

The Pennsylvania State University

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**EXAMINATIONS OF BWR-CORRODED ZIRCALOY-2 WATER RODS WITH XANES
AND XRD TO INVESTIGATE THE ROLE OF NICKEL IN ENHANCING HYDROGEN
PICKUP AT HIGH BURNUP**

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by

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ABSTRACT

Zirconium-based alloys have been used in nuclear reactors as fuel cladding and structural materials since the development of nuclear energy. Zircaloy-2, a *Sn-Fe-Cr-Ni* alloy was widely in service for years, and still is today in boiling water reactors (BWR). Among the many challenges the materials face during operation in the nuclear reactor, hydrogen pickup during corrosion of the metal components is of great concern due to the embrittlement properties of the zirconium hydrides. Zircaloy-2 materials show great corrosion resistance in the boiling environment but many in-pile fuel cladding and structural components, such as water rods and channel boxes, revealed accelerated ingress of hydrogen at high burnup when exposed for additional cycles in the reactor, while Zircaloy-4 components did not. The industry is driven toward increasing the fuel burnup in the reactors, as it reduces operation costs, and therefore it is necessary to prevent this effect from happening in modern alloys. Because the main difference between Zircaloy-2 and Zircaloy-4 is the removal of nickel replaced by additional iron in Zircaloy-4 - nickel was linked to increased hydrogen pickup as early as the 1960's - nickel was thought responsible for this acceleration of hydrogen pickup during the additional cycles in the reactors. In a previous study, metallic nickel was measured in the oxide layer near the metal interface of high hydrogen pickup Zry-2 water rods. In this work, additional materials were selected at low and high elevations in the Zircaloy-2 water rods corroded for 3 and 4 cycles in a BWR (Limerick-1) with low and high hydrogen pickup respectively; and were examined by microbeam X-ray absorption near-edge spectroscopy (XANES), microbeam X-ray diffraction (XRD), and scanning electron microscopy (SEM) in an effort to verify and understand further this observation.

Cross-sectional samples were prepared from the two water rods and investigated at the Advance Photon Source (APS) at Argonne National Laboratory (ANL). In each material, the oxidation state of nickel atoms in the thick oxide layers was measured as a function of distance from the metal interface by XANES. The results confirm the presence of metallic nickel in the oxide layer of the high elevation material/high hydrogen pickup material (4 cycles) where 30-35% metallic nickel was seen in the near oxide (up to 10-12 μm from the metal interface), as previously observed in two other high hydrogen pickup materials. At low elevation in the high hydrogen pickup water rod, the correlation was not directly verified (nickel atoms were fully oxidized in the oxide layer past 3-4 μm from the metal/oxide interface) but we argue that the high hydrogen content observed at that location results from the diffusion down the water rod of hydrogen absorbed at higher elevation, driven by the concentration and temperature axial gradients.

A detailed analysis of the XANES signal from the metallic nickel atoms in the oxide layer of the high hydrogen pickup material suggest that these nickel atoms are no longer bonded to zirconium atoms, which shows that the metallic nickel which can affect hydrogen pickup consists of atoms in solid solution or in small clusters in the oxide layer, rather than in second phase precipitates. This is in agreement with recent APT examinations of high burnup Zry-2 materials with high hydrogen pickup in which the nickel atoms were seen uniformly distributed in the oxide layer and only small clusters were observed.

Additionally, metallic nickel in the outer oxide region close to the water interface was observed in most materials, with the highest metallic fraction (up to 75%) in the low hydrogen content samples. Nickel and iron high fluorescence counts near the oxide/water interface confirmed that the nickel atoms at that location corresponded to deposits from the corrosion of other reactor components on the water rod oxide surfaces. However, these metallic nickel atoms near the water interface of the thick oxide layers ($> 25 \mu m$) do not seem to affect the hydrogen uptake in the Zry-2 materials as they were mostly observed in the low hydrogen pickup samples.

Many cracks (lateral and through thickness) were seen in the oxide layers of the materials with SEM imaging of the prepared samples, especially in the high hydrogen pickup water rod at high elevation. In all four materials investigated, the oxide layers were rather uniform, but extensive circumferential oxide thickness variations could be observed between different regions of the water rods.

An increase in oxidation kinetics during the 4th cycle was seen at mid/high elevation, where the irradiation flux is the most intense, by comparing the oxide thicknesses of the 3-cycles to 4-cycles GNF water rods and was correlated to the presence of nickel in the oxide layer. As such, irradiation seems to play an important role in accelerating corrosion (as previously reported) and in stabilizing metallic nickel in the oxide layer (and in turn enhancing hydrogen pickup).

Concurrently to the XANES examinations, X-ray diffraction patterns were collected in the oxide layers of the cross-section samples as a function of distance from the bulk metal in order to investigate the oxide microstructure (phase content, grain size, texture) of in-reactor Zry-2 materials at high burnup with low and high hydrogen pickup fraction. The oxide layers formed on the BWR Zry-2 water rod consisted of small and highly oriented monoclinic oxide grains, with a small fraction of tetragonal grains, maximum near the metal interface (3-6%). Grain growth was observed in all materials as the oxide thickens, especially at high elevation, with grain sizes at 17-20 nm near the bulk metal and 33-38 nm in the outer region. Additionally, small grains compose the oxide region near the metal/oxide interface of the high elevation/high hydrogen pickup material which is coherent with accelerated corrosion taking place during the 4th cycle.

In all materials, an orientation relationship was apparent between the (111) *m*-ZrO₂ and the (10 $\bar{1}$ 0) α -Zr crystal planes, and for a significant fraction of the oxide grains throughout the whole oxide layer, the (200) *m*-ZrO₂ direction is close to the oxide growth direction. This is coherent with previous XRD examinations of autoclave and in-reactor corroded Zr-alloys.

After a thorough review of the presented results and of the literature available, the author proposed a mechanism for the enhancement of hydrogen uptake in Zry-2 materials in BWR at high burnup. A combination of a thick, porous oxide layer, of high fluence, of high irradiation flux and of low linear power – especially for fuel rods – are thought to be necessary conditions for the stability of metallic nickel in the near oxide layer of Zry-2 materials during additional cycles at high burnup. These metallic nickel atoms then catalyze the hydrogen absorption surface reaction at cracks and pores surfaces near the metal interface, as previously suggested, resulting in increased hydrogen pickup by the material.

In turn, the results presented in this study support that the acceleration of hydrogen pickup observed in Zry-2 materials at high burnup in BWR is not likely to occur in the modern Ni-free Zr alloys.

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Chapter 1

Literature review

This chapter presents a bibliographical review of the knowledge on zirconium alloys used in the nuclear industry, with an emphasis on Zircaloy-2 (Zry-2) and Zircaloy-4 (Zry-4) alloys used in Light Water Reactors (LWRs). LWRs are introduced in the first section, followed by the history of the development of zirconium alloys. Then, the waterside corrosion of these alloys in the reactor is reviewed, succeeded by the hydrogen ingress phenomenon. Lastly, the objective of this study is presented.

1.1 Introduction to Light Water Reactors

Since their development in the late 1950s, commercial nuclear reactors have been built and used all around the globe. While many reactor designs are possible using various coolants, the majority of the existing power plants are Light Water Reactors (LWRs) which use pressurized water as both the coolant and neutron moderator. Out of the 437 operational reactors, and of the 56 under construction today in the world, 364 and 50 respectively are LWRs [1]. Their predominance results from their simplicity and lower costs of construction. Two types of reactors constitute the LWRs: the Pressurized Water Reactor (PWR) and the Boiling Water Reactor (BWR). In a PWR, the water is pressurized to about 15.5 MPa (156 atm) to prevent boiling as it travels into the reactor core at approximately 290°C and exits at the bottom at approximately 320°C [2]. The water then exchanges heat with a secondary water coolant system in a steam generator before returning to the core. The secondary system is under lower pressure so that the water transforms into steam, and the produced steam drives a turbine to produce electricity. Two coolant systems are necessary to maintain the primary coolant in a subcooled liquid state. On the

other hand, the water in a BWR is pressurized to 7.2 MPa (75 atm) and enters the core from the bottom at about 270°C - 275°C [3]. As it runs upward in the reactor, the water reaches 285°C - 290°C and transforms into steam directly in the core. The steam gets separated from the water to drive the power-generating turbine, while the water is returned to the core. The steam is then condensed and in turn reinjected into the core [2, 4]. Due to the single-coolant system, the main advantages of the BWR relative to a PWR include lower fuel and coolant temperatures, and structural components operating at lower pressure. On the other hand, PWRs are easier to monitor by controlling the flow of the liquid water, and offer no contamination of the secondary loop, power generating and condensing systems.

In both reactors, the fuel is enriched uranium (between 3% to 5% of ^{235}U concentration) in the form of uranium oxide (UO_2) pellets, stacked on top of each other and encased in rods that are about $3.6 \text{ m} - 4 \text{ m}$ high and $9.5 \text{ mm} - 14 \text{ mm}$ in diameter [5]. The UO_2 fuel provides the benefits of a chemically inert crystal structure, which is stable over the whole temperature range of the solid state of the material, with a high melting point and a relative resistance to irradiation [6]. The fuel rods are then gathered using metallic grid spacers to form the fuel assemblies. Each assembly may contain 64 to 289 fuel rods, and a typical 1100 MWe (megawatt electric) nuclear core may contain 150 fuel assemblies. In addition to the fuel rods, control rods are injected into the core to help govern the fission rate or shut down the fission chain reaction by absorbing neutrons. For BWRs, they consist of boron carbide cruciform rods inserted in between fuel assemblies, and for PWRs they are silver-indium-cadmium alloy rods inserted in selected fuel assemblies. Lastly, water rods may be added at the center of the fuel bundles to increase moderation and to flatten the neutron flux - which provides a more even fuel consumption - as water flows inside. Their diameter is slightly larger than that of the fuel rods with an outer diameter about [7]. In LWRs, the nuclear fuel cladding tube into which the UO_2 pellets are inserted, is made of zirconium alloys, as are some of the structural elements of the nuclear core

and the water rods. The fuel cladding represents the first barrier for release of fission products. However the cladding may corrode in the aggressive aqueous environment of the reactor. For Zr alloys, an adherent oxide forms on the surface of the cladding which limits further corrosion. Its properties are of major importance for extensive use in the power plant [8]. Figure 1-1 illustrates the fuel assemblies of PWRs and BWRs.

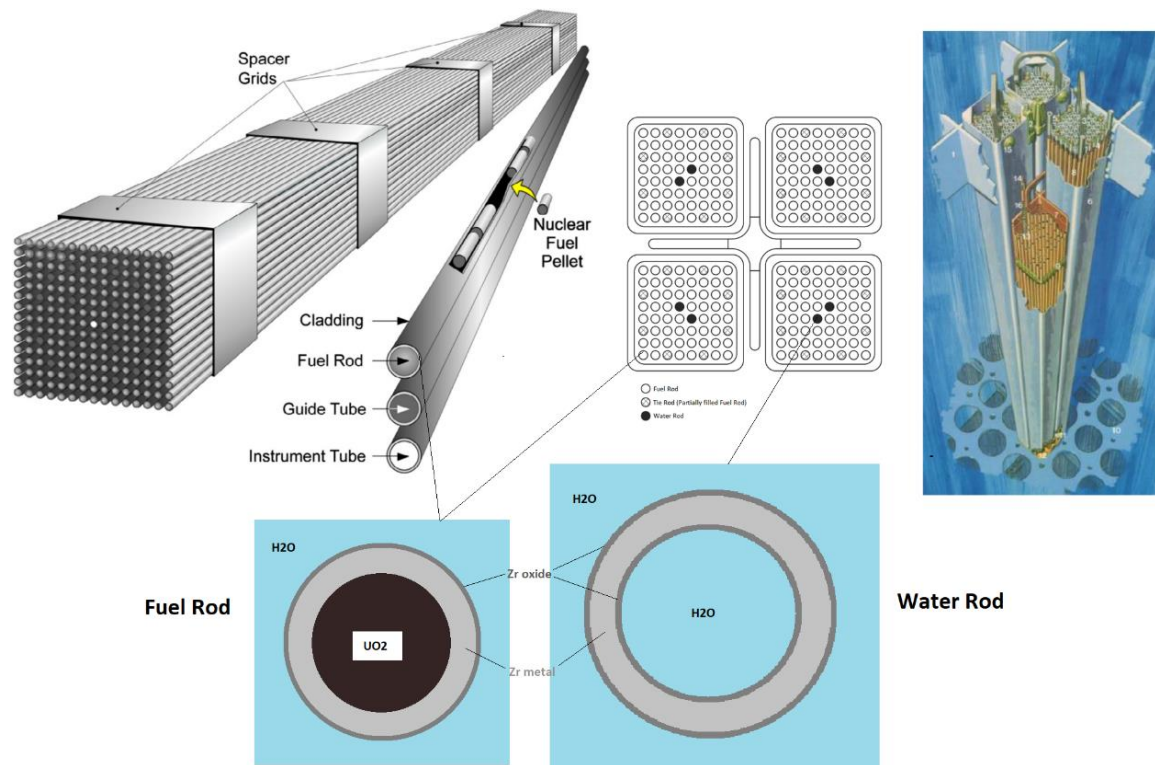


Figure 1-1: Illustration of the fuel assembly of a LWR with fuel rods (top left) and of a BWR fuel assembly with fuel rods, water rods and control rods (top right). The fuel rod and water rod corruptions are also illustrated, with an oxide forming on the rod surfaces in contact with the coolant (adapted from [7, 9, 10]).

In order to improve the economics of nuclear power plants and reduce nuclear waste, there is a drive to increase the fuel utilization – known as burnup – in the reactor. It can be expressed in terms of actual energy released (in gigawatt-days) per mass of initial fuel (in metric tons of uranium or heavy metals in case of mixed fuel) [11]. Increasing the fuel utilization allows a power station to reduce its frequency of refueling, its volume of fresh fuel required and spent fuel waste – which in turn limits the potential for diversion of plutonium for nuclear weapons

from those waste. However, it implies longer time in the aggressive reactor environment for the fuel and cladding, and detrimental effects such as the acceleration of corrosion on Zry-4 beyond 30 GWd/tU have been observed. Thanks to significant efforts in the industry that led to the optimization of existing alloys and the development of modern alloys such as ZIRLO and M5, the burnup of nuclear fuel already improved from $30 - 40 \text{ GWd/tU}$ to $60 - 65 \text{ GWd/tU}$ [11]. With a drive to further increase the burnup, more knowledge on the effects of longer reactor exposure on the fuel cladding materials is necessary, especially the detrimental effects that arise with increased radiation damage and increased concentration of fission products [12, 13]. As such, the focus of this work is to study the effect of Ni in accelerating hydrogen ingress at high burnup in Zry-2.

1.2 Zirconium alloys in the nuclear industry

1.2.1 History of the development of zirconium alloys

When the project of nuclear submarine propulsion started in the 1940's, groups of scientists were asked to investigate metals for use in nuclear reactor cores. The material specifications were to resist high temperature corrosion and intense radiation for long periods of time without failure, and without interacting with the neutron flux. Also to be used as cladding, the heat transfer properties are of importance to increase the thermal efficiency of the reactor. Additionally, nuclear naval fleet ambitions required reasonable production cost in large quantities. At that time, few engineering data were available on zirconium and its production was very limited. However, when tested it was found that its corrosion properties were reasonable and when its high transmission of neutrons (low absorption cross section for thermal neutrons) was noted, zirconium was selected among stainless steel, aluminum, and beryllium [8, 14].

Early on, the Kroll process enabled to produce high-purity zirconium with adjustable composition and properties. The new high-purity sponge zirconium proved to have poor corrosion resistance and lower mechanical properties compared to the crystal-bar produced material. In fact, pure zirconium was shown to have the worse corrosion properties, and any small additions of alloying elements was beneficial [15]. Therefore, the development of a zirconium-based alloy started. The first of the Zircaloy series, later called Zircaloy-1 (Zry-1), was a $Zr-2.5Nb$ alloy. Tin was added to counteract the effect of N , involuntarily picked up during material processing. Zry-1 showed improved corrosion resistance relative to the pure metal but still underwent breakaway corrosion i.e. increasing corrosion kinetics with time [15, 16]. When the beneficial effects of iron, nickel, and chromium additions (present in stainless steel) were found [17], a second alloy was proposed: Zircaloy-2 ($Zr-Sn-O-Cr-Fe-Ni$). Because of its high corrosion resistance in boiling environment, Zry-2 is still currently used in BWRs, with the addition of an inner liner made of a higher purity Zr alloy to prevent pellet-cladding interaction (PCI) failures in the fuel rods [18-21]. Zircaloy-3 - a low tin variant - was soon abandoned after being tested. The observation that nickel additions enhance hydrogen absorption by the metal during corrosion [22] led to the development of Zircaloy-4, a variant of Zircaloy-2 in which the nickel has been replaced by additional iron. This has been the main cladding material of PWRs but can suffer enhanced corrosion past a burnup of 30 GWd/tU . Zry-4 has been replaced in PWRs by improved modern alloys such as ZIRLO (Westinghouse) and M5 (Areva, today Framatome) in the 2000's [13]. In the heavy water moderated CANDU (Canadian deuterium uranium) and the Russian RBMKs (BWR) and WWERs (PWR), $Zr-Nb$ alloys have been used instead of zircaloys [23]. It is worth mentioning that in CANDU, the exposure is much lower because only natural uranium is used which highly reduces energy content in the fuel. Due to the great results of Zry-4 and $Zr-2.5Nb$ in LWRs, ZIRLO ($Zr-Sn-Nb-O-Fe$) can be considered an intermediate between these two alloys and show better corrosion resistance in the reactor than

Zry-4 [24]. M5 is a *Zr-Nb-O* alloy with some iron and sulfur content which also show improved corrosion resistance, particularly at higher burnup, and a lower hydrogen pickup fraction [25, 26]. The addition of *Nb* to Zircalloys also provided better resistance to irradiation swelling, severe at high burnups for zircalloys which limits the lifetime in the reactors [27]. Table 1-1 gathers the main zirconium alloys, their composition, and their use in the nuclear industry.

Table 1-1: Composition (wt.%) and use of zirconium-based alloys in nuclear reactors. ASTM specifications for Zircaloy-2 and Zircaloy-4 [28-30], nominal composition for Zr-Nb [31], M5 [25] and ZIRLO [24].

	Zircaloy-2	Zircaloy-4	Zr-Nb	M5	ZIRLO
Sn	1.2-1.7	1.2-1.7	-	-	1.0
Nb	-	-	1.0-2.8	1.0	1.0
Fe	0.07-0.20	0.18-0.24	-	-	0.1
Cr	0.05-0.15	0.07-0.13	-	-	-
Ni	0.03-0.08	-	-	-	-
O	0.1-0.14	0.1-0.14	-	0.125-0.135	0.125
Use	BWRs	PWRs	CANDUs, RMBKS and WWERS	PWRs	PWRs

A second alternative to increasing fuel burnup is the development of advanced cladding material. After the Fukushima Dai Ichi accident, considerable effort has been made to create accident tolerant fuels that can provide additional coping time in case of loss of coolant accident (LOCA). A non-exhaustive list of candidates are ceramic materials such as silicon-carbide (*SiC*), high entropy alloys such as *FeCrAl* or *CrFeMnNi*, or coated *Zr* alloys [8, 12, 32-39]. When the base material is no longer *Zr*, these materials can provide larger safety margins by improving the corrosion resistance to the high temperature corrosive environment during beyond design basis accident (BDBA). However, these *Zr*-free fuels do carry a neutronic penalty and due to the

lengthy and rigorous process of licensing materials for use in nuclear power plants, as well as the expensive irradiation and corrosion tests on a multitude of different standards, the deployment of advanced *Zr*-free cladding materials is in the 15-20 year time frame [8, 12, 33]. On the other hand, coated *Zr* alloys benefit from the abundant literature on *Zr* alloys corrosion and the protective coating on fuel claddings can significantly improve the oxidation resistance during LOCA with little change to the reactor design [32]. From the many materials tested in the past 10 years, it is worth mentioning chromium coatings [32, 35, 40, 41] and nitride-based coatings (such as *TiN* and *TiAlN*) [34, 42, 43] which have shown good corrosion resistance and great adherence. However, further investigations are required for a comprehensive understanding and optimization of the coatings, especially the long-term effects in the nuclear reactor environment.

1.2.2 Metallurgy of zirconium alloys

Zr is a transition metal of atomic number $Z = 40$ and natural atomic mass $A = 91.22$ amu. Pure zirconium is a soft, ductile, and malleable greyish-white material with two solid phases up to the melting temperature of 2128 K (1860°C) and a boiling point at 4650 K (4377°C). At atmospheric pressure and below 1138 K (865°C), it exhibits a hexagonal compact (hcp, space group $P6_3/mmc$) crystal structure (αZr) with lattice parameters $a = 0.323\text{ nm}$ and $c = 0.515\text{ nm}$, giving a c/a ratio of 1.593 (slightly lower than the ideal value of 1.633). Starting at 1138 K (865°C), zirconium undergoes an allotropic transformation to body-centered cubic (bcc, space group $I m\bar{3}m$) phase (βZr), stable until the melting temperature of the metal [23]. Because of this allotropic transformation, zirconium can be strengthened via rapid cooling from the βZr phase (known as β -quenching for zirconium material) [23, 44]. At high pressure, αZr transforms into another hexagonal structure ($P6/mmm$), not close-packed, called ωZr . The transition pressure is estimated to be 2.1 GPa at 300 K . It is metastable in ambient conditions when

pressure is dropped and transitions back to αZr at 470 K (197°C). Eventually, as pressure and temperature increase further, ωZr transforms into βZr and the triple point is estimated around 5 GPa and 950 K [45, 46]. Due to the high pressure required for ωZr , it is generally not observed in the microstructure of the materials for nuclear use, but Ishii's work [47] measured the presence of ωZr beneath the oxide of Zry-2 when corroded in air at 450°C. It was argued to result from the high compressive stresses in the metal from corrosion of the base metal, as explained in section 1.3.3. The pressure-temperature phase diagram for Zr from Zhang et al.'s work [46] is shown in Figure 1-2.

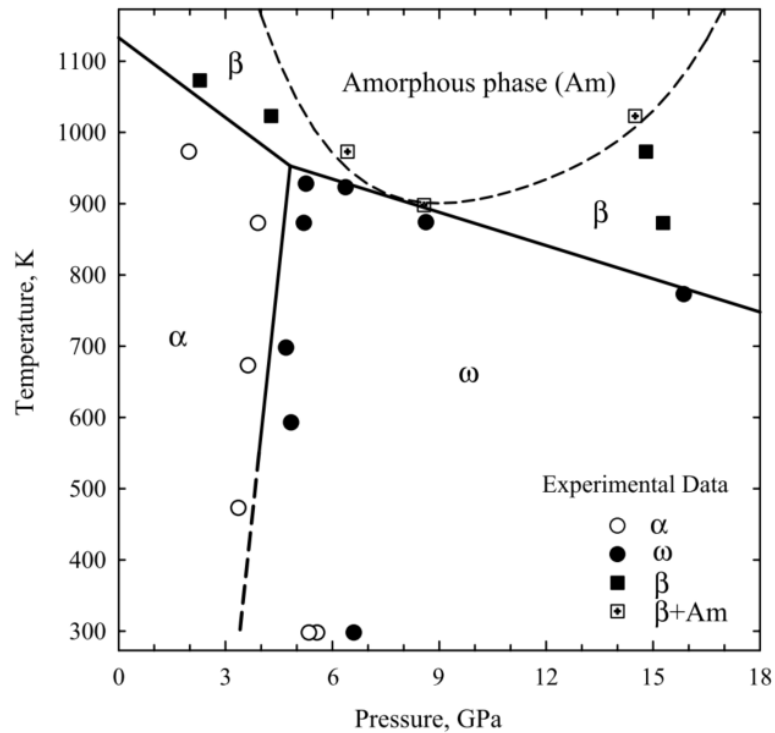


Figure 1-2: Pressure-temperature diagram of Zr for pressures and temperatures up to 1200 K, taken from Zhang et al. [46].

