine the surface grain.
- Tweaking the monochromator theta may be useful to get a higher beam intensity.
- Be sure the Laue spot does not saturate the detector. Lesser harmonics may be used to avoid saturation (although one pixel is ok)

Written December 2011
Appendix G: SEM Polishing Schedules

Schedule 1: This polishing schedule gives best results when employed for thick oxides, and may cause retention issues when used with thin oxide (under 5 µm) samples. Initial grinding can be done by hand or using the Allied auto-polisher. The 3mm disc cross-sectional samples were mounted to a 1.25 inch diameter aluminum cylinder using epoxy for use in the auto-polisher.

Grinding
(cool/flush constantly with running water)

180 grit SiC paper
- 100 rpm plate, 110 rpm head same direction
- 4 Newton individual pressure
- 2 minutes (just to flatten sample)

400 grit SiC paper
- 100 rpm plate, 110 rpm head same direction
- 4 Newton individual pressure
- 3 minutes

600 grit SiC paper
- 120 rpm plate, 130 rpm head same direction
- 9 Newton individual pressure
- 6 minutes

Polishing

1200 grit SiC paper
- 120 rpm plate, 130 rpm head same direction
- 9 Newton individual pressure
- 8 minutes (Cool/flush with running water)

1 µm mono-crystalline Diamond suspension (Leco metallographic consumable)
- Imperial cloth
- 110 rpm head, 130 rpm plate same direction
- 9 Newton individual pressure
- 10 minutes (Cool/flush with lubricant or de-ionized water)

0.05 µm Colloidal Silica (Leco metallographic consumables)
- Imperial cloth
- 110 rpm head, 130 rpm plate same direction
- 4 Newton individual pressure
- 10 minutes (Cool/flush with de-ionized water)

Rinse samples thoroughly with distilled water between steps to reduce contamination by heavier grit particles between polishing stages.
Schedule 2: This procedure works well for all oxide thicknesses and very thin oxides remain intact.

Grinding
(Cool/flush constantly with running water)

180 grit SiC paper
- 100 rpm plate, 110 rpm head same direction
- 4 Newton individual pressure
- 1-2 minutes (just to flatten sample)

400 grit SiC paper
- 100 rpm plate, 110 rpm head same direction
- 4 Newton individual pressure
- 3 minutes

600 grit SiC paper
- 120 rpm plate, 130 rpm head same direction
- 9 Newton individual pressure
- 6-8 minutes

800 grit SiC paper
- 120 rpm plate, 130 rpm head same direction
- 9 Newton individual pressure
- 8 minutes

Polishing

3 µm polycrystalline Diamond suspension (Allied High Tech polishing)
- White label cloth
- 110 rpm head, 130 rpm head same direction
- 9 Newton individual pressure
- 10 minutes (Cool/flush with lubricant)

1 µm mono-crystalline Diamond suspension (Leco metallographic consumables)
- Imperial cloth
- 110 rpm head, 130 rpm plate same direction
- 9 Newton individual pressure
- 10 minutes (Cool/flush with lubricant)

0.05 µm Colloidal Silica (Leco metallographic consumables)
- Imperial cloth
- 110 rpm head, 130 rpm plate same direction
- 4 Newton individual pressure
- 10 minutes (Cool/flush with de-ionized water)

Rinse samples thoroughly with distilled water between steps to reduce contamination by heavier grit particles between polishing stages.
Appendix H: Protocol for Analyzing Integrated Diffraction Data using PeakFit

1. Open the scan to be analyzed in Peak Fit

2. Background Removal
   (press button with a curve and a B)
   Ensure settings are:
   - Best
   - Tolerance 0.5%
   - 2nd derivative zero

=> press green check.
This should ensure uniformity of background removal
Save an ASCII (.prn) of the background removed spectrum at this point, making a note that it is a different file than the peak output summary (such as including a _nbk tag). This will ensure you can replicate the same background removed spectrum in the future.

3. Open Files for Fitting

Open data files in option I with automatic peak detection

   - No smoothing
   - Pearson VII Area
   - Check Vary Widths and Vary Peak Shapes, Amp=1.5%
   - Input the peaks that should be there from visual inspection

4. Manual Fit of peaks

Go to peak fitting (press button with I and curve)

Open Standard n-1

Fit characteristics should be governed by standards, and should have set variables in the following way:

   - no baseline
   - spectroscopy
   - Pearson VII area
   - No smoothing
   - Amp%=0
• Vary width
• Vary shape

Fit yellow line by adjusting height, width, tails and locations of peaks. Peak fitting criteria:

• Fit the peak shapes; (ensure the overall peak shape agrees.)
• No systematic problem (residuals should be small and up and down along line, rather than systematically up or down)
• Ensure that the T peak does not vary too widely in the tails (it is possible to keep I and FWHM constant and vary the tails to account for bkgd, we should keep the fwhm and tails width about constant to ensure consistent peak shape)
• If maximum amplitude is I, residuals of ~1% I are great, 2% are ok.
• Stuff on the right side of the (-111) monoclinic peak is ok not to fit well (hard to fit bkgd there). An extra peak may be added to account for the consistent extra intensity.

5. Manual Fit

Go to the Review Peak Fit button (bottom right button on 6 on the left) (Review Peak Fit); This will show the current state of the peaks without the computer trying to automatically fit further. The automatic fit can induce unwanted non-physical errors.

R2 should be > 0.99, preferably >0.999

6. Review and Save

When program stops, go to Review Fit, perform three saves:

• Save text (numeric) as prn file
• Export fit as xls file
• Go back to spectrum and save the peak positions as standard “n” scn file (this will serve as input to the next one

At this point it could be useful to print the top and bottom screens to get a good idea of the goodness of the fits.