Zirconium is the ninth most abundant metal in the earth's crust, and normally contains impurities of hafnium (Hf) with a concentration fluctuating between 1 and 3 wt.% [48, 49].

Because hafnium's propensity to thermal neutron capture is 100 times higher than for zirconium [8], zirconium must be purified to very low contents of *Hf* (less than 100 *wt.ppm*) prior to use in nuclear reactors – a challenging process due to the chemical similarities between the two. These occur generally as the mineral form zircon ($ZrSiO_4$), and sometimes as baddeleyite (ZrO_2 mineral). *Hf* and other impurities are extracted via distillation, calcination, and carbochlorination [48]. The Kroll process, developed in the 1940's for titanium, enables the production of zirconium metal by reduction of the zirconium chloride $ZrCl_4$ by liquid magnesium, and after a vacuum distillation to separate to reduced solution, so-called high purity sponge *Zr* is available. Zirconium metal can also be obtained via an electrolysis processes that may offer economic benefits, as reviewed by S. Li et al. [50], but the different techniques have yet to replace the traditional Kroll process. Eventually, high purity *Zr* is obtained by the Van Arkel process which consists of gas transport of *Zr* reacting with iodine at medium temperature followed by the iodide separation and deposition at high temperature on an electrically heated filament [23].

Once pure *Zr* sponge is available, the alloying elements are added using the vacuum arc remelting process. This technique consists of melting the pure material (called electrode) in a vacuum by means of an electronic arc while adding the desired alloying elements of interest in powder form. Because this operation is done under high vacuum, it allows for strict control of the concentrations of the beneficial and detrimental impurities [51]. The produced zirconium alloy ingots consist of a solid solution of *Zr* and some alloying elements, while the other elements separate from the matrix to form secondary phase precipitates (SPPs). The improved corrosion highly depends on the uniformity and overall concentration of the elemental additions [52]. While the overall concentration is controlled during the vacuum arc melting process, homogeneity is achieved via the initial heat treatment of the ingot. Among the alloying elements, *Sn* and *O* typically remain in solid solution (SS) in αZr , while *Fe*, *Cr*, *Ni* form SPPs as inclusions in the matrix because of their very low terminal solubility in αZr . Therefore, the ingot is usually hot

rolled (tubes) or forged (plates) at temperatures near above 1273 K (1000°C) to reach the upper αZr , the $(\alpha + \beta)Zr$ or the βZr stability regions, where the alloying elements have higher solubility, followed by a β -quench. Because of higher solid solubilities of the alloying elements in βZr , this heat treatment allows for their dissolution and homogenization in the material [23]. During the rapid cooling, the alloying elements are redistributed locally: *Sn* and *O* remain at the center of the α platelets while *Nb* and the transition metals (*Fe*, *Cr*, *Ni*) are ejected toward the grain interfaces. Plastic deformation strains have been observed as a result of the segregations, requiring further thermomechanical processes to restore ductility [53]. Moreover, as the alloy is worked to produce the desired shape of the materials via hot extrusion or cold rolling, additional intermediate annealing treatments are necessary to lower the hardness.

Annealing heat treatments are usually performed in the range of [530°C-600°C] to allow for full recrystallization (RX) of the material. The deformed grains of the bulk are fully dissolved to nucleate equiaxed defect-free *Zr* grains. The temperature of the last annealing process can be reduced to avoid full RX. This process allows for dislocations and other defects to partially remain in the material, improving its mechanical properties, and is applied to Zry-4 alloys – defined as cold worked stress relieved (CWSR or SR) materials - when utilized in PWRs, whereas BWRs use fully RX Zry-2 [23].

It has been found that the SPPs strongly correlate with the oxidation behavior of the material. Typically, larger precipitates ensure lower uniform corrosion in PWRs [54] while smaller precipitates prevent localized corrosion in BWRs [55]. The size and distribution of these precipitates are controlled by manufacturing and thermal treatment of the alloys. The β -quench heat treatment described above sets the initial size distribution of the SPPs. Successive annealing procedures on the alloy increase the size of the precipitates [56] due to grain growth by Ostwald ripening in which the smallest particles dissolve and the bigger ones grow. The process minimizes the free energy of the system by reducing the precipitate/matrix interface area [57].

The cumulative annealing parameter (CAP) was introduced to correlate hardness reduction and precipitate characteristics with all the thermomechanical processes [58]. It is defined as the integral of the thermal treatments:

$$CAP = \sum_i t_i \exp\left(\frac{-Q}{RT_i}\right) \quad (\text{Eq. 1-1})$$

where t_i the annealing time (h) and T_i the annealing temperature for the i th heat treatment, Q the activation energy, and R the molar gas constant. $\frac{Q}{R} = 40\,000\,K$ approximately for Zircalloys [59, 60].

A value for CAP around $10^{-17}h$ corresponds to a mean SPP size of $150 - 200\,nm$ [56], and was seen optimum for uniform corrosion of Zry-4 materials in PWRs [56, 61]. On the other hand, annealing parameters about 10^{-18} correspond to a mean SPP size of about $50\,nm$, and optimizes corrosion and hydrogen pickup of Zry-2 in BWRs, especially at high burnup [56, 59]. Figure 1-3 illustrates the relationship between the mean particle sizes of the intermetallic precipitates as a function of the CAP for β -quenched Zircalloys from Garzarolli et al.'s work [56]. For better approximation of the particle size, it has been argued that a Q/R value of $32\,000\,K$ should be used, and to add the ratio of $0.45/CDR$ where CDR is the cooling down rate (K/s) in the α -phase during the initial β -quench of the alloy [62].

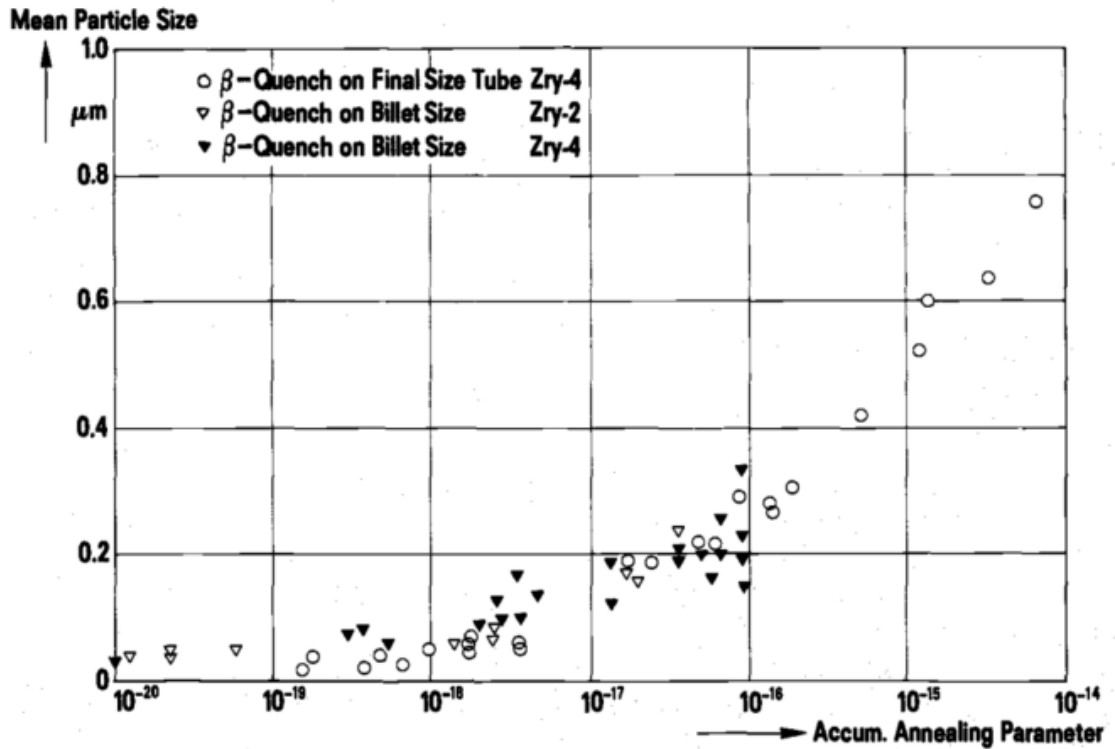


Figure 1-3: Mean intermetallic precipitate sizes as a function of the cumulative annealing parameters for β -quenched Zircaloys. Figured taken from Garzarolli et al.'s work [56].

1.2.3 Alloying elements in Zircaloys

As mentioned before, the distribution of alloying elements in the supersaturated α Zr solid solution or in second phase precipitates is determinant of the corrosion performances of Zr alloys in nuclear reactors. In this section, the different alloying elements of zircaloys and their microstructure are further detailed. The ASTM specifications for Zircaloy-2 and Zircaloy-4, found in Table 1-1, refer to five main alloying elements: *Sn*, *Fe*, *Cr*, *Ni*, and *O*. Detrimental impurities such as carbon, nitrogen, sulfur, cadmium, or cobalt, have their concentration strictly controlled during the manufacturing process [23] and are not detailed here. During reactor operations, hydrogen enters the materials during corrosion, a mechanism referred to as “hydrogen

pickup”. Hydrogen ingress is of concern because of the embrittlement of the alloy due to the precipitation of brittle zirconium hydrides (ZrH) and is further discussed in section 1.4.

As mentioned above, initially the additions of tin in zircalloys counteracted the N impurities added during the early manufacturing processes [15] but was kept in zircalloys and added to ZIRLO for its beneficial effect on mechanical properties in the power plants, especially in-reactor deformation [63, 64]. The Sn concentration range in zircalloys is 1.2 – 1.7 wt. % [28-30]. It was later found that decreasing Sn content within the specification range improves corrosion resistance without reducing mechanical properties, and so it was suggested to control the tin concentration near the lower limit of 1.2 wt. % [64]. The phase diagram of the $Zr-Sn$ system is plotted in Figure 1-4. It can be seen that Sn solid solubility starts increasing significantly past 300°C and Zr_4Sn precipitates should be present at room temperature. However, Zr_4Sn phase is not observed in zircalloys because of the slow kinetics of the precipitation and Sn is rather located in the supersaturated αZr grains, acting as an α -phase stabilizer as the temperature increases [65].

Similarly, oxygen is highly soluble in the αZr phase and acts as an α -phase stabilizer at high temperature, which strengthens the material. Nitrogen is usually preferred to oxygen to improve the mechanical properties of metals, but it has a severe detrimental effect on the corrosion performance of zirconium alloys [23]. The specified oxygen concentration range in zircalloy is 0.1 – 0.14 wt. %, or 1000 – 1400 wt. ppm [31]. When reaching concentrations above 2000 wt. ppm, the ductility of the material is negatively affected [23]. Oxygen atoms can interact with the dislocations at medium temperatures and cause age-strengthening phenomena [66, 67]. The phase diagram of the $Zr-O$ system is shown in Figure 1-5. Zirconium oxide ZrO_2 (forming at O concentrations above approximately 30 wt. %, or 300 000 wt. ppm for all temperatures until melting) is described in the next section focused on corrosion in the LWRs.

On the other hand, the transition metals (Fe , Cr , Ni) have very low solid solubility in αZr , but are soluble in βZr , and are considered β -phase stabilizers. In Zircaloy-2, they are found mostly in two types of Laves phase precipitates [68]: $Zr(Fe, Cr)_2$ – with cubic and hexagonal crystal structures – and $Zr_2(Fe, Ni)$ – with a body centered [69] tetragonal structure [70-73]. Only the $Zr(Fe, Cr)_2$ precipitates are found in Zry-4 due to the absence of Ni . Cr content is specified to be 0.05 – 0.15 wt. % in Zry-2 and 0.07 – 0.13 wt. % in Zry-4. Fe content, slightly higher in Zry-2 and compensating for the absence of Ni in Zry-4, are 0.07 – 0.20 wt. % and 0.18 – 0.24 wt. % respectively. Lastly, Ni content in Zry-2 is in the range of 0.03 – 0.08 wt. % [28-30]. These alloying elements strongly improve the corrosion resistance and hydrogen pickup in the reactor, as well as the strength of the materials due to the formation of the secondary phase precipitates in the bulk [23]. Figure 1-6, Figure 1-7, and Figure 1-8 show the phase diagram of the $Zr-Cr$, $Zr-Fe$, and $Zr-Ni$ respectively. It can be seen that $ZrCr_2$, Zr_3Fe , and Zr_2Ni are the stable precipitates at room temperature. The first precipitates to form are the $ZrCr_2$ and the Zr_2Ni types. The Zr_3Fe phase starts precipitating at a lower temperature than the other two, and as a result Fe substitutes in the already present SPPs, forming $Zr(Fe, Cr)_2$ and $Zr_2(Fe, Ni)$ particles, rather than to nucleate [65, 68]. The microstructural and compositional changes in the precipitates due to corrosion and irradiation in the reactor are discussed in later sections.

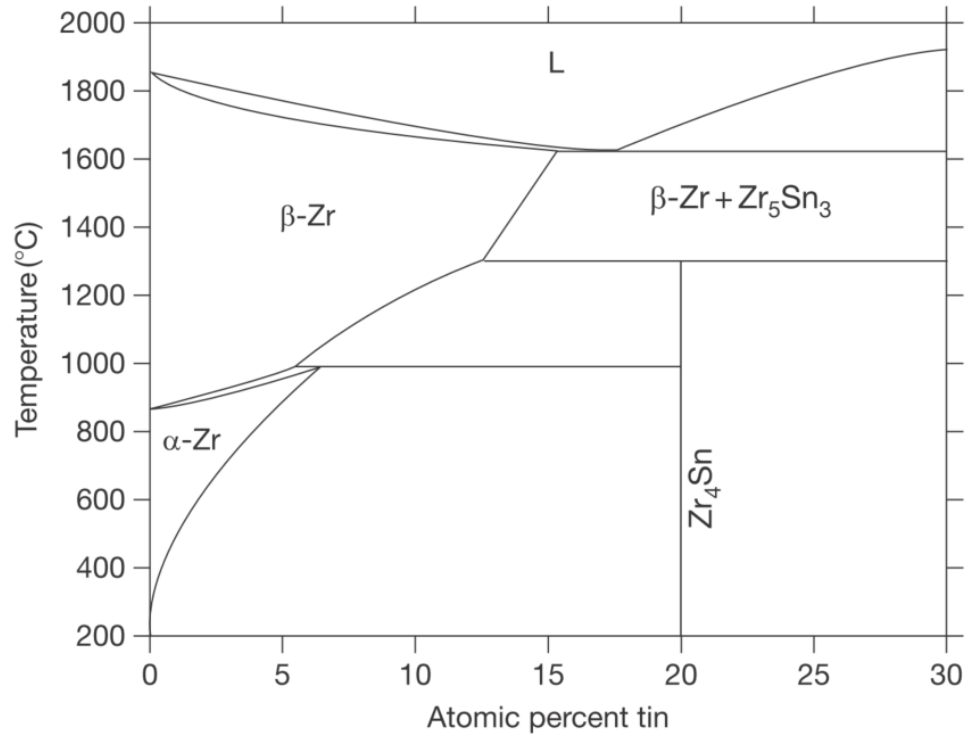


Figure 1-4: Zr-Sn phase diagram [23].

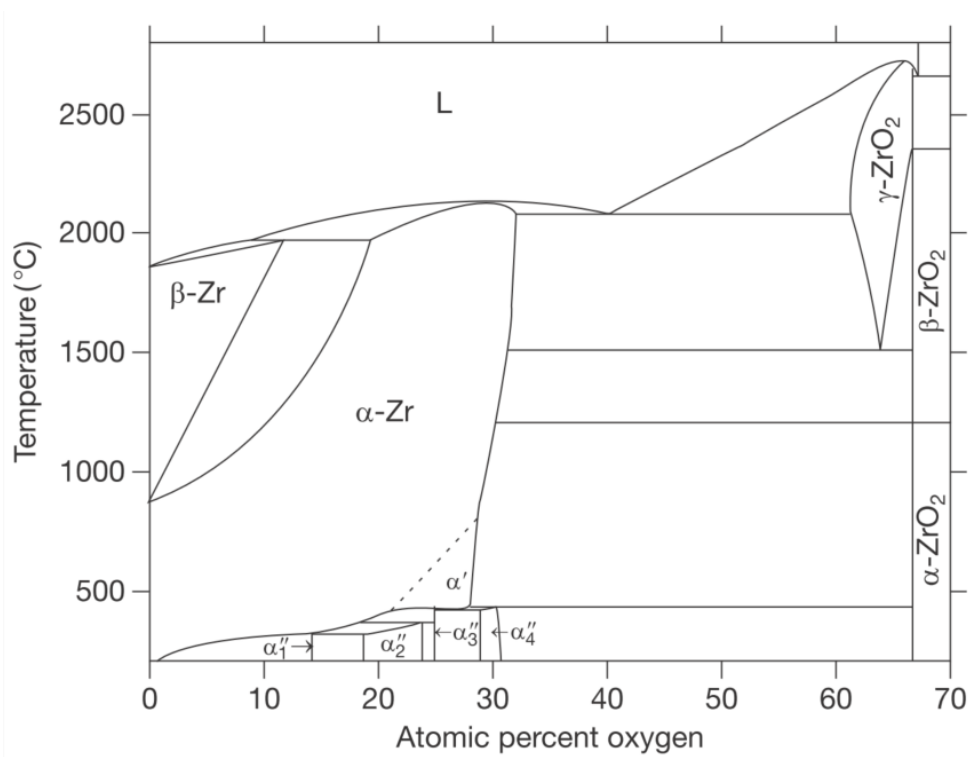


Figure 1-5: Zr-O phase diagram [23].

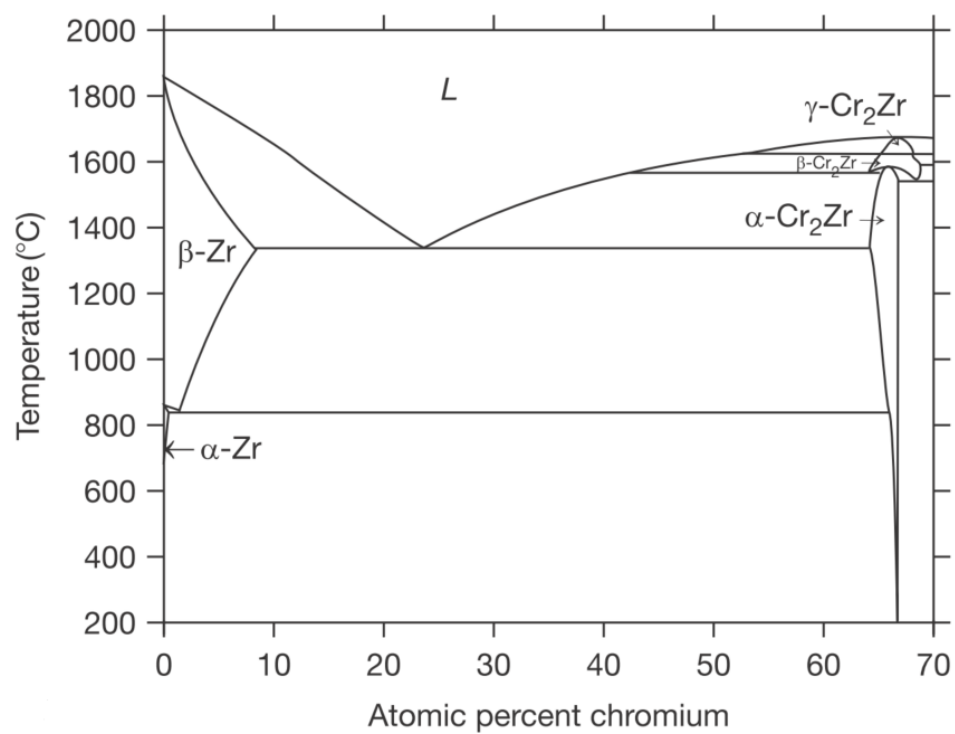


Figure 1-6: Zr-Cr phase diagram [23].

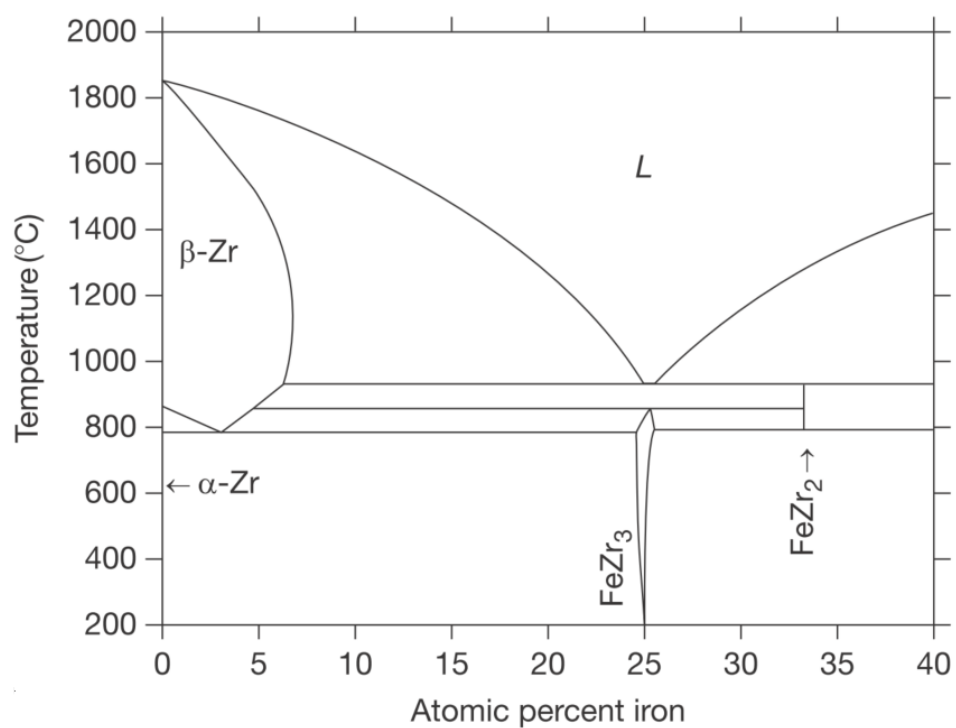


Figure 1-7: Zr-Fe phase diagram [23].

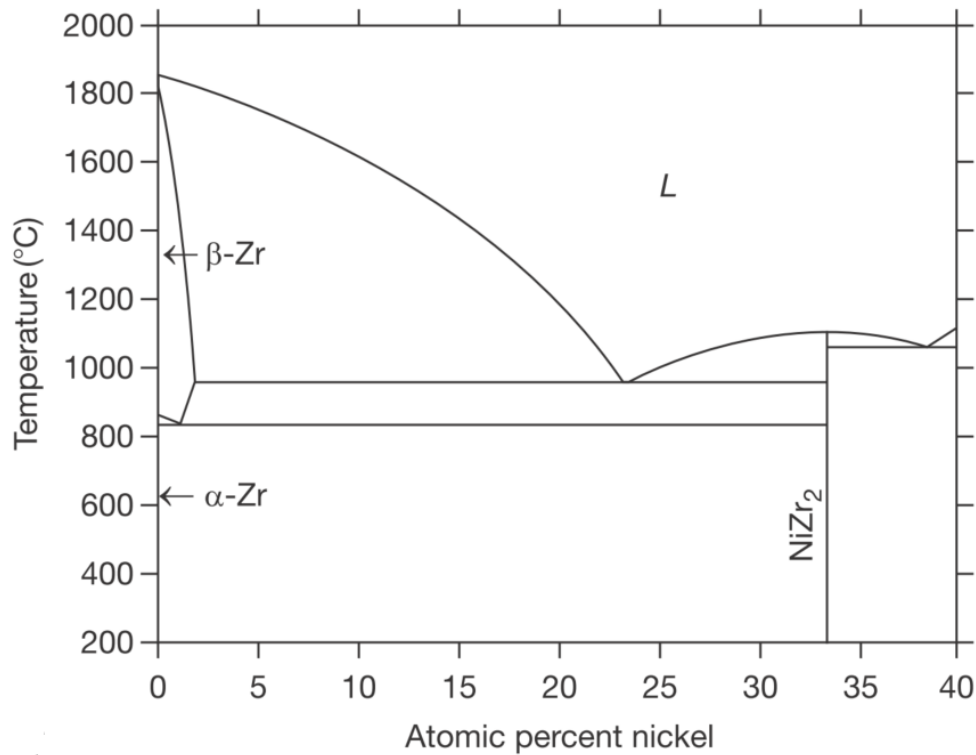


Figure 1-8: Zr-Ni phase diagram [23].

1.3 Corrosion of the Zircalloys in Light Water Reactors

1.3.1 Zirconium oxide phases

When used in the highly corrosive environment of a LWR, Zr alloys endure oxidation of the zirconium atoms and of the alloying elements by the oxygen in the coolant water. An oxide layer forms on the surface of the material which controls further corrosion. The properties of this protective layer highly depend on the microstructure and alloying content of the bulk [52]. When oxidized in a water environment, Zr exhibits predominantly the +4 oxidation state (IV), in the form of zirconium dioxide (ZrO_2), also known as zirconia. In addition, thin mono-oxide ZrO (oxidation state +2 or II) and an αZr solution saturated in oxygen ($\alpha Zr(O)_{sat}$) are present close to the metal/oxide interface in the oxide layers of zirconium alloys [74-76]. The presence of the

thin layer ($< 1\mu m$) of suboxide ZrO , with a hexagonal crystal structure, and its morphology is believed to depend on the oxidation temperature [77]. The thickness of this layer varies during the corrosion process, and a thicker sub-oxide layer is seen in $Zr-Fe-Cr$ alloys corroded in supercritical water at $500^\circ C$ compared to $360^\circ C$ [78].

ZrO_2 exhibits three main polymorphs: monoclinic ($m-ZrO_2$), tetragonal ($t-ZrO_2$), and cubic ($c-ZrO_2$). The $Zr-O$ phase diagram at atmospheric pressure from Abriata et al.'s work [79] is plotted in Figure 1-9 and described further below. Highly compacted orthorhombic phases have also been observed or predicted under extreme pressure, which are orders of magnitude higher than in nuclear reactors conditions [80, 81]. The relative stability of oxide phases further depends on temperature, concentrations of alloying elements, impurities, and defects in the material [82]. Additionally, grain size and stresses have an important impact on the oxide microstructure [83].

At low and moderate temperature, the stable phase is $m-ZrO_2$ (space group is $P2_1/c$ with the lattice parameters $a = 5.197 \text{ \AA}$, $b = 5.280 \text{ \AA}$, $c = 5.345 \text{ \AA}$, and $\beta = 99.53^\circ$) [81, 84]. The $t-ZrO_2$ has a more compact structure (space group is $P4_2/nmc$ with the lattice parameters $a = 3.629 \text{ \AA}$ and $c = 5.208 \text{ \AA}$) [81, 84] and is stabilized at higher temperature ($T > 1170^\circ C$) or higher pressure ($P > 2.5 \text{ GPa}$) [85], or with small crystallite size [86] or alloying elements [87-89]. In nuclear reactors where the temperature is well below the transition temperature, some $t-ZrO_2$ has been observed, especially close to the met/ox interface [90-92], due to compressive stresses and small crystallite size in the oxide [86, 93], impurities [94], and oxygen vacancies [95, 96]. Eventually, $c-ZrO_2$ is observed at temperatures above $2370^\circ C$ (space group is $Fm3m$ with the lattice parameters $a = 5.128 \text{ \AA}$) for stoichiometric compounds (66.7% *at. %* of oxygen) [81, 84] and at lower temperature (starting at $1525^\circ C$) in sub-stoichiometric oxide (with eutectoid

point at 63.6 at. % of oxygen as seen in Figure 1-9) [79]. These three crystal structures are shown in Figure 1-10 [84] with the oxygen atoms in red and the zirconium atoms in blue.

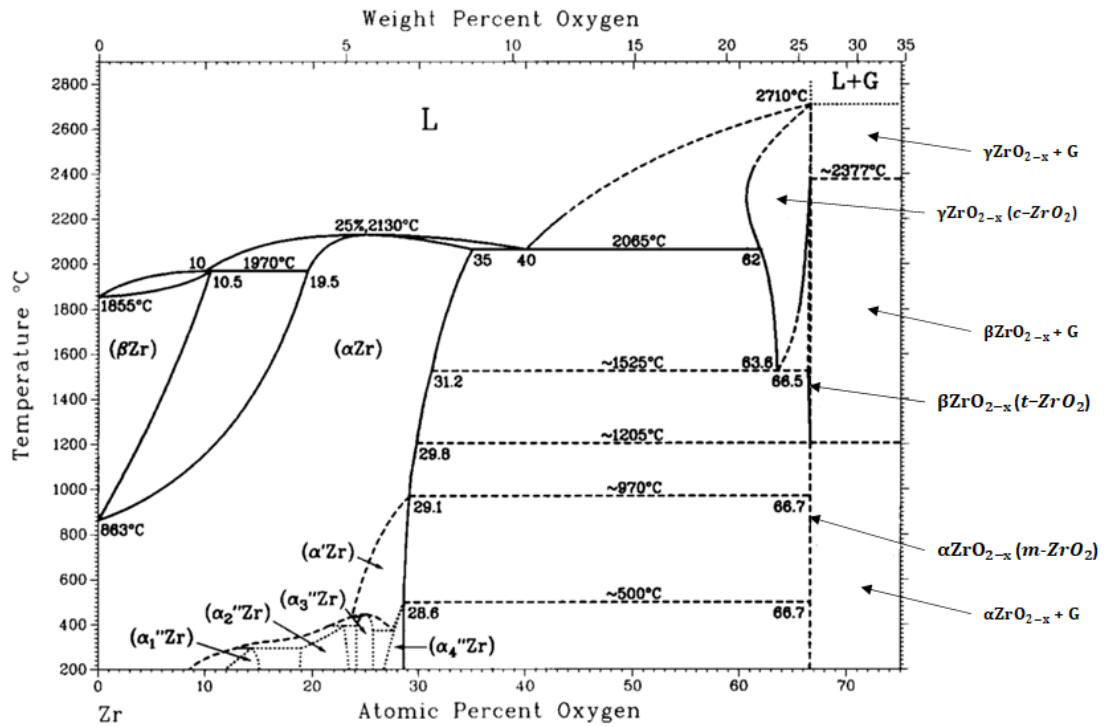


Figure 1-9: Zr-O phase diagram. Adapted from [79]

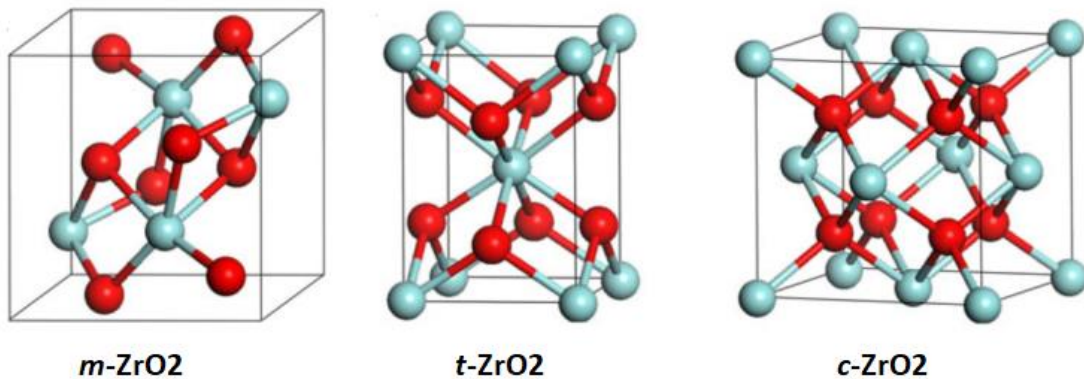


Figure 1-10: Crystal structures of ZrO_2 (monoclinic, tetragonal, and cubic). Zr atoms are shown in blue while O atoms are in red. Illustration taken from [84].

1.3.2 Corrosion process of zirconium alloys in Light Water Reactors

Like most metals, *Zr* atoms are oxidized by the coolant during operation in nuclear reactors. The driving force for the oxidation to occur is measured by the change in Gibbs free energy ΔG of the system. The Gibbs free energy change at constant temperature is defined by: $\Delta G = \Delta H - T\Delta S$ where ΔH is the change in enthalpy, T the absolute temperature and ΔS the entropy change. Negative values for Gibbs free energy change signify a spontaneous reaction, with the probability of the reaction occurring increasing as ΔG becomes even more negative [97]. The Ellingham diagram – a plot of the free energy of formation of oxides – for common elements in an oxygen environment is presented in Figure 1-11 [98].

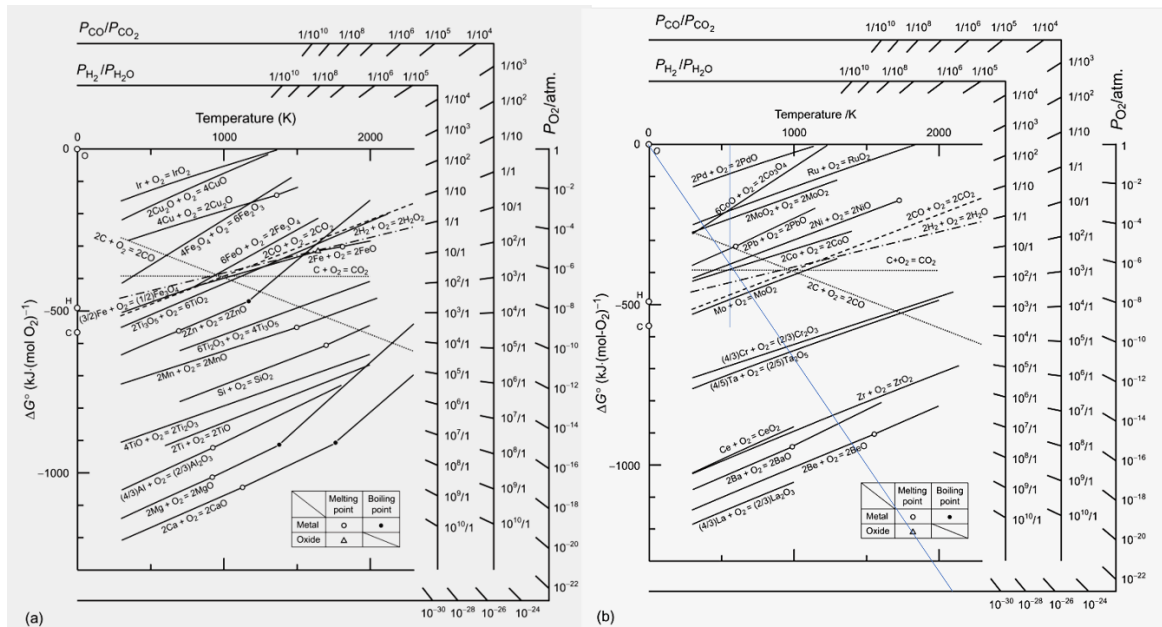


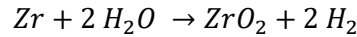
Figure 1-11: Ellingham diagram for common oxides with the Richardson nomographic scales to determine the equilibrium oxygen partial pressure: a) Al, Ca, Cu, Fe, Ir, Mg, Mn, Si, Ti, Zn; b) Ba, Be, Ce, Co, Cr, La, Mo, Ni, Pb, Pd, Ru, Ta, Zr. Taken from [98].

The Richardson nomographic scales are also plotted in Figure 1-11 to determine the equilibrium oxygen partial pressure P_{O_2} of the redox reactions at the specified temperatures. To determine P_{O_2} , a line is drawn from the origin of the Ellingham diagram ($T = 0$, $\Delta G = 0$ i.e. top left corner) to the point on the oxidation line of interest at the specified temperature. The oxygen

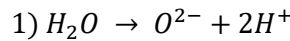
equilibrium partial pressure is then the intersection of the drawn line and the P_{O_2}/atm scale. An example is shown with the blue lines drawn on Figure 1-15-(b) for the redox reaction of nickel: $2Ni + O_2 = 2NiO$ at $T \approx 560 K$ which yields $P_{O_2}/atm \approx 10^{-34}$. The hydrogen and the carbon monoxide equilibrium partial pressures are obtained in a similar manner with the difference that the first point of the drawn line is at $(\Delta G = \Delta G_H, T = 0)$ and $(\Delta G = \Delta G_C, T = 0)$ respectively.

As can be seen from the plot in Figure 1-11, the free energy during *Zr* oxidation is more negative and therefore more spontaneous than metals such as *Fe, Cr, Ni, Pd, Ti* or *Zn*. As a result, *Zr* oxidation is highly spontaneous, and the alloying element get oxidized later than the *Zr* matrix. The delayed oxidation of alloying elements compared to the host has been observed in zircalloys [99-101] and is discussed in more detail in section 1.1.1.

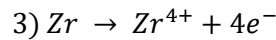
The overall chemical reaction of water corrosion of *Zr* is given by:



This reaction is the result of multiple step reactions and processes occurring at different locations in the material as reviewed by Couet, Motta, and Comstock in [13] and [102], and illustrated in Figure 1-12 [13]. In the case of zirconium alloys, the oxide is stable and adherent to the metal surface and forms a layer through which charged species need to travel for further corrosion to take place. At the oxide/water interface, dissociation of the water occurs, providing O^{2-} anions:

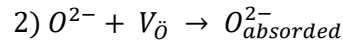


At the metal/oxide interface, oxidation of the zirconium provides Zr^{4+} cations:

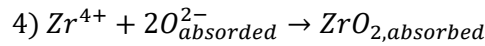


Contrary to what is observed in steels, no metal migration through the layer is observed - Zr^{4+} cations have little mobility in zirconia [103] - and thus oxygen has to travel through the oxide. The transport of oxygen anions is driven by the concentration [104] and electric potential gradients [13]. While the concentration gradient results from the coolant water being the source

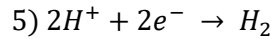
for oxygen atoms at the oxide/water interface, the electric fields arise from the ambipolar diffusion of electrons and anions [105] and local space charging in the oxide [106]. Oxygen vacancies are present in the oxide (the ZrO_{2-x} oxide is sub-stoichiometric [104]) due to the oxide forming at the cheapest oxygen cost it can in the oxygen starved metal/oxide interface. At the water interface, O^{2-} anions are absorbed from the environment to fill the vacancies:



The transport of O^{2-} is equal to the transport of O^{2-} vacancies, $V_{\dot{O}}$, and the vacancy current is preferably used. Once the $O_{absorbed}^{2-}$ reach the metal interface, they react with the cations to form new layers of oxide:



If the electrons can move outward to the cathodic sites, they reduce the H^+ to form dihydrogen:



The location of the cathodic sites of the reaction is unknown and may happen withing the oxide rather than at the water interface as H atoms diffuse toward the metal [107, 108]. Supposing that the electrons cannot migrate easily through the oxide, the alternative way to close the reaction is for H to reach the oxide/metal interface, combine with electrons and be absorbed in the metal – the process of hydrogen pickup. The H atoms which make their way into the material dissolve or form zirconium hydrides ZrH in the metal [109]. The mechanism by which the absorption and transport of hydrogen occurs is not fully understood, as discussed in further detail in 1.4, and is of great concern in Zr alloys due to the brittle properties of zirconium hydrides [107, 110]. The oxide electronic conductivity is therefore of great importance: if the H_2 recombination occurs close to the water, little hydrogen will be picked up during corrosion. This was shown in Couet's work where the hydrogen pickup in Zry-4 and Zr-2.5Nb alloys was seen to increase as the oxide electronic conductivity decreased [111].

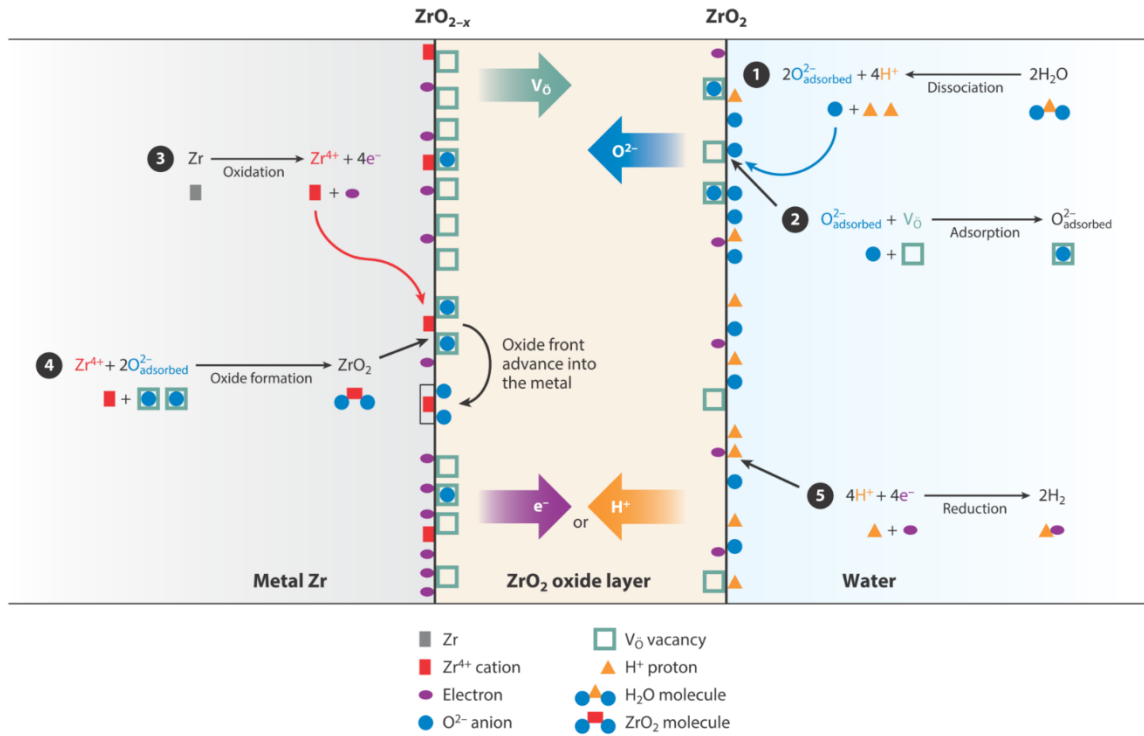


Figure 1-12: Oxidation process of zirconium alloys in a water environment. Surface reactions 1 to 5 happen in series, but the steps controlling the corrosion rate are the transport of charged species (oxygen, electrons, and hydrogen). Figure and caption taken from [13].

The decrease in oxidation rate as the oxide thickens in *Zr* alloys [112] means that the corrosion kinetics are limited by the oxygen or electron transport through the oxide layer. Wagner's oxidation theory of pure metals predicts that this hypothesis leads to parabolic scaling kinetics of the form $\delta = K * t^{1/2}$ (with δ the oxide thickness, K a constant and t the exposure time) under the hypothesis of local chemical potential equilibrium of charged species [113, 114]. However, oxidation of *Zr* alloys is frequently sub-parabolic exhibiting exponents n lower than $1/2$ ($\delta = K * t^n$ with $n < 0.5$). This is thought to be the result of alterations to the oxygen anions and electrons mobility because of oxide microstructure and the presence of local space charge in the oxide [13]. The coupled current charge compensation (C4) model developed by Couet et al. [102] is based on the theory developed by Fromhold [115] in which the electron current and potential space charge in the oxide clearly affect the corrosion rate. The theory hypothesizes a

global zero net current (oxygen and electron current compensate each other) but allows for local concentration differences which form electric fields across the oxide, in turn affecting the movement of charge species. Importantly, although an overall zero net current is necessary to maintain charge neutrality, a local imbalance can occur, resulting in a space charge. The C4 model was successfully applied to *Zr-Nb* corrosion where the oxidized niobium ions compensate positive space charges in the oxide by accommodating additional oxygen vacancies [102].

As corrosion kinetics vary from one alloy to the other when corroded in the same environment [116], it has been a challenge to provide a unified model for the sub-parabolic corrosion behavior in *Zr* alloys. Although the charge effect approach incorporating effects of oxidized alloying elements may resolve this issue [13], the conductivity of specific oxide microstructure and precipitate composites needs to be determined for a quantitative evaluation. The corrosion rate values for *Zr* alloys are further discussed in the next section, along with the description of oxide microstructure and growth.

1.3.3 Oxide growth and stability

In order for the metal to resist the temperature oxidation environment of nuclear reactors, the oxide formed on zirconium metal must form an adherent oxide barrier. Due to differences in molar density of *Zr* and *ZrO₂*, stresses accumulate as the oxide grows. The Pilling-Bedworth ratio, which measures the volume expansion during the oxidation of metals [117], is defined as:

$$PBR(Zr) = \frac{\text{Volume unit cell } (ZrO_2)}{\text{Volume unit cell } (Zr)} = \frac{21.7 \text{ cm}^3 \cdot \text{mol}^{-1}}{14.0 \text{ cm}^3 \cdot \text{mol}^{-1}} = 1.55$$

(Eq. 1-2)

Because $PBR(Zr) > 1$, it is expected that compressive stresses develop in the oxide and tensile stresses in the metal [117-119]. Although the vast majority of this volume difference is

accommodated in the direction of the growing oxide ($1\ \mu\text{m}$ of metal creates about $1.55\ \mu\text{m}$ of oxide), if this ratio is not perfect, some implanted stresses may develop. For pure *Zr*, the behavior of the oxide barrier can vary considerably as some samples maintain a black protective oxide while other samples suffered oxide spalling with a non-protective white oxide early on [15, 16, 120]. The high linear corrosion rate in the presence of the white flaky oxide is usually referred to as the *breakaway* regime, and typically characterized by uneven oxide growth [52, 120, 121]. In contrast, the protective black oxide offers reduced corrosion kinetics until a so-called transition manifested by an abrupt increase in oxide growth. The transition is thought to occur because of the stress accumulation and recrystallisation process in the oxide, making the oxide lose its protectivity as cracks and pores provide the water coolant with a direct access to the metal interface [13, 122, 123]. Specifically, compressive stress accumulation in the oxide eventually creates lateral cracks that interconnect existing pores throughout the near oxide. This percolating condition enables the water to reach the metal interface, leading to increased corrosion kinetics [13, 120, 124].

Once transition occurs, either a non-protective oxide layer develops leading to *breakaway* behavior (*Zr-0.5X* type alloys), or a protective oxide is built under the cracked porous oxide layer, slowing down further corrosion similar to that of the pre-transition regime (zircalloys, *Zr-Nb*, ZIRLO, M5) [13, 120]. In an extensive study of the oxide microstructure of Zircaloy-4, ZIRLO, and *Zr-2.5%Nb* alloy tubing specimens corroded in autoclave (water, 360°C) by Yilmazbayhan [125], the transitions were seen respectively at $1.8\ \mu\text{m}$, $2.0\ \mu\text{m}$ and $2.5\ \mu\text{m}$ and the oxide remains adherent and protective as subsequent transitions occurs, leading to an oxide composed of periodic layers. In another study on *Zr* alloys sheets corroded in water at 360°C by Sakamoto [126], the transition was seen at $2.5\ \mu\text{m}$ for Zircaloy-2 and at about $3\ \mu\text{m}$ for *Zr-2.5%Nb*. The transition thickness is seen to be constant for a specific alloy throughout multiple cycles [13, 125].

The long-term exposure in the reactors leads to thick oxides composed of many periodic layers about $2\text{--}3\text{ }\mu\text{m}$. In PWRs, end of life oxides of up to $100\text{ }\mu\text{m}$ on Zircaloy-4 can occur. In contrast, mainly because the corrosion temperature is much lower in BWRs (288°C), oxide thickness of Zry-2 is typically around $30\text{--}60\text{ }\mu\text{m}$ [59, 127]. An illustration of the uniform oxide formed on Zry-4 and the *breakaway* oxide formed on pure Zr is shown in Figure 1-13 [120].

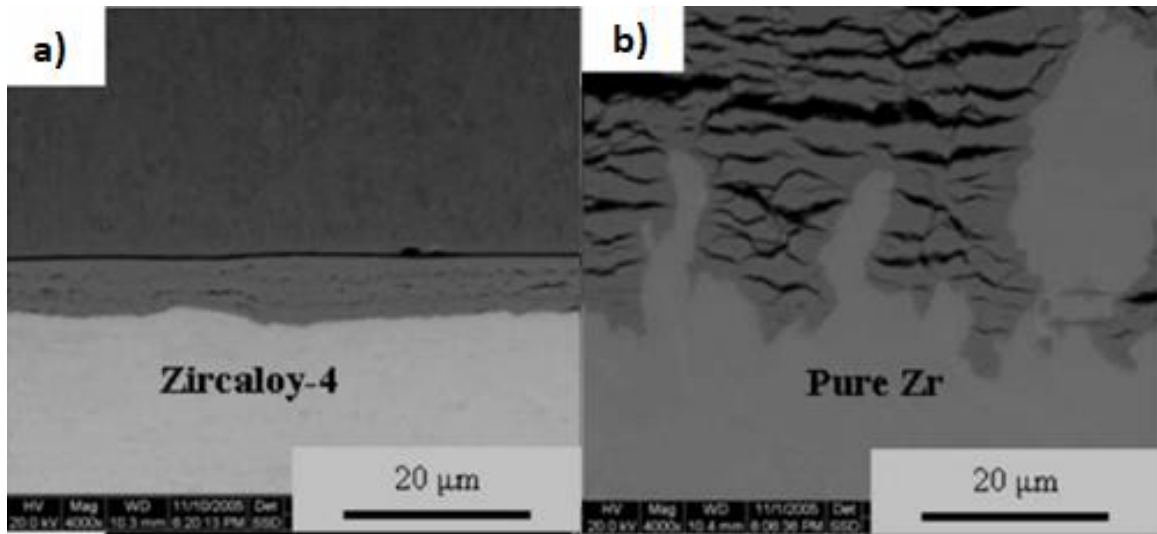


Figure 1-13: SEM micrographs of oxide layers formed in 360°C water: a) uniform corrosion with multiple transitions in Zircaloy-4 after 353 days; b) breakaway behavior in crystal bar Zr after 3 days [120].

As mentioned in the previous section, the corrosion kinetics of Zr alloys are sub-parabolic:

$$\delta = Kt^n \quad (\text{Eq. 1-3})$$

with δ the oxide thickness, K constant, t the exposure time and $n < 0.5$.

These oxide growth rates apply in between transitions, leading to a cyclic sequence of sub-parabolic oxidations. The value for n varies from 0.2 to 0.5 depending on the alloy composition and microstructure, with values closer to 0.3 – 0.35 (cubic) and lower for Zircaloys [128-130]. As exposure time increases, the cycles eventually disappear, and a linear corrosion rate is established. The different kinetic regimes are schematically represented Figure 1-14, produced

from the illustrations in [13, 131-133]. The later linear rate is regarded as the superposition of asynchronized pre-transition growths of various material regions [134]. In the case of long-term corrosion, a second linear regime with increased kinetics has been observed [132].

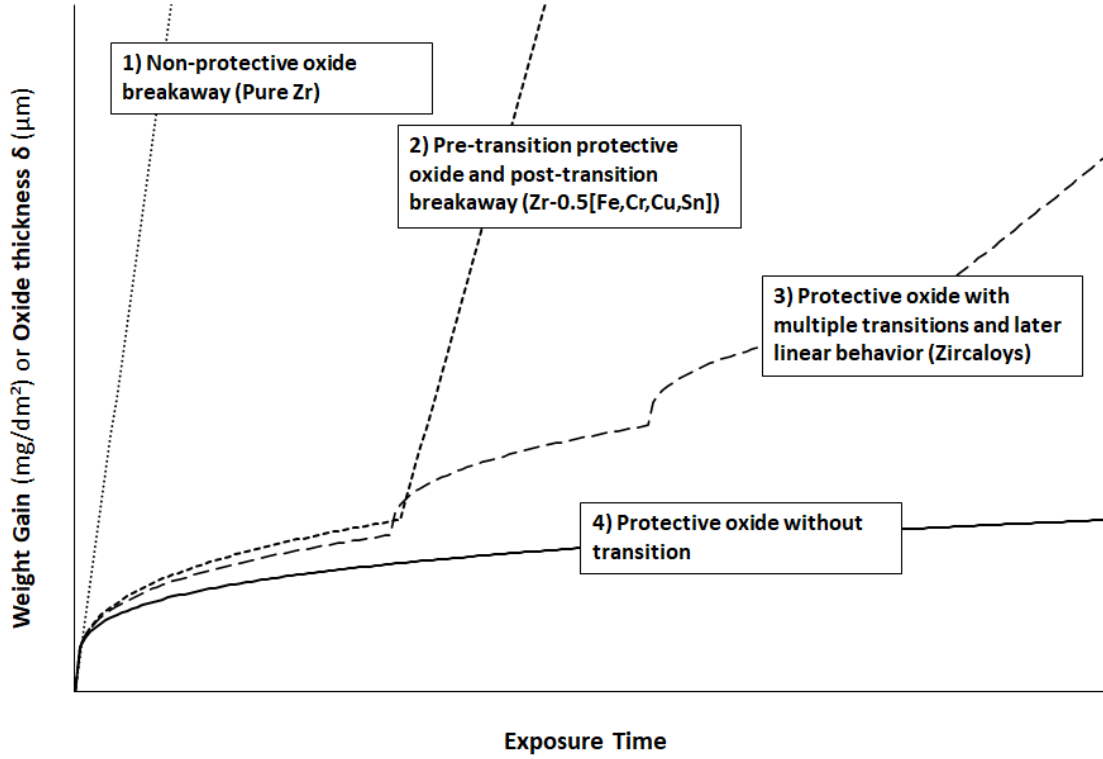


Figure 1-14: Schematic representation of the different corrosion regimes of Zr alloys. After references [13, 131-133].

Because there is little oxide dissolution and the vast majority of the oxygen which arrives at the oxide metal interface is used to create new ZrO_2 rather than being dissolved into solid solution, the oxide thickness can be interchanged with the weight gain (wg) of the material (Figure 1-14) which is easier to access experimentally, especially for autoclave samples. The relationship between weight gain and oxide thickness (assuming uniform oxide growth) is:

$$wg = \delta \times \rho(ZrO_2) \times \left[1 - \frac{M(Zr)}{M(ZrO_2)} \right]$$

(Eq. 1-4)

with zirconia's density $\rho(ZrO_2) = 5.68 \text{ g.cm}^{-3}$, and zirconia and zirconium molar masses $M(ZrO_2) = 123.22 \text{ g.mol}^{-1}$, $M(Zr) = 91.22 \text{ g.mol}^{-1}$, so that:

$$wg [\text{mg.dm}^{-2}] \approx 14.7 * \delta[\mu\text{m}]$$

(Eq. 1-5)

The aggressive environment present in the reactor may cause additional degradation processes to affect the protective oxide layers. These include, non-exhaustively, stress-corrosion cracking (SCC), corrosion fatigue, irradiation creep and thermal stresses (due to the difference in thermal expansion between the oxide and the metal) [82] and may lead to accelerated corrosion rates as burnup and exposure time increase. Also, long-term irradiation enhances corrosion kinetics of Zircalloys [132, 135].

Lastly, while uniform corrosion is typically observed on Zry-4 used in PWRs, nodular and shadow corrosions are observed on Zry-2 materials corroded in BWRs [134, 136]. Nodular corrosion is described as the formation of small circular *Zr* oxide blisters as illustrated in Figure 1-15-(a) and Figure 1-15-(b) [112]. This nodule-like oxide growth occurs more spontaneously in BWRs because of the water boiling and the more oxidizing coolant (due to differences in water chemistry of the reactors as described further in section 1.4.3) [137]. The mechanism for nodular corrosion is yet to be fully understood but Cox [130] suggested that regions of *Zr* metal depleted in alloying elements may suffer local increased kinetics due to nearby noble precipitates. Nodular corrosion is also more prevalent during high temperature testing in autoclave (500°C) [138, 139]. Similarly, shadow corrosion may occur when *Zr* alloys components are located near other components made of noble metal alloys; it consists of a local galvanic corrosion where the oxide growth mirrors the shape of the noble alloy [134]. For example, a stainless steel control blade too close to a zirconium-based fuel rod may lead to shadow corrosion as seen in Figure 1-15-(c) and Figure 1-15-(d) [134].

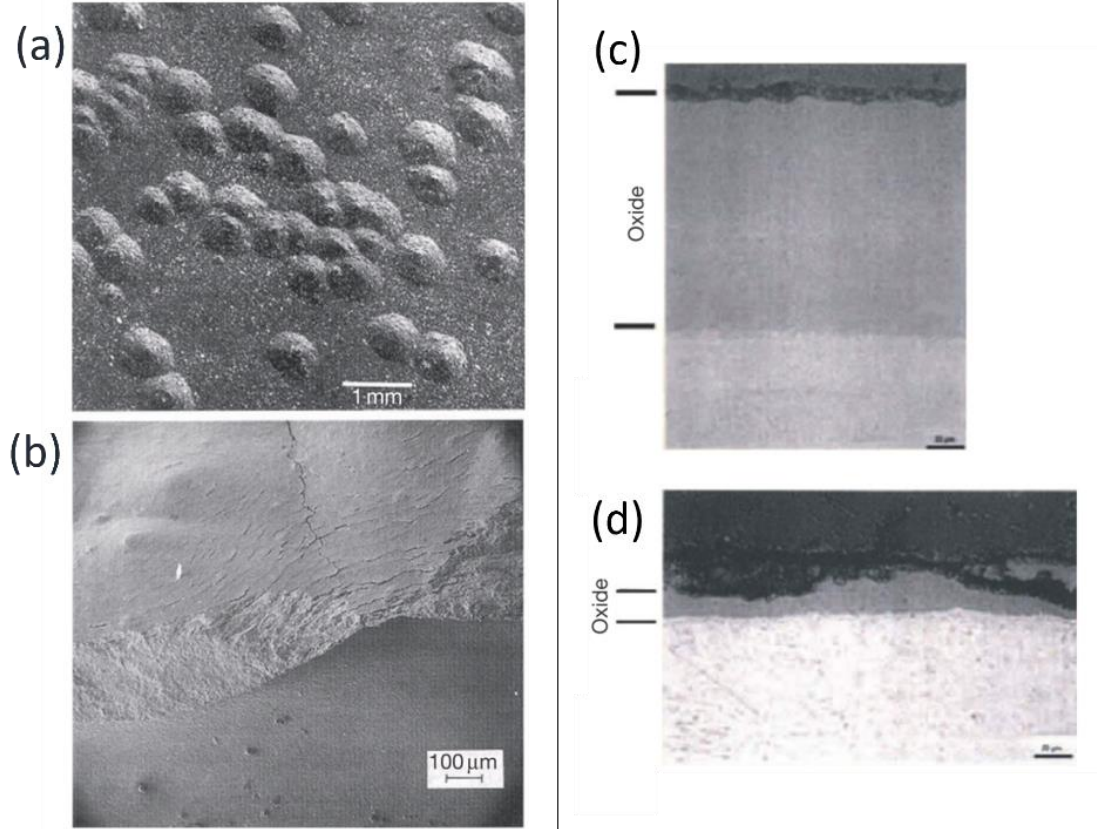


Figure 1-15: (a) Nodules formed on Zr alloy oxide corroded in 500°C steam at 10.3 MPa, seen in cross-section in (b) [112]; Zr oxides near (c) and away (d) from a stainless steel control blade, showing the effect of shadow corrosion [134].

1.1.1 Oxidation of alloying elements in Zircalloys

In previous sections, the oxidation of the host atoms in zirconium alloys was reviewed. The alloying elements also can play a significant role in improving *Zr* alloys corrosion. In fact, any small addition of alloying elements was seen to improve the poor corrosion properties of high purity *Zr* in water [15]. Ensor [52] found that unstable oxide growth developed in regions of low alloying element contents. The size of the second phase precipitates and the ratios of elements (*Fe/Cr* and *Fe/Ni*) are also known to influence the corrosion rate of zircalloys, especially at high burnup where the content and microstructure of SPPs suffered long-term exposure to irradiation

damage [140]. In this section, the oxidation of the alloying elements of zircalloys corroded in LWRs is reviewed.

From the Ellingham diagram of common elements, as illustrated in Figure 1-11 [98], it is predicted that the alloying elements (*Sn*, *Cr*, *Fe*, *Ni*) oxidize later than the *Zr* atoms, i.e. when the oxide front passes, the *Zr* atoms are preferentially oxidized. Some researchers have found that, likely driven by its higher nobility compared to *Zr*, it nucleates into small metallic precipitates in the oxide before quickly oxidizing and substituting again [141]. Tin is fully oxidized (*II*, or +2) within the first 0.5 – 1 μm of oxide, favoring oxygen vacancy creation (and hence increasing the corrosion rate) because of its lower oxidation state compared to *Zr(IV)*, and reaches the (*IV*, or +4) oxidation state in further oxide [141-143].

Secondly, the delayed oxidation of the intermetallic precipitates, *Zr(Fe,Cr)₂* and *Zr₂(Fe,Ni)*, has been verified in many *Zr* oxides over the last decades, with the degree of delay following the nobility of the elements: *Cr* < *Fe* < *Ni* [13]. Electron microscopy examinations of zirconium oxide layers established that SPPs remain metallic upon incorporation of the alloy [101, 144] and undergo full oxidation as the oxide thickens, as shown by in-depth X-ray diffraction near-edge spectroscopy studies on Zry-2 and Zry-4 [99, 100, 145, 146]. The mechanism by which these precipitates get oxidized past the metal/oxide interface is still unclear. In the precipitates, the *Zr* atoms oxidize first, followed by the less noble of the two alloying elements in the precipitate while the other segregates to the particle boundary. The oxidized products are believed to comprise amorphous oxide along with cubic, tetragonal, and monoclinic *ZrO₂* [101, 147]. For *Zr(Fe,Cr)₂* type SPPs, *Cr* atoms oxidize while *Fe* segregate to boundaries and into the matrix and may nucleate to form a *bcc* iron phase [143, 148, 149]. Partial segregation and precipitation of *Cr* has also been observed and chromium oxidation is believed to occur mainly before transition of the corrosion regime while iron mainly oxidizes post-transition [148].

As a result, *Cr* is fully oxidized within $1 - 2 \mu m$ [146], and *Fe* within $2 - 5 \mu m$ [99, 131, 145] of the metal/oxide (*M/O*) interface in Zircalloys.

For the $Zr_2(Fe, Ni)$ particles, *Fe* oxidizes while *Ni* segregates and dissolves in the matrix [147, 150]. Kuri's work revealed some *Ni* remaining metallic in the oxide layer of in-reactor corroded Zry-2 fuel cladding (burnup of $45 MWd/kg$) in the form of *Ni*-bearing SPPs whereas all *Ni* in oxide solid solution is oxidized [151]. Shivprasad's study of in-reactor corroded Zry-2 water rods ($45 - 75 MWd/kg$) showed partially metallic nickel up to $10 - 15 \mu m$ deep while iron was fully oxidized within $5 \mu m$ of the oxide-metal interface [99]. Shivprasad [91] also studied the oxidation state of *Ni* and *Fe* in autoclave corroded Zry-2 and observed a high metallic nickel fraction throughout the whole thin layer of oxide ($2 - 4 \mu m$) while iron was fully oxidized within $2 - 3 \mu m$. This partially metallic nickel in the oxide layer is suspected to be the cause for enhanced hydrogen pickup at high burnups and this relationship is further investigated in the present study, as detailed in section 1.5.

The knowledge of the oxidation state of the transition metal additions in the oxide of zircalloys is partial. Chromium oxidation is suspected to be mostly (*III*, or +3) forming the compound Cr_2O_3 more commonly [146, 152]. However, density functional theory (DFT) calculations by Than [153] suggest oxidation states (*II*, or +2) and (*IV*, or +4) at low and high oxygen pressure in $t-ZrO_2$. The *Fe* oxidation state is a mixture of (*II*, or +2) and (*III*, or +3), forming compounds of FeO , Fe_2O_3 and Fe_3O_4 [148, 152-154]. *Ni* is seen as Ni^{2+} ions (*II*) predominantly forming the compound NiO (substituting with an oxygen vacancy in ZrO_2) [151], though metallic *Ni* (observed experimentally under certain conditions in Zry-2 [99, 151]) and Ni_2O_3 are predicted to be the most stable defects in $t-ZrO_2$ at low and high oxygen pressures respectively [153].

Lastly, it should be noted that TEM investigations implied that $Zr_2(Fe, Ni)$ particles oxidized earlier than $Zr(Fe, Cr)_2$ in Zry-2 when corroded in air at $450^\circ C$ [47] and in $ZrSnNbFeCrNi$ alloys when corroded in 18.6 MPa lithiated water at $360^\circ C$ [147], though Ni and Fe are more noble than Cr . Because the Gibbs free energy of Zr is so much lower than that of the alloying elements and the Zr/M ratio is widely different for the two precipitates, the energy of Zr_2M type particles may be below that of the ZrM_2 [152]. It was also suggested that the Pilling-Bedworth ratio between the intermetallic particles and their oxidized compounds influences the corrosion of the precipitates, with NiO having a smaller unit volume than Cr_2O_3 [152]. Moreover, the particle diameter influences the oxidation behavior of the SPPs. Small precipitates are fully dissolved faster than larger ones in BWRs due to irradiation damage, participating in enhanced corrosion kinetics [140]. On the other hand, Cox [130] suggested that galvanic corrosion may appear between very large SPPs and the matrix, enhancing the zirconium corrosion rate and delaying the oxidation of the particles.

1.2 Hydrogen pickup in Light Water Reactors

1.2.1 Ingress of Hydrogen in zirconium alloys during corrosion

The absorption of hydrogen by the metal during corrosion in aqueous environments was one of the first observations made during the development of zirconium alloys [130]. This hydrogen absorption is commonly referred to as hydrogen pickup and may limit the lifetime of the materials due to the precipitation of brittle zirconium hydrides that degrade the mechanical properties of the alloys [155] and may alter their corrosion resistance [156, 157]. In the water environment, hydrogen is continuously produced during the corrosion reaction of the base metal: $Zr + 2 H_2O \rightarrow ZrO_2 + 2 H_2$ (see section 1.3.2); and a portion of this hydrogen enters the

material [127]. Upon entering the material, hydrogen is present both in solid solution of the alloy and in the form of zirconium hydrides platelets once the hydrogen solid solubility limit in αZr is exceeded [158, 159]. Using tritium as a tracer, Cox [160] observed that the hydrogen released from the corrosion process was the main source for ingress in the Zr alloys. Similarly, Hillner's work [161] showed that substantial hydrogen additions to the coolant had little impact on the hydrogen absorption of zircaloy-2. For this reason, the hydrogen pickup fraction (HPUF), f_H , has been used to characterize the hydrogen pickup behavior of Zr alloys. It is the ratio of hydrogen ingress over oxygen intake in the materials and as described in detail in the next section.

The hydrogen solubility in αZr is rather low at room temperature ($< 1 \text{ wt. ppm}$) but increases to about $70 - 120 \text{ wt. ppm}$ at reactor temperatures [162-164]. When the hydrogen content exceeds the terminal solid solubility (TSS), second phase hydride particles precipitate, which are mostly composed of face-centered cubic δ -hydrides (fcc, space group $fm\bar{3}m$) [165, 166]. Other phases such as the face-centered tetragonal γ - or ϵ -hydrides have also been observed in zircalloys [165-167]. These hydrides are brittle and can severely lower the overall fracture toughness, impact strength and ductility of the alloys [109, 158, 168]. The $Zr-H$ phase diagram from Zuzek's work [166] is shown in Figure 1-16.

Additionally, hydrogen atoms are highly mobile in the solid solution of the Zr alloy but become rather immobile after precipitation [127, 165]. In solid solution, hydrogen responds to the effects of concentration (Fick's law) and temperature (Soret effect) gradients, as well as stresses in the metal [169-171]. The resulting flux is the combination of all three effects:

$$J_{diffusion} = J_{Fick} + J_{Soret} + J_{stress}$$

(Eq. 1-6)

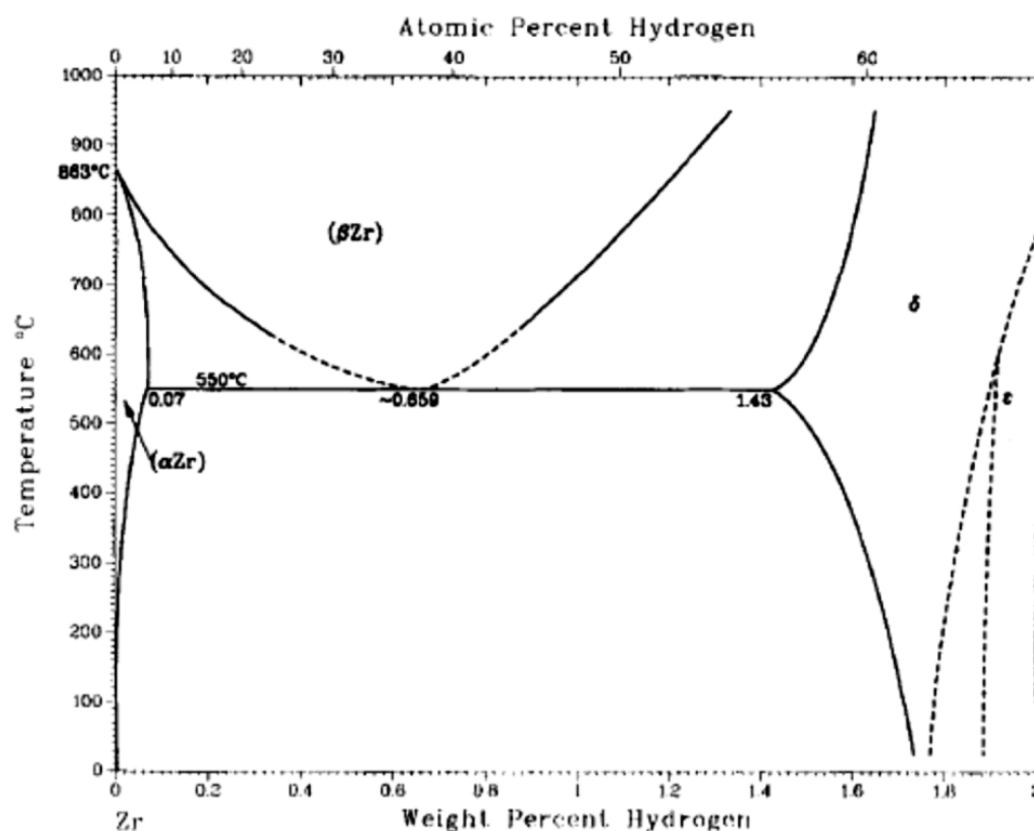


Figure 1-16: Zr-H phase diagram [166].

Fick's law of diffusion provides a driving force into the metal due to the source of hydrogen ingress located at the outer surface of the material. In fuel rods, the higher fuel temperature leads to hydrogen being pushed toward the outer surface of the cladding tube, as H is attracted to cold regions [172]. In water rods (where the coolant flows inside the tube as well), no radial temperature gradient is present. An axial gradient is still present due to the temperature difference between the inlet and outlet water (see section 1.1) but is rather low due to the dimensions of the rods, and lower corrosion temperature tends to reduce the overall hydrogen ingress at the cold elevations. On the other hand, the high radial temperature gradient in tube cladding opposes the hydrogen intake from the outer surface (as verified by higher H content in water rods [173]) but may lead to the formation of circumferential hydride rims [157, 174].

In case of oxide spallation, hydride blisters have been observed at the location of the loss of material by reason of the cold spot generated [175]. Moreover, the hydride rims may undergo radial reorientation under thermomechanical cycling effects which further reduce mechanical properties by reason of facilitated crack propagation as reviewed in [127]. Brittle failure behavior was shown to appear in hydrided Zircaloy-4 cladding tubes as hydride rims thicker than $100\ \mu\text{m}$ strongly reduced the ductility of the alloy [174]. This rim thickness corresponded to hydrogen contents exceeding $600 - 700\ \text{wt. ppm}$, although reorientation and other detrimental effects (such as accelerated corrosion) appear at lower hydrogen content [134, 162, 176]. Enhanced corrosion kinetics have been attributed to hydrides near the metal/oxide interface that would hamper stress accommodation as oxide grows leading to earlier transitions [82, 162]. SEM examinations by Ensor suggested that local advanced oxide growth was correlated with the presence of hydrides in the metal underneath [162]. Similarly, Jublot et al.'s work shows apparent enhanced corrosion when a thin layer of hydrides ($8\ \mu\text{m}$) was precipitated on the surface of Zry-4 prior to oxidation [177].

1.2.2 Hydrogen pickup fraction for Zircalloys

As previously observed, most of the hydrogen picked up by zirconium alloys in the nuclear reactors originates from the corrosion reaction with water liberating H^+ ions [127, 160, 161]. The hydrogen pickup fraction, f_H , is normally used to evaluate and compare H ingress in between materials. It is defined as the ratio of hydrogen absorbed over oxygen intake:

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

(Eq. 1-7)

The HPUF is calculated from weight gain (oxygen content) and hydrogen content measurements. While the weight gain measurements are straightforward, accurately accessing the hydrogen content is challenging. Destructive techniques such as Vacuum Hot Extraction (VHE) or Inert Gas Fusion (IGF) – mainly used in early research as fast and inexpensive – have inherent uncertainties due to the use of *sister* samples and possible hydrogen local concentrations variations due to the small sample sizes [131, 178, 179]. Cold Neutron Prompt Gamma Activation Analysis (CNPGAA) provide more accurate measurements (less than 5 *wt.ppm* error) without affecting the corrosion kinetics but is slow and requires a neutron source [180]. Once hydrogen content is measured, one can calculate the HPUF [107]:

$$f_H = \frac{H_{absorbed}}{H_{generated}} = \frac{10^{-6}(m_s^t C_H^t - m_s^i C_H^i)}{2 \frac{(m_s^t - m_s^i)}{M_O} M_H} \quad (\text{Eq. 1-8})$$

with C_H^i , C_H^t the concentrations of hydrogen in the sample initially and at the time of measurement (in *wt.ppm*), M_H , M_O the atomic masses of the hydrogen and the oxygen atom and m_s^i , m_s^t the masses of the sample initially and at the time of measurements. For the instantaneous HPUF, f_H^i , the measurements are at times t and $t + \Delta t$.

This expression of HPUF requires three assumptions [131]: (1) the oxide did not spall allowing the direct relationship between weight gain and oxide thickness; (2) the weight gain is due to oxygen only and does not consider the H uptake; (3) all H absorbed comes from the corrosion reaction. As mentioned before, (1) and (3) have been observed experimentally in zirconium alloys corroded in nuclear reactors although it should be noted that some oxide spallation has been seen in Zry-4 and Zry-2 [130, 181, 182]. (2) enables to simplify the calculations but leads to some measurable error in case of high HPUF (the hydrogen pickup represents 11.1% of the weight gain for $f_H = 100\%$) [107]. On the other hand, the hydrogen

pickup fraction of a fuel or water rod materials is estimated using the total oxide thickness δ and the thickness of the rod L (assuming no oxide spallation as well and low curvature of the rod) with the following equation:

$$f_H = \frac{H_{absorbed}}{H_{generated}} = \frac{C_H}{\frac{\rho_{ZrO_2}}{\rho_{Zr}} \cdot \frac{4M_H}{2M_O + M_{Zr}} \cdot \frac{\delta}{L - \alpha\delta}} \quad (\text{Eq. 1-9})$$

with C_H the concentrations of hydrogen in the rod material (in *wt. ppm*), M_H , M_O , M_{Zr} the atomic masses of the hydrogen, oxygen, and zirconium atom, ρ_{ZrO_2} , ρ_{Zr} the density of zirconia and zirconium and $\alpha = \frac{1}{PBR(Zr)}$ with $PBR(Zr)$ from (Eq. 1-2).

The general trends of HPUF in zircaloys in relation to corrosion kinetics are presented below:

- Hydrogen pickup fraction follows the oxidation kinetic periodicity [91, 107, 183].
- During a cycle, H uptake sharply increases early, followed by a slow increase or small oscillations as oxide thickens and then increases to a local maximum just before the oxide transition in zircaloys [91, 107, 183, 184].
- Total hydrogen pickup fraction increases with corrosion time up to multiple cycles and then stabilize for long-term corrosion [21, 107, 127, 185]. Deviations from the plateau to enhanced pickup fraction have been observed at high burnup in Zry-2 (section 1.4.5) [59].
- Hydrogen pickup is inversely proportional to the electronic conductivity of the protective oxide layer [102, 111].
- Hydrogen pickup fraction is higher for alloys with slower oxidation kinetics (lower values of corrosion exponent n – see section 1.3.3) [13, 107, 186, 187]. But hydrogen content may be less significant overall since slower kinetics reduce the amount of hydrogen available for ingress.

The hydrogen pickup appears to change during the corrosion of the alloys, as affected by the kinetics and structure of the oxide. The transport of hydrogen through the ZrO_2 layers is not well understood and is still the subject of discussions. Observing the diffusion of hydrogen through the oxide layer is challenging due to the experimental difficulty of measuring the H spatial distributions. Using Secondary Ion Mass Spectroscopy (SIMS), experimenters have suggested that the compressive stress in the inner oxide layer prevents H diffusion [188], while the external layer is highly permeable to hydrogen due to the higher porosity and crack density [189-193]. These observations have been supported by the measurements of tritium spatial distributions with high concentrations close to the outer surface which then sharply decrease with depth [193, 194]. Additionally, SPPs and oxide grain boundaries are thought to be preferred pathways [195-197]. Recent 3D spatial distribution measurement techniques such as high-resolution SIMS [198] may provide better insight into the migration of hydrogen but extended experimental data on zircaloy materials is still incomplete. Moreover, computational modelling of the hydrogen uptake in Zry-2 and Zry-4, such as finite elements [199, 200], or thermodynamics and *ab initio* calculations [201] may provide insights to the driving forces for H ingress in Zr alloys. However, important aspects such as hydride dissolution and precipitation or enhanced H pickup by Zry-2 compared to Zry-4 are not yet integrated.

In unirradiated autoclave samples corroded at temperatures between 280°C and 400°C in steam and water, H pickup was about 20% – 40% for Zry-4 and 40 – 60% in Zry-2 [107, 184, 185]. The hydrogen pickup fraction was lower within the first cycles, with f_H below 10% for Zry-4 and 15% for Zry-2, before increasing to higher values by 100 – 150 mg/dm^2 [91, 131]. As detailed later in this chapter (see section 1.4.4), the higher hydrogen pickup in zircaloy-2 is attributed to the presence of Ni in the alloy [22, 178]. It should be noted that the total hydrogen content in an alloy is fully characterized by the HPUF and the corrosion kinetics. For this reason, the average content is significantly lower in zircaloy-2 compared to zircaloy-4 for up to

30 MWd/tU due to thinner oxides [59, 127]. However, strong accelerations of hydrogen pickup at higher burnup can lead to concentrations as high as 1000 – 1500 $wt.ppm$ in Zry-2 [59, 99, 173], with detrimental effects to the ductility of the materials. As detailed later, this specific observation is investigated further in this study on Zircaloy-2 alloys with hydrogen content varying from 250 $wt.ppm$ to more than 1700 $wt.ppm$ (see Table 2-1). In the following sections, the effects of water chemistry, alloying elements and irradiation on hydrogen pickup are reviewed.

1.2.3 Effects of LWRs water chemistry

The water chemistry of the coolant has been modified to serve multiples purposes in PWRs and BWRs. In PWRs, the coolant contains dissolved hydrogen, boric acid, lithium hydroxide ($LiOH$), and zinc [137, 161]. Hydrogenated (or hydrogen) water chemistry (HWC) reduces the concentration of oxidizing species (enhanced by radiolysis of the water molecules in the reactor, see section 1.4.5) in the coolant enabling lower corrosion of structural components [134, 161]. Boron, in the form of boric acid, was added to the coolant as a burnable poison to offer reactivity control thanks to its high neutron absorption properties [137]. Lithium hydroxides additions enable the control of the pH, lowered by the additions of boric acid. Additionally, boron is believed to counteract the increase in Li -induced increased corrosion kinetics [137, 202]. High pH operations in PWRs with $LiOH$ offers the advantages of lower plant radiation levels (reducing shutdown time) [203], lower uniform corrosion of structural materials and limit the deposition of CRUD of fuel rods [161, 204]. CRUD (for *Chalk River Unknown Deposit*) are deposits of Fe and Ni oxides due to the corrosion and dissolution of steam generator pipes in the primary circuit [82, 137, 205]. They are known to locally accelerate corrosion kinetics and alter heat transfer when deposited on the fuel cladding [137, 206], and may affect neutron balance in reactor via

sequestration of the boron in CRUD pores [82]. Additionally, *Zn* injections help preventing stress corrosion cracking (SCC) of the primary coolant structural components [207] and reduce radiation field in the power plants [208], especially in hydrogen water chemistry conditions. The formation of a very stable *Zn*-chromite based inner layer with *Zn* injections improves protectivity of the oxide and prevents the uptake of activated ^{60}Co by the oxide layers of stainless steel structural materials in the reactor [209]. Additionally, Hillner observed that at the *Zn* concentrations suggested for PWRs applications, no significant detrimental effects were observed on corrosion kinetics and hydrogen pickup [161]. However, it may increase CRUD depositions on fuel cladding [206] as incorporation of the *Zn* atoms may release some *Fe* and *Ni* atoms in the coolant.

In BWRs, modified coolant chemistry is not as systematic for all power plants as PWRs water chemistry is and involves mainly: hydrogen water chemistry (HWC), zinc (*Zn*) and noble metal (NB) additions [137, 210]. Similarly to PWRs, injecting *H* and noble metals (typically *Pt* and *Rh*) into the coolant of BWRs diminishes the probability of intergranular stress corrosion cracking (IGSCC) in stainless steel and other structural components in the cooling system [211, 212], and injecting *Zn* further reduces the IGSCC as well as radiation dose [137]. Investigations by Shimada *et al.* [212] and Kim *et al.* [210] suggest that the modified water chemistry had little effect on the corrosion and hydrogen pickup in Zircaloy-2 at moderate burnup. However, at higher burnup, water chemistry may have a significant impact on the onset of accelerated hydrogen pickup in Zry-2 as suggested by Shimada *et al.* [212], but accessible data is still scarce. This study is part of the effort to provide additional data for investigating the enhanced hydrogen pickup behavior at high burnup in BWRs.

1.2.4 Effects of alloying elements with a focus on nickel

As described previously in this chapter, the additions of alloying elements to zirconium offered greater corrosion resistance and mechanical properties for nuclear reactor use relative to pure *Zr*. The effects of those elements (*Sn*, *Cr*, *Fe*, *Ni*) on hydrogen pickup in zircalloys are now reviewed.

While *Sn* additions improve the mechanical properties of the *Zr* alloys [63, 64], tin influence on hydrogen uptake is not clear. Berry *et al.* [178] found little to no effect of tin additions in Zry-2 when corroded in (327°C, 407°C) water and 477°C steam. In a different study of *Zr-Fe*, *Zr-Sn* and *Zr-Sn-Fe* alloys corroded in 400°C steam and 360°C water, Kass [179] observed that tin additions slightly increase the hydrogen pickup fraction in the binary alloy but significantly increased the weight gain kinetics. On the other hand, the addition of *Sn* reduced HPUF when added to *Zr-Fe* without worsening the poor corrosion resistance of the alloy. Thus there is not much evidence that tin plays a significant role in the hydrogen pickup mechanism.

The transition metals (*Cr*, *Fe*, *Ni*) are present in the alloy in the form of SPPs and many researcher have studied the hydrogen pickup sensibility to the alloying content and SPPs size [22, 178, 179, 185, 196, 213]. Baur *et al.* [213] studied the hydrogen pickup in Zry-4 samples with various precipitate sizes (from 20 nm to 400 nm) corroded in water at 350°C and found that the HPU was strongly affected by the precipitate size. The hydrogen pickup was strongly increased for the large precipitate samples (> 120 nm) when an electrochemical potential was applied. It should be mentioned that isolating the precipitate size is challenging and the observations may result from other differences between the tested samples. In a different study, Hatano *et al.* [196] observed that Zry-2 and Zry-4 samples with precipitate size of about 200 nm had better hydrogen pickup behavior than the samples with large SPPs (particle diameters ranging from 600 nm to almost 2000 nm) when corroded in 350°C – 450°C steam. It was argued that the hydrogen

pickup was controlled by the oxide electronic resistivity and that the precipitates may act as preferred pathway for H transport in the oxide [196, 213]. Couet [106] studied the electronic conductivity of Zr alloys and confirmed the inverse relationship between HPU and oxide resistivity. It is explained by the fast e^- migration outward when the oxide resistivity is low, so that the cathodic reaction occurs at the outer surface of the oxide. In contrast, when the movement of electrons is hampered by an insulating oxide, the cathodic recombination may happen much closer to the metal/oxide interface, favoring H intake by the bulk [106].

Similarly to Sn , the effect of Fe on hydrogen pickup in Zr alloys is somewhat variable, with beneficial effects near zircaloy concentrations. Kass [179] observed an increase in hydrogen pickup when a significant amount (1.54 wt. %) iron was added in binary or ternary alloy, while a 0.29 wt. % addition to pure Zr improved corrosion resistance but did not affect the hydrogen pickup fraction. In contrast, Berry *et al.* [178] observed improved hydrogen pickup behavior in Fe -enriched Zry-2, as well as for Cr -enriched Zry-2. Conversely, Ni detrimental effects on hydrogen pickup were witnessed early in Ni -enriched Zry-2 by Yeniscavich *et al.* [22], and more recently in Ni -enriched Zry-4 by Ensor [185]. The hydrogen pickup fraction as a function of corrosion of the latter work [185] is shown in Figure 1-17. The higher H pickup fraction during corrosion of Zry-2 compared to Zry-4 has been attributed to the presence of Ni in the alloy.

Different mechanisms have been proposed to explain the influence of transition metals on hydrogen pickup. As mentioned above, Hatano *et al.* [196] suggested that the intermetallic precipitates act as shortcut for H diffusion through the oxide. This hypothesis has been challenged by *Ab-initio* thermodynamic calculations [214] that predicted H trapping by $Zr_2(Fe, Ni)$ in αZr - restricting H diffusion into the metal if near the oxide interface – and unfavorable H sites in $Zr(Fe, Cr)_2$ precipitates compared to αZr – which would facilitate H ingress. Recent experimental and computational studies by Jones *et al.* [215] suggested that for

both precipitates in αZr , the matrix surrounding the particles act as trapping sites for H , hampering H mobility in the bulk. This observation supports the beneficial input of Fe and Cr on hydrogen pickup in Zry-2 but does not predict the detrimental effect of Ni .

Similarly, Garzarolli *et al.* [59] hinted at metallic Ni bands forming in the oxide matrix, due to dissolution of the precipitates under fluence (see section 1.4.5) and segregation at oxide grain boundaries, that would act as H windows for fast pathway across the oxide [216]. However, due to the high electronic conductivity of the metallic Ni , such bands offer faster highways for the electrons outward so that the cathodic reaction would occur further away in the oxide, in turn reducing H pickup [13].

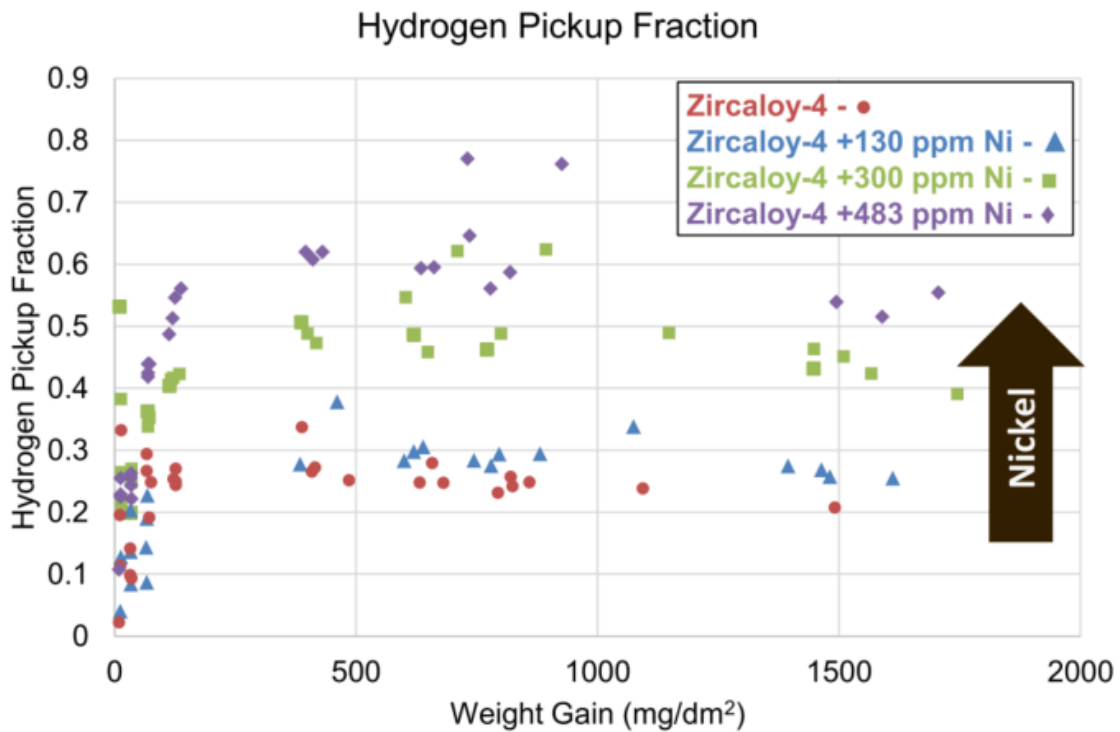


Figure 1-17: Hydrogen pickup fraction as a function of weight gain for four Zry-4 with different Ni enrichments exposed to 360°C water in autoclave. The hydrogen pickup fraction was corrected for hydrogen weight gain. Figure and caption taken from Ensor's work [185].

The role of *Ni* in enhancing hydrogen pickup may not involve facilitating the transport of *H* but, rather, acting as a catalyst to the hydrogen ingress surface reaction as proposed by Arimescu and Shivprasad in the case of high burnup [91, 173, 217]. *Ni* propensity to increase the surface reaction of hydrogen absorption has been observed on many occasions on different materials and *Ni* is commonly used as a catalyst for *H* ingress reactions [218, 219]. It should be noted that Ni^0 acts as a catalyst, requiring that *Ni* remains metallic near free surfaces, pores, or cracks in the oxides. This hypothesis is supported by recent DFT calculations by Than *et al.* [153]. The authors simulated the defect formation energies associated with *Ni*, *Cr* and *Fe* in tetragonal zirconia to predict the defect clusters and charge concentrations in the material. Their results reveal that *Cr* and *Fe* atoms form clusters with an oxygen vacancy as charged atoms ($Cr^{2,3,4+}$, $Fe^{2,3+}$) for the O_2 partial pressures studied, whereas *Ni* atoms form a $Ni^0 - V_{\bar{O}}$ defect at low oxygen pressure (the conditions close to the metal/oxide). Additionally, subsequent simulations in the same study [153] showed that H_2 molecules would dissociate in the vicinity of this cluster, supporting that *Ni* would enhance the surface reaction of hydrogen absorption.

Another mechanism involving oxidized *Ni* has been suggested by Kuri *et al.* [151, 220] who studied the oxidation and location of the alloying element in the oxide of zircalloys with experimental investigations of in-reactor (BWR) corroded Zry-2 fuel rod and computed DFT calculations in monoclinic zirconia. The authors predicted the substitution of Zr^{4+} by Ni^{2+} in *m*- ZrO_2 and the associated oxygen vacancy $V_{\bar{O}}$ to balance charges. This $Ni^{2+} - V_{\bar{O}}$ substitution was also predicted by DFT calculations in *t*- ZrO_2 at moderate oxygen partial pressure, while Ni^{3+} substitution (with no vacancy) is expected at higher pressure [153]. It was suggested that ($Ni^{2+} - V_{\bar{O}}$) compounds may offer nucleation sites for trapping hydrogen ions which would then short circuit the dielectric barrier between the anode and cathode. This in turn would cause fast migration of *H* into the metal [151].

The process or processes by which *Ni* increases hydrogen uptake in zirconium alloys are yet to be verified, although various theoretical explanations have been offered. Clarifying and identifying the processes implied, especially at high burnup, are the objectives of this study as presented in section 1.5. In the next section, the irradiation effects on *H* pickup are reviewed.

1.2.5 Effects of irradiations

When in service, zirconium alloys are subject to the high neutron flux necessary to nuclear reactor operations. Zirconium was selected because of its low neutron absorption cross section, but the energetic particles still hit the atoms in the material and the coolant. In this process, fast neutrons may knock atoms off of their lattice positions, producing vacancies and interstitials in the metal, or splitting the water molecules (radiolysis) affecting the electrochemical potential for corrosion [134, 137]. Such processes can lead to microstructure and elemental structure changes which in turn impact the corrosion kinetics and the hydrogen pickup, as well as the physical properties of the material. [6, 137]. The neutrons interact elastically with the alloy atoms that may be displaced in the lattice several times during service. As such, irradiation damage is commonly quantified in terms of displacements per atom (dpa) to allow comparison between different neutron spectra and charge particle irradiations. The neutron spectrum is integrated over the fast neutron energy range $E > 1 \text{ MeV}$ and exposure time and is referred to as neutron fluence ($\times 10^{21} n/cm^2$). The neutron flux can also ballistically eject atoms from the precipitates, modifying their structure and even dissolving them, and in LWRs coolant, irradiation may dissociate water molecules – a process called radiolysis [31]. Radiolysis of H_2O during operation can lead to high concentrations of oxidizing species near the material surfaces which in

turn enhance the corrosion process; this effect led to the addition of hydrogen in the coolant of LWRs, thus reducing the concentration of oxidizing species [134].

Irradiation-induced defects lead to the formation of dislocation loops in the material. These loops hamper the movement of dislocations resulting in hardening of the alloy. Additionally, loss of ductility, referred to as embrittlement, has been observed in cases of local strain and deformation due to dislocation channeling [137]. However, it should be noted that, in contrast with the embrittlement and hardening due to hydride precipitation, the concentration of these irradiation-induced effects saturates after about one month in the reactor and can be reversed by annealing treatment of the material [112, 137].

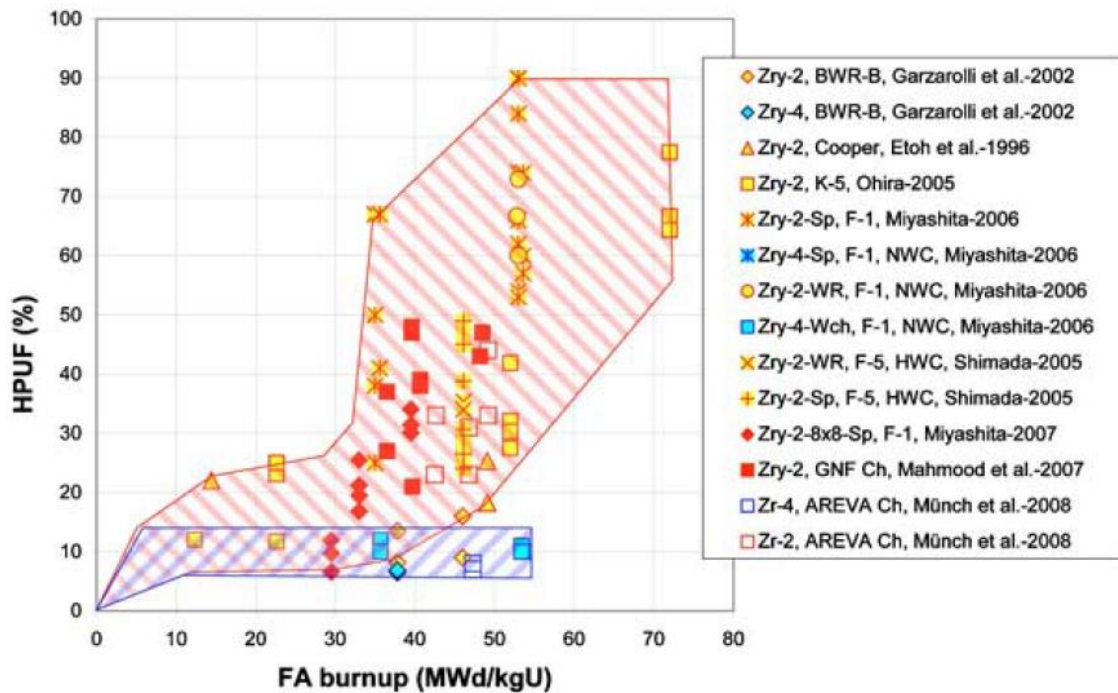


Figure 1-18: Hydrogen pickup fraction as a function of fuel burnup for multiple Zry-2 (red area) and Zry-4 (blue area) structural components. Figure taken from Garzarolli's review [59] who compiled the data from [21, 212, 221-225].

On the other hand, irradiation effects on corrosion kinetics in zirconium alloys start appearing for oxide thicknesses larger than 5 – 6 μm as discussed in [130]. Above this thickness, irradiation-induced acceleration of the corrosion has been observed with kinetics deviating from

autoclave measurements [134, 226]. The second main effect of concern for Zircaloy-2, and which is the subject of this study, is the acceleration of hydrogen uptake at high burnups as reviewed by Garzarolli *et al.* [59]. Compiling hydrogen pickup data as a function of burnup for many zircaloy cladding and structural components that became available in the 2000's [21, 212, 221-225], Garzarolli *et al.* [59] highlighted that Zry-2 materials may reach 70% to 90% of total hydrogen pickup fraction at burnup above 35 GWd/tU , while in Zry-4, HPUF was contained below 15%. The compiled data of hydrogen pickup fraction as a function of burnup is shown in Figure 1-18 [59].

The combination of accelerated corrosion and hydrogen pickup lead to high hydrogen content in the material well above the terminal solubility limit, highly degrading the physical properties of the materials (as described in 1.4.1). The mechanism underlying the acceleration of oxidation is believed to result from the amorphization and dissolution of the SPPs in the material in BWR environment and the accumulation of hydrogen in the material [227, 228]. In these studies, precipitates of small diameters were seen fully dissolved at burnups as low as 30 MWD/kgU or at fluence of $8.5 \times 10^{21} n/cm^2$. It has been observed that the precipitates first become amorphous or partially amorphous under irradiation while losing most of its *Fe* content, and are almost completely dissolved when the fluence exceeds $12 \times 10^{21} n/cm^2$ [21, 229-231]. In other studies, $Zr(FeCr)_2$ and $Zr_2(FeNi)$ were found partially dissolved but *Fe*-depleted [151, 232]. Hence, at high fluence, the *Fe*, and eventually *Ni* and *Cr* are likely to be forced into the saturated *Zr* matrix. Once in solid solution, reprecipitation of *Fe* and *Cr* into small clusters (1 – 5 nm) and segregation of the alloying elements at grain boundaries have been reported [149, 233].

Kuri *et al.* [151] observed the partial oxidation of the *Ni*-containing precipitates in Zry-2 cladding tube corroded in BWRs to an average burnup of about 45 MWD/tU , while the dissolved *Ni* was found fully oxidized. Similarly, Shivprasad *et al.* [91] observed the presence of metallic nickel past multiple oxide transition thicknesses in water rods with enhanced hydrogen pickup at

high burnups, but the authors were not able to differentiate signal from *Ni* in SPPs from the signal produced by *Ni* in solid solution. Moreover, Nissen *et al.* [173] suggested that hydrogen pickup in fuel cladding and water rods of Zry-2 was highly enhanced in the case of high/low power. The authors postulated that if the initial high power regime was long enough to ensure a “thick oxide film” [31] of about $11 - 13 \mu\text{m}$, then enhanced hydrogen pickup may occur in the low power period, due to lower heat flux in the cladding and lower water flow. This observation is difficult to verify and reproduce due to the paucity of information on reactor power history available in literature. Moreover, as described in the IAEA report [31], the “thick oxide film” effect which consists of enhanced corrosion and hydrogen pickup once a certain thickness of initial oxide is reached, is not well understood nor verified. Still, irradiation and power history appear to play a crucial role in dictating hydrogen uptake at high burnup in Zircaloy-2, but a better understanding of the process and its relationship with nickel is crucial for optimization of modern *Zr* alloys materials with increased resistance at high burnups. In the next section, the objectives and outline of this study are presented.

1.3 Objectives of the study

In section 1.4.5, it was shown that Zry-2 cladding is subject to high acceleration of the hydrogen pickup during long exposure in the BWR environment (Figure 1-18). Although the mechanism resulting in this increase is not fully understood, nickel is believed to be the cause of this enhancement (section 1.4.4). Verifying and understanding this hypothesis would help rule out that this could occur for *Ni*-free *Zr* alloys such as the modern alloy ZIRLO and M5. The first-of-a-kind observation by Aditya Shivprasad [91, 99] using microbeam XANES analysis of in-reactor corroded Zry-2 water rods, of which this study represents a continuation, is detailed below and shown in Figure 1-19:

- The quantitative metallic nickel fraction (30% – 40%) remains in the oxide up to 10-12 μm from the oxide-metal interface in of Zircaloy-2 materials with high H pickup fraction, i.e. which were in the reactor for much longer, as compared to Zry-2 with low pickup fraction. The materials were selected so that pairs of low and high H pickup fraction materials with same heat treatment and similar corrosion environment (the materials with high pickup fraction stayed for an additional fuel cycle in the reactor). Because the materials were taken from water rods material, the effect of radial heat flux is not considered.
- No similar difference between high and low pickup fraction materials was seen for iron. The iron atoms are fully oxidized within 5 μm of the oxide metal interface for all the materials studied, with no significant differences between the low and high H pickup fraction alloys.

Because of the complexity of the processes involve in the nuclear reactors, the presence of a significant amount of metallic nickel up to multiple oxide transition thicknesses and its apparent correlation to acceleration of hydrogen pickup at high burnup are yet to be explained. Additionally, information on the oxide chemistry and infrastructure as a function of depth - especially the oxidation state of the low-concentration alloying elements - in Zry-2 materials that were used in reactors to high burnups is limited in literature but of great value. In an effort to understand the mechanism underlying this acceleration of hydrogen pickup, materials taken from different locations in the same sister BWR water rods (provided by Global Nuclear Fuel - GNF) studied by Shivprasad [91, 99] are being investigated. The samples were selected so that the effects of elevation, fluence, and water chemistry may be investigated. The water rods materials and the experimental details can be found in chapter 2.

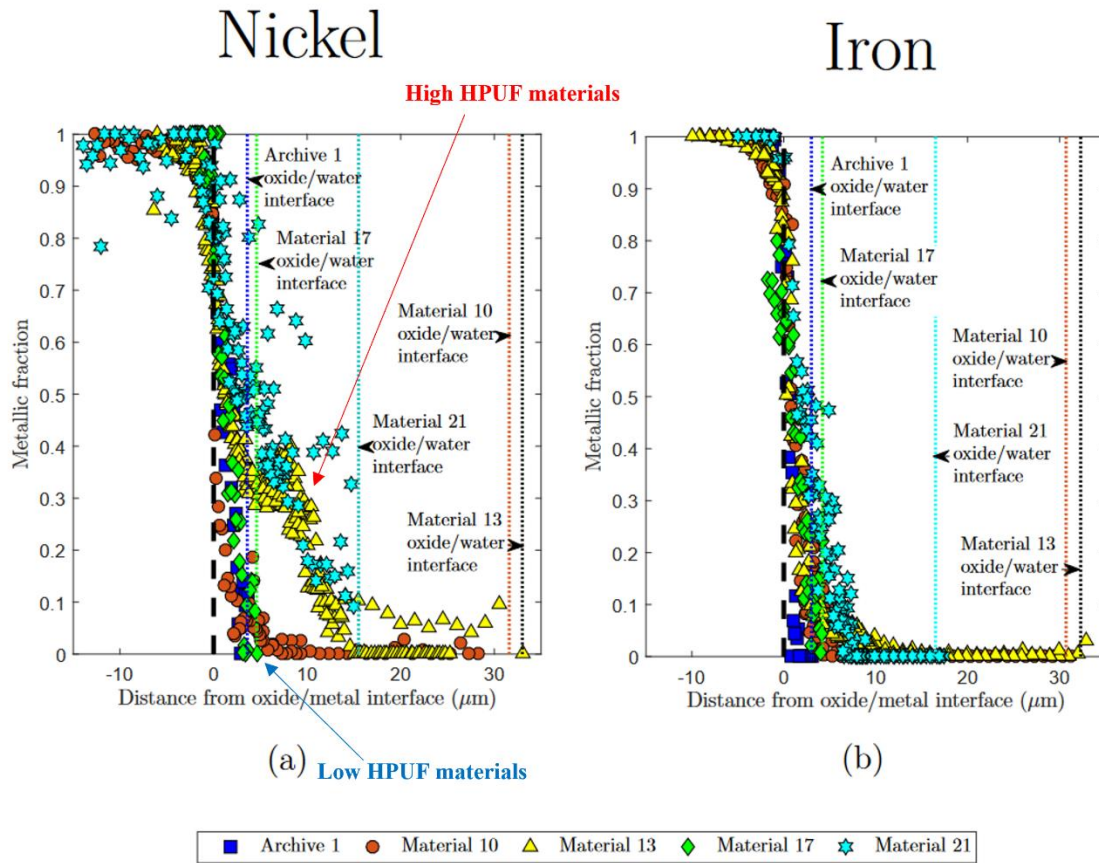


Figure 1-19: Nickel and iron oxidation state as a function of distance from the metal/oxide interface (negative values are the metal region, and positive ones the oxide layer) for Zry-2 water rod corroded in BWRs for 3 to 4 cycles. Materials 13 and 21 suffered significant H pickup while archive 1 and materials 10 and 17 did not. Figure adapted from Shivprasad's work [91, 99].

Firstly, in-depth X-ray absorption near-edge spectroscopy (XANES) measurements of the oxidation state of *Ni* on the in-reactor corroded water rods materials were carried out at beamline 34-IDE of the Advance Photon Source (APS) at Argonne National Laboratory (ANL). The results are presented in chapter 3. The in-depth microstructure of the metal and the oxide was investigated via X-ray Diffraction at beamline 34-IDE at the APS as well and the results are presented in chapter 4. Chapter 5 is dedicated to discussions on the experimental results and the role of *Ni* in enhancing hydrogen pickup at high burnup, before concluding in chapter 6.

Chapter 2

Material selection and experiments details

In this chapter, the selection of materials from in-reactor corroded water rods is first presented. This is followed by a description of the cross-sectional sample preparation for in-depth analysis of the oxides. Then, section 2.3 and section 2.4 depict the X-ray absorption near-edge spectroscopy (XANES) and X-ray diffraction (XRD) analysis (respectively) using the synchrotron radiation at beamline 34-ID-E of the Advance Photon Source (APS) at Argonne National Laboratory (ANL).

2.1 Zircaloy-2 water rods corroded in Boiling Water Reactors

Because of Shivprasad's previous work [99] on two sets of Zry-2 water rods corroded in BWRs (Limerick-1 or Dresden-2), a focused set of 4 materials from different axial positions in the Limerick-1 water rods was chosen to investigate further the observation of metallic nickel far in the oxide of high hydrogen pickup materials. Cross-sectional samples were produced at Pacific National Laboratory (PNNL) and examined with synchrotron radiation at the Advance Photon Source (APS) located at Argonne National Laboratory (ANL). Additionally, scanning electron microscopy imaging of the samples was performed at Pennsylvania State University (PSU). The material selection enables to separately investigate the effects of neutron fluence, corrosion temperature and water chemistry on the enhancement of H pickup at high burnup. The effect of radial heat flux is not investigated in this study as the samples are taken from water rods. Initial examination of the water rods was done at the hot cell facility of General Electric (GE) Vallecitos Nuclear Center (VNC) in California, and the resulting characteristics of the selected in-reactor corroded materials are presented in Table 2-1. All materials were composed of Zircaloy-2 with

the nominal original composition: $Zr-1.9Sn-0.18Fe-0.10Cr-0.07Ni$. After a β -quench, these materials have undergone an α -anneal heat treatment consisting of a single vacuum anneal at $577^{\circ}C$, which resulted in the low CAP value of $2.19 * 10^{-19}h$. As described in 1.2.2 and *Figure 1-3*, this CAP value corresponds to precipitates sizes of $40 - 100 nm$, which is consistent with the post-irradiation TEM measurements on materials from the same water rods available in Shivprasad's study [99]. The chemistry of the coolant in Limerick-1 reactor consisted of hydrogenated water (HWC) with additions of zinc and noble metals - as described in detail in section 1.4.3.

Because the materials are water rods, the total oxide thickness for these materials corresponds to the sum of the inner oxide (not present in fuel rods) and outer oxide thicknesses and was used for the hydrogen pickup calculations. The oxide thicknesses were measured using metallography at GE VNC hot cell facility. Oxide thickness measurements using Zr K-edge fluorescence at the synchrotron and SEM at Penn State were consistent with the metallographic measurements but revealed clear oxide thickness differences between the inner and outer parts of the samples. Although generally uniform, the oxide layers contained some thickness variations, locations which were both thinner and thicker than the measured average were seen as further described in section 3.2. The presence of nodular corrosion is often seen during Zry-2 corrosion in a BWR environment (see section 1.3.3) and was observed in some of the water rod materials studied by Shivprasad [99], along with the asymmetry of inner and outer oxide layers growth.

Hydrogen content of the materials was assessed using the destructive inert gas fusion method in a LECO RH-2 hydrogen analyzer at GE VNC hot cell facility. The samples were melted in a graphite crucible, which allows hydrogen to bond with highly heated ejected carbon atoms. Because hydrogen is located in many hydrides in zirconium, a tin flux was added to the furnace to help reduce the hydride compounds. A high purity nitrogen gas flux (the inert gas carrier) then sweeps the evolved gases of the specimens from the fusion chamber to a thermal

conductivity detector. The change in the ability of the gas to draw heat away from a body is related to the hydrogen content through a series of calibration standards [234].

Table 2-1: Zircaloy-2 materials selected for XANES/XRD and 3DAP measurements. All materials were cut from 2 water rods used in Limerick-1 (USA) boiling reactor for 3 and 4 cycles. Initial examinations were performed at GE VNC hot cell facility. The total oxide thickness for the water rods corresponds to the sum of the inner oxide (not present in fuel rods) and outer oxide thicknesses.

Sample Preparation	XANES/XRD Cross-section Samples			
ID	Material 9	Material 11	Material 12	Material 14
Composition at fabrication	$Zr - 1.95Sn - 0.18Fe - 0.10Cr - 0.07Ni$			
Type / Heat treatment	Zry-2 / Alpha annealed			
Cumulative Annealing Parameter (CAP) (hours)	2.19×10^{-19}			
Water Chemistry	Hydrogen Water Chemistry (HWC) – Zinc – Noble Metal (NM)			
Fluence: $E > 1 \text{ MeV}$ ($\times 10^{21}n/cm^2$)	7.5	12.6	9.3	15.6
Elevation from bottom (in inches [in m])	20 [0.51]	110 [2.79]	20 [0.51]	112.5 [2.86]
Total oxide thickness (μm)	40	50	40	82
H content (wt. ppm)	250	329	600	1721
HPUF (%)	12.8	13.4	30.6	42.8
Exposure time (days)	2036	2036	2703	2703
Bundle-average burn-up (GWd/tU)	52.5	58.5	65.6	72.1

Materials 9 and 11 were cut from the same low hydrogen content water rod as material 10 [99], which was taken out of the reactor after 3 cycles of 2 years (2036 days total), at the following elevations from the bottom: 20 in (or 0.51 m) and 110 in (or 2.79 m) respectively. The corresponding fluence for fast neutrons ($E > 1 \text{ MeV}$) was estimated to be $7.5 \times 10^{21}n/cm^2$

at material 9's position, and $12.6 \times 10^{21} n/cm^2$ at material 11's location. As a result of the elevation differences in the boiling reactor, material 9's corrosion temperature was considered to be $275^\circ C$ (the water input temperature) whereas material 11 was corroded at the coolant saturated temperature of $288^\circ C$ (exit temperature). The total oxide thickness was $40 \mu m$ for material 9 and $50 \mu m$ for material 11. The hydrogen content was low at 250 wt. ppm and 329 wt. ppm , leading to low pickup fractions of 12.8% and 13.4% respectively. Lastly, the fuel assembly average burn-up was estimated to be 52.5 GWd/tU at 20 in (material 9) and 58.5 GWd/tU at 110 in (material 11) in the water rod.

The other two materials, 12 and 14, were cut from the same high hydrogen content water rod as material 13 [99], which was removed after an additional cycle of 2 years leading to a total of 4 cycles (2703 days) spent in the reactor. For comparison between the two rods, the elevation of material 12 is identical to that of material 9 (20 in) and the elevation of material 14 is very similar to that of material 11 at 112.5 in . Consequently, the corrosion temperature was estimated at $275^\circ C$ for material 12 and $288^\circ C$ for material 14. The total oxide thickness of material 12 was $40 \mu m$, corresponding to that measured on material 9. On the other hand, material 14 suffered enhanced corrosion with a total oxide thickness of $82 \mu m$. Hydrogen content in material 12 was about twice that of materials 9 and 11 at 600 wt. ppm , leading to the large hydrogen pickup fraction of 30.6%. In material 14, hydrogen load reached the substantial value of 1721 wt. ppm , with the high pickup fraction of 42.8%. The fuel assembly average burnup was estimated to be 65.6 GWd/tU at 20 in (material 12) and 72.1 GWd/tU at 112.5 in . Such high hydrogen content at high burnup is way above the revised regulation limit by the NRC for LOCA (rule 10 CFR 50.46c) [235] which accounts for the degradation of the material properties with hydrides (see section 1.4.1). This sample selection allows for a direct comparison between the low hydrogen pickup (9 and 11) and high hydrogen pickup materials (12 and 14) due to their symmetric

location in the boiling reactor. Additionally, the four materials (9, 11, 12, and 14) can be confronted to those previously investigated by Shivprasad [99], i.e. materials 10, 13, 17, and 21.

2.2 Cross-section sample preparation for in-depth XANES and XRD analysis

Due to the low but detectable radioactivity present in the water rods, sample preparation was performed by Danny Edwards and Alan Schemer-Kohn at Pacific North National Laboratory. Although the water rod did not contain fuel, some radioactivity is present in the material because of the activation of isotopes by the neutron flux and the absorption of leaked fission products during service. The main radioactive isotope still present after years of storage is cobalt-60 (^{60}Co) resulting from multiple stages of activation of iron (mostly released from the steel structural components and then deposited on the water rod, see section 1.4.3). Additionally, very small traces of other radioactive nuclides can be detected such as potassium-40 (^{40}K) (naturally occurring nuclide), and the fission products: caesium-134 (^{134}Cs) and caesium-137 (^{137}Cs).

Cross-sectional samples were prepared from the water rod materials presented in *TABLE 2-1* for examinations at Argonne National Laboratory (ANL). The sample preparation was similar to that of previous in-depth studies of zircaloy oxides [52, 99, 100, 120, 125, 236] and is illustrated in Figure 2-1. Slices about 1 *mm* wide and a few *mm* high were cut from the water rod and then placed into a molybdenum rod (2 *mm* diameter). The assembly was then inserted into a brass tube with an outer diameter of 3 *mm*, and filled with GATAN G1 epoxy to hold the structure in place. Once the epoxy set, samples about 500 μm thick were sliced from the filled tube and polished for surface examinations. The polishing procedure consisted of initial polishing with 500 grit *SiC* paper, followed by consecutive polishing using a cloth with decreasing

diamond compound (15, 9, 6, 3, and $0.25\ \mu\text{m}$) and lapping oil (from DP Brown). An image of one of the samples taken with an optical microscope and one with a scanning electron microscope are shown in Figure 2-2-(a) and Figure 2-2-(b) respectively.

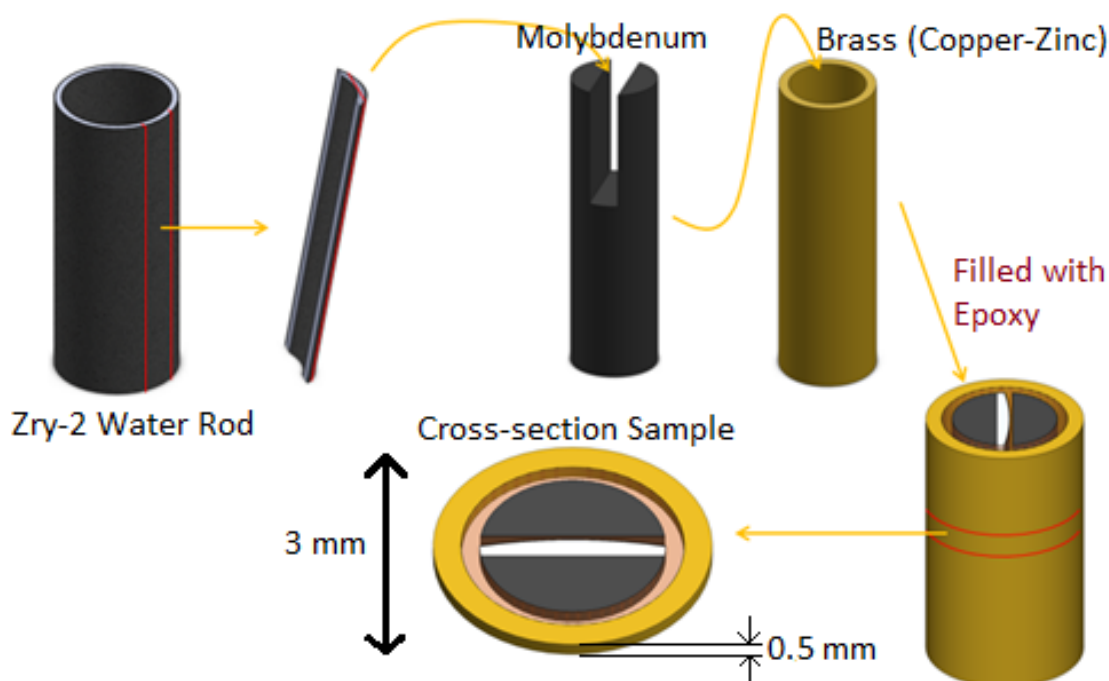


Figure 2-1: Cross-section sample preparation from the in-reactor corroded water rods. The water rod is cut and placed in molybdenum and brass, filled with epoxy to hold the structure, and then sliced into a cross-section sample. Figure adapted from [91, 131].

Because of the experimental setup at beamline 34-ID-E at the APS (ANL), the sample holder was an extruded aluminum plate about 20 mm wide and 3 mm high. Up to four samples were glued on one plate using GORILLA superglue. Because of the low but detectable radioactivity from the irradiated samples, a full encapsulation of the sample holders was needed for examination at the APS. A DuPont Kapton Type HN polyimide film (ordered via CS Hyde Company) of thickness 0.5 mil ($12.7\ \mu\text{m}$) was used for encapsulation of the samples, sealed on the side with a 1.0 mil ($25.4\ \mu\text{m}$) thin DuPont Kapton tape with silicone adhesive (ordered via CS Hyde Company as well). Figure 2-3 presents the final two encapsulated sample holders used for the XANES and XRD analysis. 8 cross-section samples were prepared (2 from each material)

but one of the samples from material 12 failed during initial SEM imaging at PNNL. Therefore sample holder 1 contains 4 specimens (9-A, 11-A, 12-A, and 14-A) and holder 2 contains only 3 samples (9-B, 11-B, and 14-B).

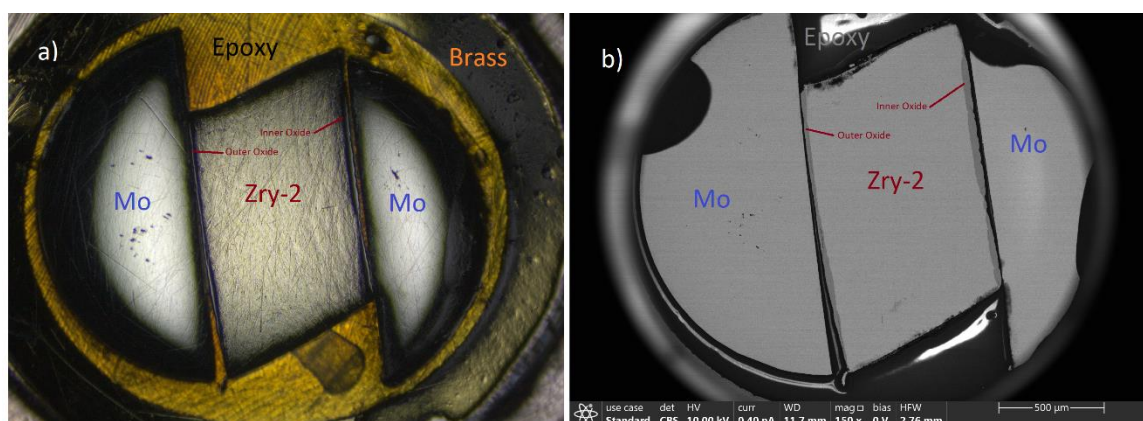


Figure 2-2: Optical (a) and SEM (b) images (acquired at Penn State) of one of the Zry-2 cross-section samples prepared at PNNL. The inner and outer oxides of the water rod material can be seen in dark grey on both images, with the Zry-2 bulk and Mo rod in light grey.

Molybdenum, brass, and aluminum were selected as the materials to be used in the samples because the X-ray fluorescence peaks of the elements that compose these materials (molybdenum, aluminum, copper, zinc) do not overlap with the X-ray fluorescence peaks of the elements of interest (zirconium and nickel). Epoxy was chosen because of its good reliability in service. Although epoxy may slightly attenuate the X-ray fluorescence intensity passing through it [237], this is not a factor in this case because the samples were cut from the middle of the prepared brass tube (Figure 2-1) and polished so that no epoxy is left on the examined surface of the bulk or oxide. Lastly, the DuPont Kapton polyimide film is known to have good resistance to radiation damage [238] and to be mostly transparent to X-rays [239]. Therefore it withstands long exposure time to the high incident photon flux without failure (thus ensuring the sample remains fully encapsulated throughout the experiment) and does not alter the X-ray signal from the

sample. Tests at beamline 34-ID-E prior to irradiated samples examinations by scientist Wenjun Liu confirmed that the *Zr* and *Ni* fluorescence signal was not affected by the presence of a thin layer (tests done up to 1 *mil* – or about 25 μm - thickness) of Kapton on top of the sample. As was the case during previous examinations at beamline 2-ID-D [91], no degradation was observed on the Kapton film after the XANES scans (up to 20 *h* around one location) across the oxide layer of the irradiated samples. The cross-section samples prepared at PNNL were then shipped to the APS (ANL) for XANES and XRD analysis.

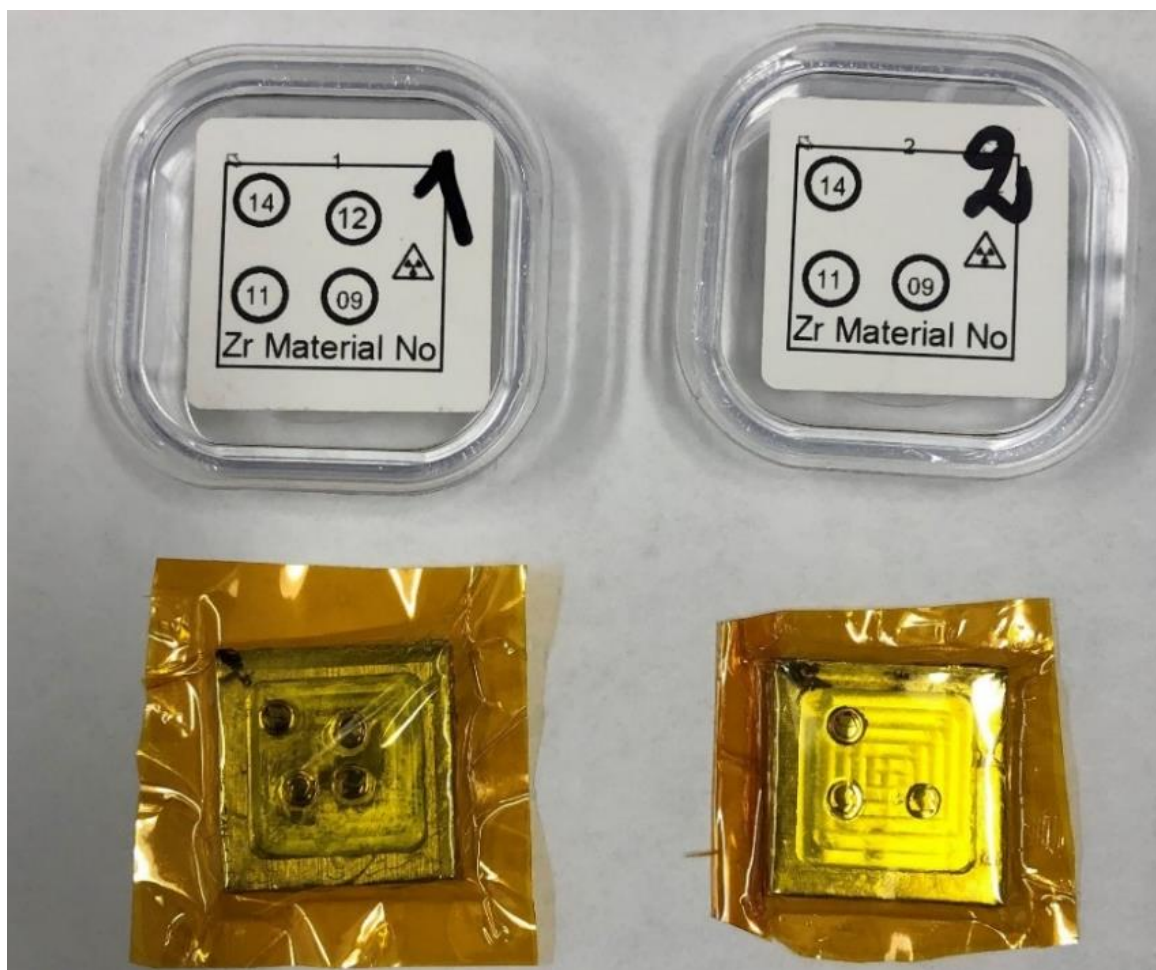


Figure 2-3: Cross-section samples glued (GORILLA superglue) on extruded aluminum plate and encapsulated with DuPont Kapton film (0.5 mil, or 12.7 μm thick).

2.3 Ni oxidation state analysis via XANES using synchrotron radiation

2.3.1 Purpose and layout of the XANES measurements at the APS

The observation of a correlation between the oxidation state of nickel in the oxide layer of Zircaloy-2 materials and the increase of hydrogen pickup at high burnup in BWR [91, 131] has yet to be verified. Therefore, a set of four additional materials was selected (Table 2-1) for examination at a second beamline (34-ID-E) at the APS (ANL), while the samples were prepared at PNNL. The purpose of the XANES analysis is to characterize the oxidation state of nickel atoms incorporated into the oxide layer as a function of depth into the oxide of additional Zircaloy-2 materials. The purpose of these measurements is to better understand the role of the alloying element in enhancing hydrogen pickup at high burnup in BWRs. We focus especially on the most recent oxide layers formed i.e. the layers close to the oxide/metal interface, where metallic nickel has been observed in high hydrogen ingress water rods [91, 131]. As presented in section 2.1, materials that exhibited different hydrogen pickup fractions and elevation (operational temperature, coolant steam quality and fluence) in the nuclear reactor were selected so that the oxidation state of *Ni* across the oxide can be analyzed in each case.

Because the concentration of nickel in the alloy is so low (less than 0.1 wt. %) and the oxidation state varies across the thin (less than 50 μm) oxides, it is necessary to use synchrotron capabilities to study nickel atoms in the oxide layers. The high flux microbeam at 34-ID-E station at the Advance Photon Source (APS) at Argonne National Laboratory (ANL) allows for *Ni* XANES examinations and was selected after changes were made to 2-ID-D station (used in previous work [91, 131]). The synchrotron offers the combination of high spatial resolution as well as the ability of detecting small amounts of *Ni*, as low as 0.01 wt. %. The spatial resolution results from a high coherent photon flux with the following characteristics:

- *Beam size:* $\Delta x * \Delta y \sim 0.3 \mu m * 0.3 \mu m$
- *Energy resolution:* $\Delta E \sim 0.5 \text{ eV}$ at 8 keV
- *Photon flux:* $\phi \sim 10^9 \text{ to } 10^{11} \text{ photons/sec}$

The oxide thickness of the materials selected is about 20-40 μm , and a fine scan ($\Delta x = 0.25 \mu m$) across 20 μm with an 80 eV energy range at $\Delta E \sim 0.5 \text{ eV}$ takes approximately 14 hours. To optimize beamtime at the APS, we established 3 types of scans to be carried out on each sample (similarly to what has been done in previous work [91]):

- *Fine scan:* 5 μm into the metal and 10 μm into the oxide with $\Delta x = 0.25 \mu m$.
- *Semi-fine scan:* 10 μm to 20 μm into the oxide with $\Delta x = 0.5 \mu m$.
- *Coarse scan:* 20 μm to the outer surface with $\Delta x = 1.0 \mu m$

Because the metallic nickel was previously observed mostly in the most recent 10-12 μm of oxide built, high resolution was maintained for the region near the metal/oxide interface. This allowed us to do 2 scans for each material (1 on samples 9-A, 9-B, 11-A, 11-B, 14-A, and 14-B, and 2 on sample 12-A) during the two 5-day trips to the APS. The principles of XANES, the experimental setup and the data analysis are presented in the following sections while the results are detailed in chapter 3.

2.3.2 Principles of X-ray Absorption Near-Edge Spectroscopy

In this section, we describe the principles of oxidation state measurements via X-ray Absorption Near-Edge Spectroscopy. XANES, along with EXAFS (Extended X-ray Absorption Fine Structure), are the two main subsets of X-Ray absorption spectroscopy (XAS), also known as X-ray absorption fine structure (XAFS) [240]. XAS is based on the excitation of inner electrons to higher energy level by the absorption of incident photons, known as the photo-electric effect (depicted in Figure 2-4-(a) [240]). A minimum energy - corresponding to the

binding energy of the particle to the nucleus - is required to bring the electrons from the inner shell to the conduction (or continuum) band, producing absorption edges at incident energies specific to the element and to the inner shell from which the electron left. This minimum energy, called the absorption edge energy, ranges from a few keV to a few hundred keV , and is highest for heavy nuclei and for the innermost electrons (K shell) as the binding energy is maximized in those cases. Therefore, the photoelectric effect is dominant for high-Z materials and is the reason for their use in gamma-ray shields [241].

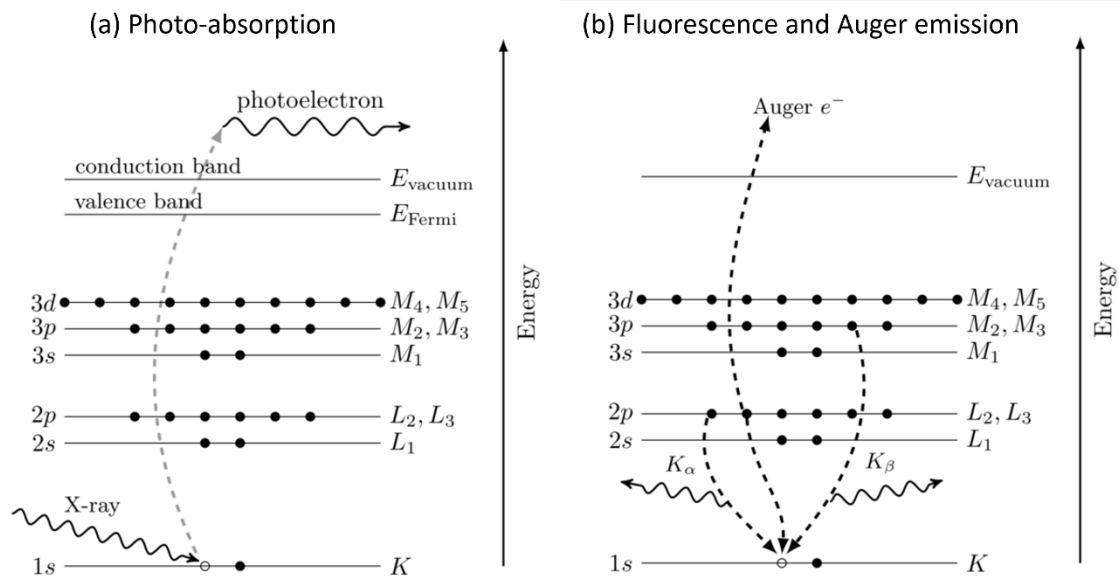


Figure 2-4: (a) Schematic of the photoelectric absorption: an incident photon excites an electron of the K shell to energies above the conduction band [240]. (b) Schematic of the decaying of the excited atom by X-ray fluorescence (K_α and K_β) or Auger electron emission [240].

The photon absorption cross-section of lead (Pb) as a function of incident energy is shown in Figure 2-5-(a) [2]. The K-edge and the L-edge can be seen and correspond to the excitation of an electron of the K shell and of the L shell respectively. L_1 , L_2 and L_3 sub-edges correspond to L-edge electron transitions with different spin and orbitals [2]. Additionally, it can be seen that the absorption cross-section of electrons strongly decreases as the incident photon energy increases only to reach local maxima at the edges. This is because the probability for the

electron transition to the excited state strongly decreases as the wavelength of the light decreases (i.e. the photon energy increases) compared to the orbital radius. As detailed in section 2.3.5, this continuous sharp decrease is filtered out during analysis using pre-edge and post-edge lines to normalize the data.

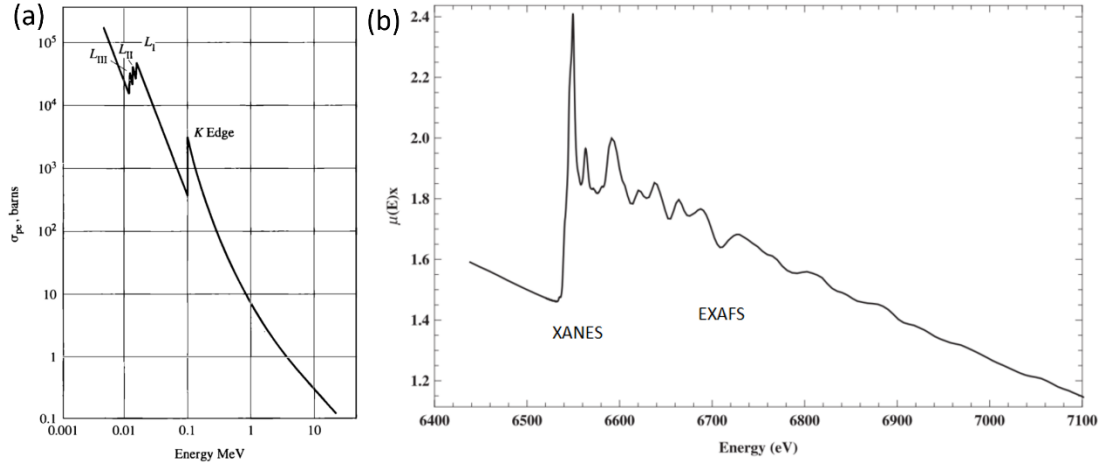


Figure 2-5: (a) Cross-section of the photoelectric absorption as a function of the incident photon energy for lead (Pb) [2]. (b) Experimental Mn XAFS spectra at the K-edge of MnO (adapted from [242]).

An example of the pre-normalization absorption spectra around the K-shell absorption edge (K-edge) of *MnO* is shown in Figure 2-5-(b) [242]. The spectrum is separated into two regions corresponding to the two XAS techniques: the near-edge region (XANES) and the Extended X-Ray Absorption Fine Structure (EXAFS) region. While XANES provides information about the local environment, energy bandwidth, and valence state of the atom, EXAFS is mostly used for investigation of the interatomic distances, near neighbor coordination and lattice dynamics [243]. The EXAFS region is marked by oscillations of the absorption coefficient that originate from the modulation of the absorption coefficient due to scattering the photoelectron on the neighboring atoms. As seen in Figure 2-6-(a), when the energy of the incident X-ray (E) exceeds the energy of the core electron (E_0), the probability of absorption by the atom sharply increases which leads to the edge jump spectrum (blue curve). The absorption

results in the ejection of the core level electron (the photoelectron) with a wavelength proportional to the square root of the excess of energy $E - E_0$: $\lambda \propto \sqrt{E - E_0}$. Because the absorbing atoms are surrounded by other atoms that can interact with the circular photoelectron wave, some photoelectrons may scatter back to the absorbing atoms (Figure 2-6-(b)) and modulate the absorption coefficient. This modulation leads to the fine structure curve (red) and can be described as the modification of the transition rate for the absorption of the X-ray photon due to the presence of the scattering atoms [240]. It is worth mentioning that fine structure oscillations are more defined for crystalline materials [244, 245]. Both XANES and EXAFS can be used to study the structure of a wide variety of crystal and amorphous materials since the rise of synchrotron X-ray sources in the 1970's. In the present work, we investigate only the XANES part (80 eV total range around the edge) to characterize the oxidation state of *Ni* in Zry-2 oxide layers.

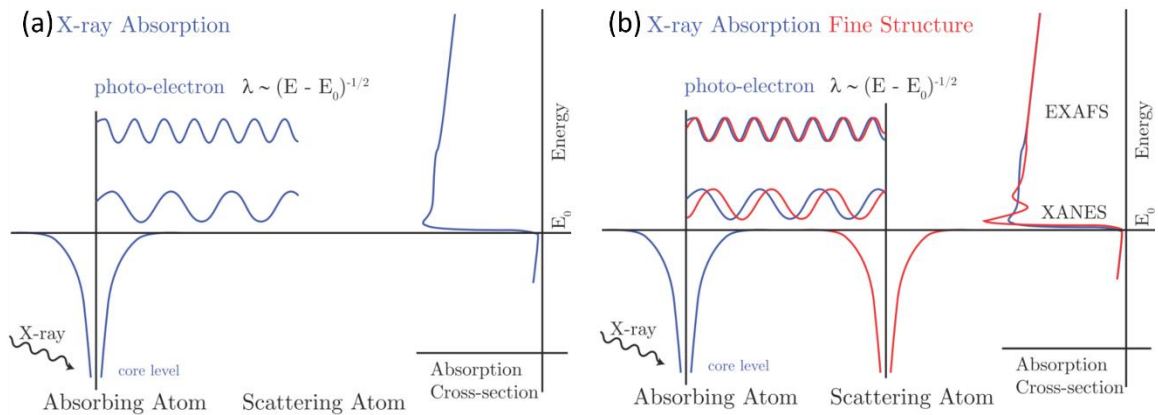


Figure 2-6: (a) Schematic of the X-ray absorption process. The incident X-ray with energy E above the core level E_0 is absorbed by the atom (blue), and a photoelectron is ejected with the wavelength $\lambda \propto (E - E_0)^{-1/2}$. (b) Schematic of the origin of fine structure in the absorption spectrum due to the scattering neighbor atoms. The photoelectron can scatter from a neighbor atom (red) and return to the absorbing atom which modulates the amplitude of the photoelectron wave-function at the absorbing atom. This in turn modulates the absorption coefficient, causing fine structure in the absorption spectrum. Figures adapted from [240].

The sensitivity of the XANES part of the spectrum to the oxidation state of the absorbing element is depicted in Figure 2-7 with the example of *Fe* XANES spectra of *Fe* in ZIRLO (acquired at the APS on an autoclave ZIRLO sample), *bcc Fe*, iron (II) oxide *FeO*, iron (II,III) oxide *Fe₃O₄* and iron (III) oxide *Fe₂O₃* (obtained from the XAFS Data Library [246-249]). It can be seen that the edge energy and peak intensity increase as *Fe* atoms are oxidized, while the pre-edge and post-edge features evolve. Those changes arise from two phenomenon [240, 242]:

- As the atom oxidizes, it loses electrons near the atom core, resulting in less shielding of the nucleus. Therefore the energy required to excite an electron from the inner shells to the continuum spectrum increases. This is reflected as a shift in the edge position toward higher energy as the atom oxidation state increases.
- Secondly, the oxidation of the atoms alters the local environment so that hybridization of electron orbitals and multi-scattering of the photoelectrons modify the edge and pre-edge intensities as well as the post-edge oscillations.

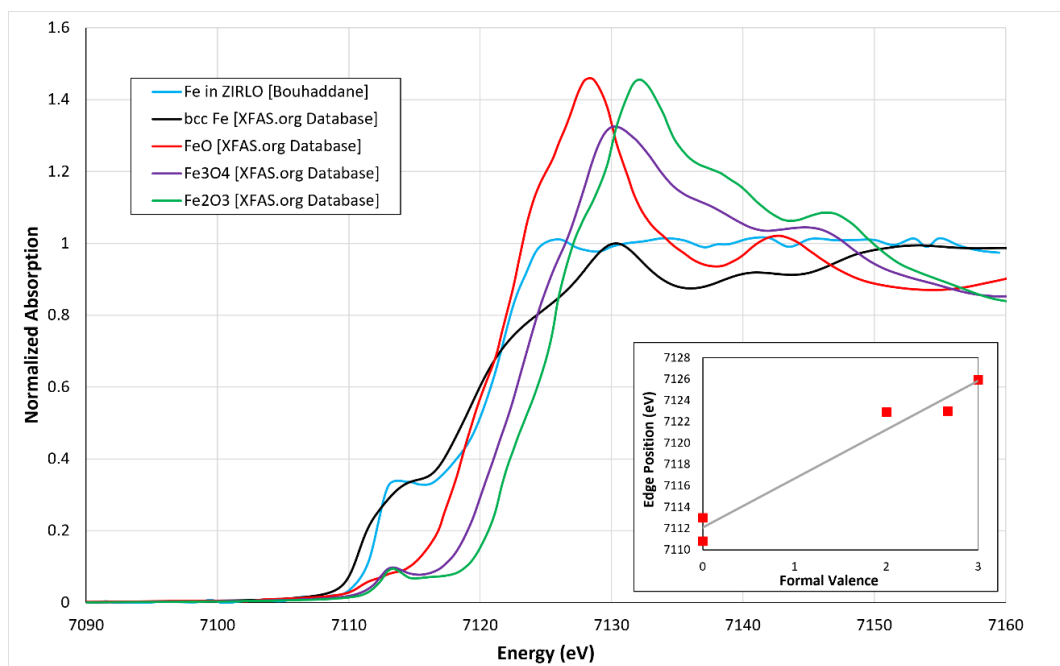


Figure 2-7: Experimental *Fe* XANES spectra for *Fe* in ZIRLO (collected at the APS on an autoclave ZIRLO sample), *bcc Fe*, *FeO*, *Fe₃O₄* and *Fe₂O₃* (from [246-249]). The inset plot represents the edge energy as a function of the *Fe* atom valence (oxidation state).

As described in more detail in sections 2.3.4 and 2.3.5, these spectral changes enable the experimenter to study the oxidation state of the element of interest in zircaloy oxides using a linear combination analysis with reference standards. Such spectral changes are seen in Figure 2-8 (from Ensor's work [145]) which contains the *Fe* XANES spectra (K edge) collected across the oxide layer formed on a Zry-4 sample corroded in 274°C water. As the scan advances in the oxide (darker blue curves), the metallic *Fe* pre-edge feature is lowered while the edge energy and the white line intensity increase, reflecting the oxidation of the *Fe* atoms in the oxide layer. Additionally, XANES is sensitive to the coordination environment of the atoms of interest, as can be seen from the differences between the spectra for *Fe* in ZIRLO and *bcc Fe* in Figure 2-7. Iron atoms in *bcc Fe* have different bonds and coordination compared to the iron atoms in precipitates or in solid solution in ZIRLO. In this case, the pre-edge feature, the edge intensity, and the post-edge oscillation differ while the edge position remains essentially the same.

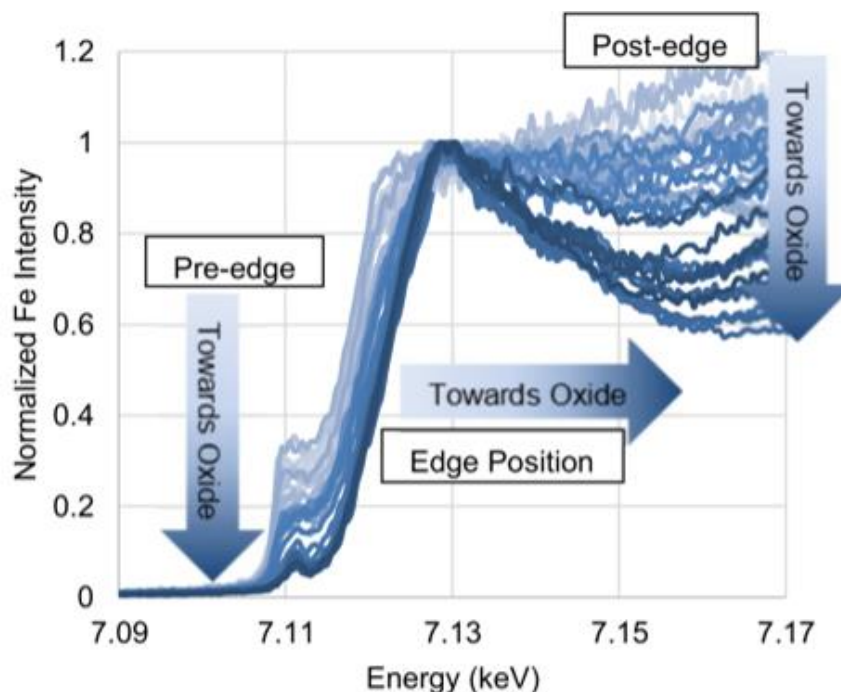


Figure 2-8: Normalized *Fe* XANES (K-edge) spectra across the oxide layer of a Zry-4 material corroded at 274°C. As the scan advances in the oxide layer (darker blue curves), the absorption spectrum is modified. The metallic iron features disappear in favor of oxidized *Fe* features, indicating oxidation of the *Fe* atoms. Figure taken from [145].

Two modes of measurements are available for XANES: transmission or fluorescence. In transmission mode, the experimenter collects the photon flux before and after it goes through the sample and directly measures the absorption coefficient μ for the material from the logarithm of the ratio of intensities. However, in order to have a meaningful signal, a significant portion of the beam must be absorbed when going through the material and thus the sample must be sufficiently thick or concentrated (large $\mu_{transmission}(E)$) [250]. In fluorescence mode – which was the setup used for our experiment (see section 2.3.3) – the experimenter studies the fluorescence spectra from the excited atoms. As described above, once the electron leaves the inner shell (Figure 2-4-(a), the atom is likely to emit characteristic X-rays - typically with a slightly lower energy than the corresponding absorption edge - to bring an electron from the continuum band (L and M shells mostly) back to the vacancy level in the inner shell (Figure 2-4-(b)). The other process involves the rearrangement of electrons from other shells resulting in the ejection of a second electron (Auger emission). The fluorescence mode is required for Zircalloys because the concentration of diluted alloying elements are too low concentrations to be characterized in transmission. Under the dilute sample assumption (few nickel atoms in the zirconium bulk or oxide), the fluorescence intensity is linearly related to the absorption coefficient (independently of incident energy) [242, 251]:

$$\mu_a \propto \frac{I_f}{I_0}$$

(Eq. 2-1)

For thick concentrated samples, the fluorescence intensity no longer shows a linear dependence to the absorption coefficient and “self-absorption” distortions appear in the spectra [242]. However, correction algorithms can be used to account for this self-absorption phenomenon as described further in section 3.1 with the correction of the distorted *fcc Ni* standard.

2.3.3 Experimental setup for μ XANES analysis in fluorescence mode

In this section we present the experimental setup for the XANES analysis at beamline 34-ID-E at the Advanced Photon Source (APS) at Argonne. The sample holder was modified from that used in previous work [91] to conform to the requirements of beamline 34-ID-E. The basic experimental setup was maintained, as shown in Figure 2-9 and Figure 2-10. The sample is aligned so that the metal/oxide interface is parallel to the incident beam. The synchrotron photon flux then hits the sample at a 14° incident angle. The fluorescence spectrum is collected using an X-ray detector positioned near the surface of the samples. A 90° angle between the incident beam and the detector is usually preferred as it reduces the elastic scattering yield reaching the detector [242]. Additionally, the nickel standard samples were tilted at 45° to the incident beam and to the X-ray detector in order to minimize spectra distortions due to “self-absorption effect” [240].

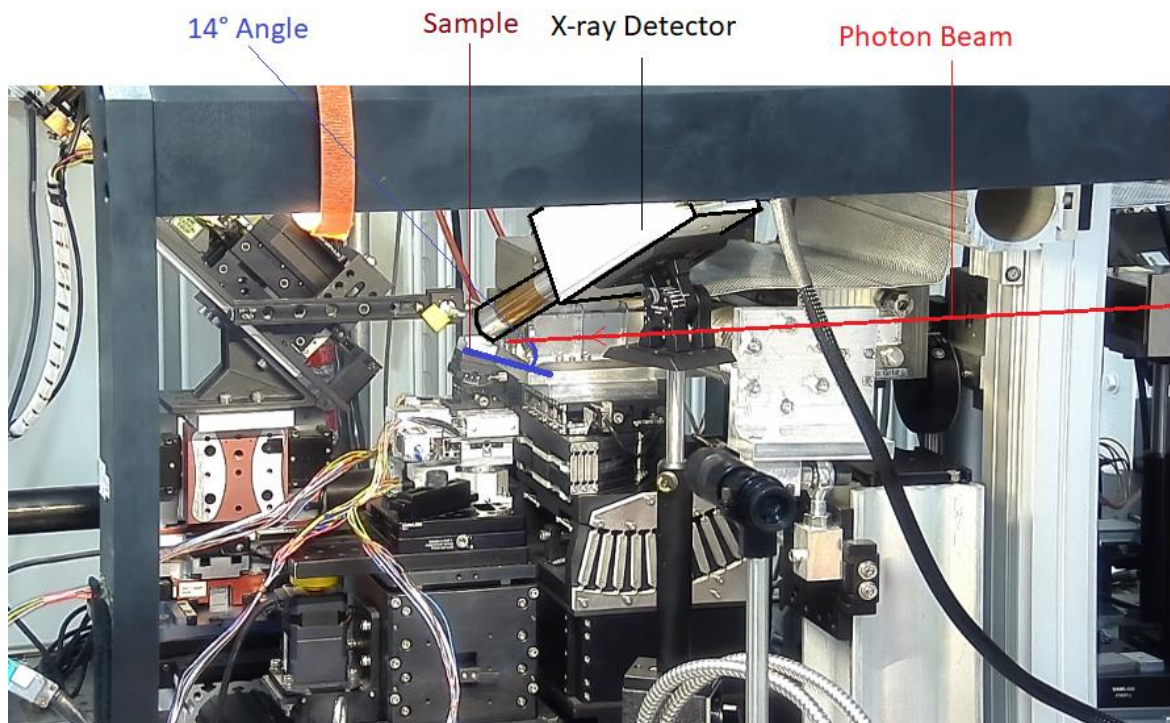


Figure 2-9: Experimental setup for XANES analysis at beamline 34-ID-E.

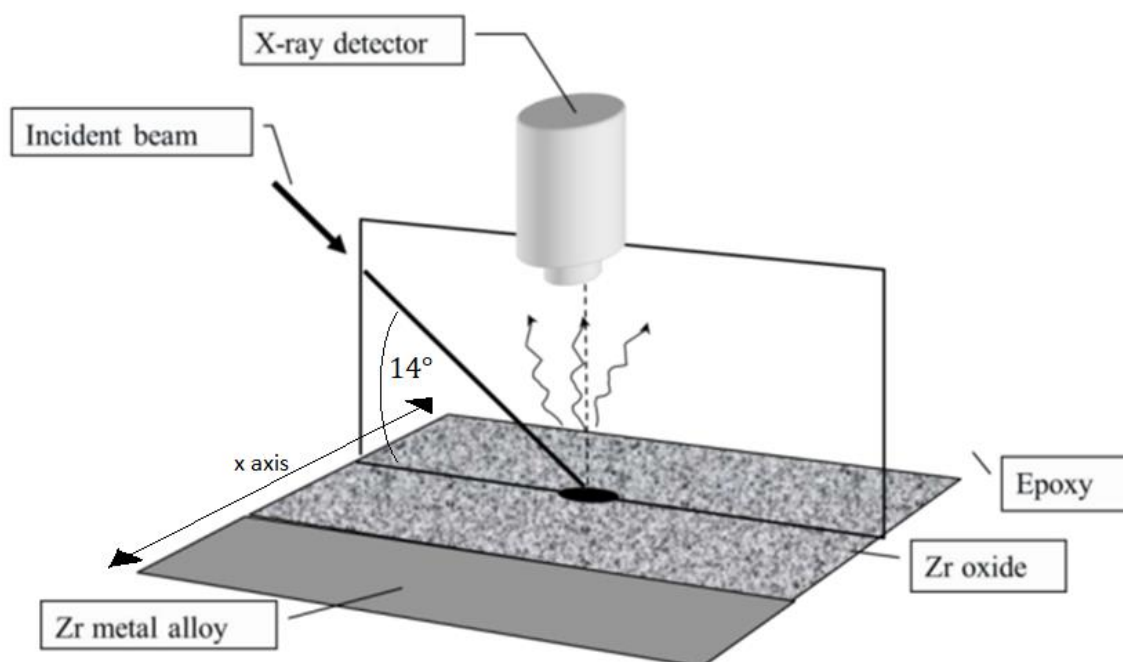


Figure 2-10: Schematic of the experimental geometry for XANES at beamline 34-ID-E at the APS. During the XANES scan across the oxide layer, the sample is moved along the x axis (set perpendicular to the metal/oxide interface) [91].

In order to analyze the oxidation state of nickel across the oxide layer, the sample is moved along the x axis and the fraction of metallic Ni can be determined as a function of depth in the oxide. The precise location of the interface is obtained from zirconium K-edge fluorescence scans, as has been done previously [52, 89, 91, 131]. Indeed, the Zr fluorescence counts decrease slightly in the oxide as the density of Zr atoms is reduced by the incorporation of O atoms. In the epoxy, Zr fluorescence count falls to a background level. Because the photon energy can reach 20 keV at beamline 34-ID-E while keeping $\Delta x < 0.5 \mu m$, it was possible to use the K-edge Zr fluorescence (at $E = 18 \text{ keV}$) [252], whereas previous experimenters had to rely on the low intensity low energy L-edge Zr fluorescence or on X-ray diffraction at beamline 2-ID-D to ascertain the position of the beam relative to the oxide layer during measurements. An example of the zirconium fluorescence spectrum acquired at beamline 34-ID-E (APS) across an oxide layer formed on material 11 at $E = 20 \text{ keV}$ is shown in Figure 2-11-(a). In comparison with previous

L-edge *Zr* fluorescence spectra taken with an X-ray energy near 9 *keV* (Figure 2-11-(b) [89]), it is clear that in both cases the metal and oxide limits are delineated by the higher *Zr* absorption in the oxide layer. We note also that the overall counts are much higher at higher energy, which results in a less noisy spectrum, but the difference between metal and oxide counts is smaller. However, it was seen post-experiment with XRD phase analysis and *Ni* oxidation state determination that the metal/oxide interface was shifted by 1-3 μm from the *Zr* K-edge fluorescence value. It is hypothesized to originate from the difference in sampling volume at 20 *keV* compared to 8.34 *keV* as described further below and in chapter 3.

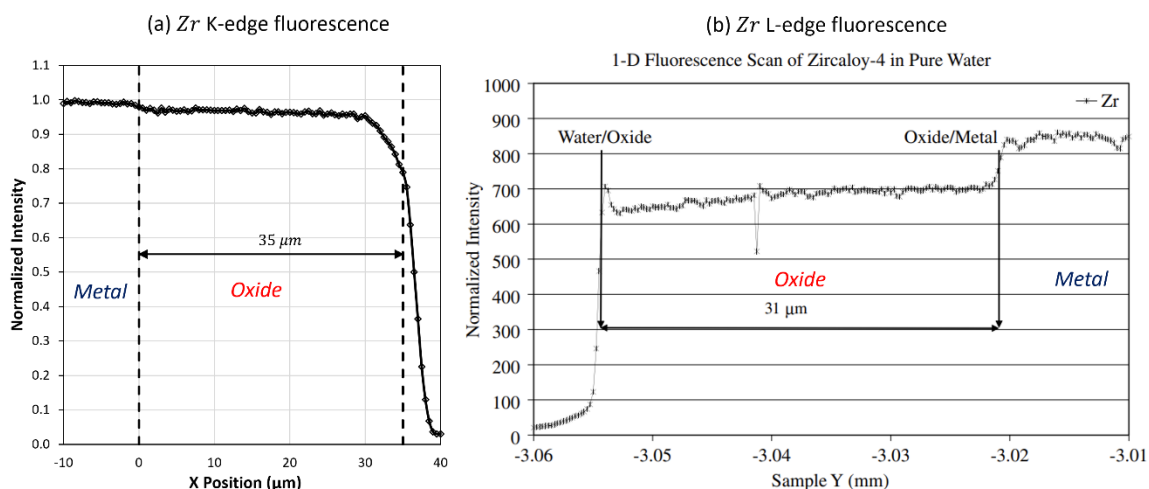


Figure 2-11: (a) Zr K-edge fluorescence of sample 11-A at the XANES scan location (collected at beamline 34-ID-E, APS). The bulk (metal) is on the left, the 35 μm thick oxide on the right. (b) Zr L-edge fluorescence in a Zry-4 sample corroded in 360°C water for 784 days (collected at beamline 2-ID-D, APS) [125]. The metal part is seen on the right with the 31 μm thick oxide on the left.

Lastly, the 14° angle between the incident beam and the sample surface was chosen so that the penetration depth was only few μm below the surface. Indeed, the footprint of the 0.3 μm * 0.3 μm beam on the sample is about 0.3 μm * 1.2 μm with this low incident angle, and the penetration depth at $E = 8340 \text{ eV}$ is about 3.1 μm in *Zr* and 4.7 μm in *ZrO₂* - compared to 19.5 μm at normal incidence [253]. The sampling depth (95% of X-ray intensity) is estimated to be three times the penetration depth. Therefore, the sampling volume at the *Ni* K-edge is at least

of $3.5 \mu\text{m}^3$. Assuming a mean size of about 100 nm (section 1.2.2) for the $\text{Zr}_2(\text{Fe}, \text{Ni})$ precipitates, the average particle volume is of the order of $10^{-3} \mu\text{m}^3$, or three orders of magnitude lower than the sampling volume. Therefore the Ni fluorescence signal arises both from nickel atoms in precipitates and in solid solution.

At the Zr K-edge ($E = 20 \text{ keV}$), the penetration depth at 14° incident angle is about $5.0 \mu\text{m}$ in Zr and $7.8 \mu\text{m}$ in ZrO_2 leading to a larger sampling volume than at the Ni K-edge energy [253]. This difference is thought responsible for the few μm uncertainty around the metal/oxide interface when compared with post-experiment to the XRD and Ni XANES measurements. However, it was fast and reliable to locate the interface in the encapsulated irradiated samples using the Zr K-edge during the experiments (section 3.2).

2.3.4 Reference standard

As described previously, XANES spectra are sensitive to the oxidation state of the absorbing elements and to its crystallographic coordination geometry or nearest neighbors (Figure 2-7) [242]. Therefore, a characteristic XANES spectrum standard is obtained for each element in a given phase with a given electronic state. When the sample consists of a mixture of the absorbing atoms in different oxidation states and sites, the X-ray absorption signal is in principle the weighted average of the absorption signal from these atoms in different locations and in different phases. This is true if the measured data is not nonlinearly distorted, i.e. sample thickness or “self-absorption” effects are not present (more details on the “self-absorption” phenomenon are available in section 3.1) [242]. When self-absorption is present, a correction algorithm such as the one described by Reddy [251] needs to be applied prior to data fit. Because the concentrations of the alloying elements of interests are so low in zirconium alloys, one can expect the fluorescent signal to depend linearly on the elemental concentration - thick dilute

conditions – such that the linear combination fit of the data can be performed in a straightforward manner. Thus standards of the element of interest in the different possible phases are required to obtain the relative contributions of each phase from the spectra. Additionally, the XANES spectrum of a reference sample (such as *fcc Ni* foil) is used for calibration of the energy to compare spectra collected at multiple beamlines with different X-ray detectors and experimental setup [254]. In the case of nickel, the standards selected consist of two metallic compounds and four oxides: *fcc Ni* and *Ni* in Zry-2; *NiO*, *NiFe₂O₄*, *Ni₂O₃* and *Ni(II, III)* in *ZrO₂*. These are listed in Table 2-2. Because of the geometry at beamline 34-ID-E, all standard signals were collected in fluorescence mode. The *Ni* standards are described below while the XANES spectra obtained are presented in section 3.1.

Table 2-2: List of standards used for nickel XANES examinations of in-reactor corroded Zry-2 water rods.

Nickel standards		
Compound	Physical State	Provenance
<i>fcc Ni</i>	Foil	Sigma-Aldrich
<i>Ni</i> in Zry-2	Bulk	Zry-2 Water Rod
Nickel (II) oxide (<i>NiO</i>)	Powder	Sigma-Aldrich
Nickel ferrite (<i>NiFe₂O₄</i>)	Powder	Sigma-Aldrich
Nickel (III) oxide (<i>Ni₂O₃</i>)	Powder	Sigma-Aldrich
Ni (II, III) in <i>ZrO₂</i>	Bulk	Zry-2 Water Rod

The *fcc Ni* standard consisted of a metallic foil provided by Sigma-Aldrich. Because this was a pure *Ni* sample, the XANES fluorescence signal suffered “self-absorption” distortions that were corrected using ATHENA software [255] in which the FLUO correction algorithm has been implemented [256]. Once corrected, the *fcc Ni* foil standard spectrum corresponded to the

fcc Ni spectra available in literature. However, the “self-absorption” distortions introduce large post-edge noise and so the *fcc Ni* standard spectrum from [249] was used after alignment of the edge energy. The *fcc Ni* foil standard can be seen in Figure 2-12-(a). The second metallic compound was that from *Ni* atoms in Zry-2 which was obtained from averaging the XANES signals from 10 locations in the metal part of material 9. This allowed for the reduction of noise in the standard data as seen in section 3.1. Although *Ni* is metallic in both standards, the XANES signals are dissimilar because of the different near-neighbors of the nickel atoms in both phases as explained in section 3.1. Indeed, the *Ni* atoms in Zircaloy-2 are bonded with *Zr* atoms both in solid solution in the *Zr* matrix or in intermetallic precipitates of the $Zr_2(Ni, Fe)$ type.

The first three nickel oxide standards - *NiO*, *NiFe₂O₄*, and *Ni₂O₃* - with respective oxidation state - *Ni²⁺* or *Ni(II)*, *Ni²⁺* or *Ni(II)* [257], and *Ni³⁺* or *Ni(III)* - were all in the powder form and provided by Sigma-Aldrich. In order to prevent the effects of “self-absorption” in fluorescence mode, the grain size of the powders was minimized, and the oxides were diluted to 5-10 wt.% into zirconia powder. The mixture was then glued with Nail polish glue and sealed on an aluminum plate (20 mm × 20 mm × 3.175 mm) using DuPont Kapton tape (provided by CS Hyde Company). The resulting standard sample is shown for *NiO* in Figure 2-12-(b). Similarly to the metallic standard *Ni* in Zry-2, the fourth oxide standard labeled *Ni(II, III)* in *ZrO₂* consisted of the average of 10 XANES spectra collected between 20 and 25 μm from the metal/oxide interface in the oxide layer of material 9. It was included during data processing of the metallic fraction and used instead of the 3 powder oxides described above for the final fit of the XANES spectra. The author believes it represents more accurately the XANES signal arising from oxidized nickel atoms in Zry-2 oxide compared to the nickel oxide standards and reduced fitting errors. However, both analyses yielded similar results as further detailed in section 3.1 and 3.4.1.

The standard XANES spectra were then collected during the experiments at the APS and normalized with the ATHENA program [255] for oxidation state analysis of the nickel atoms in the oxide formed on the Zry-2 water rods.

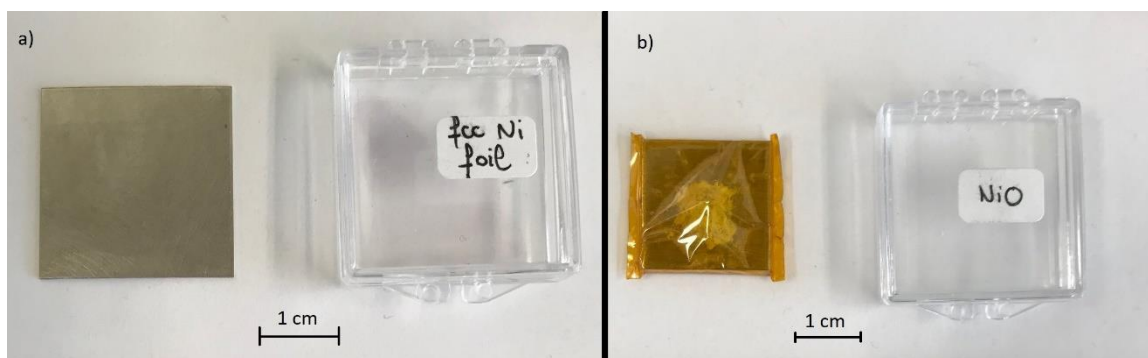


Figure 2-12: Images of the fcc Ni foil (a) and NiO powder diluted in ZrO_2 powder and sealed on an aluminum plate with Kapton tape (b).

2.3.5 Oxidation state analysis using ATHENA

Once the XANES spectra were collected from the Zry-2 cross-section samples or the nickel standards, the data were imported into the ATHENA program for analysis. ATHENA software has been used in many studies and is a useful tool for X-ray absorption analysis [255] and relies on the IFEFFIT algorithm [258]. The pre-fit processing of the XANES spectrum consisted of the determination of the edge energy and of the pre-edge and post-edge (or normalization) functions. This initial processing is described below and illustrated in Figure 2-13 with the example of Ni_2O_3 .

The first step consists in dividing the fluorescence counts by the incident beam intensity because of the small synchrotron pulse variations with time. Then, following previous work [52, 91, 131, 255, 259], the edge position E_0 was defined as the maximum of the derivative of the spectrum with respect to energy. The pre-edge function was linear and fit to the region 15 – 20 eV before the absorption edge while the normalization function was polynomial and regressed

to the data in the region $15 - 20 \text{ eV}$ past the edge (Figure 2-13-(a)). The normalization constant $\mu_0(E_0)$ is calculated by extrapolation of the pre-edge and post-edge functions and defined as the difference between the two curves at the edge position, also called the “edge step”. The extrapolated pre-edge function is then subtracted from the whole spectrum, which put the pre-edge portion of the data on the ($y = 0$) axis. The resulting spectrum is then divided by $\mu_0(E_0)$ to obtain the “normalized” data (Figure 2-13-(b)). Lastly, the difference in slope and quadrature between the pre-edge and post-edge lines was subtracted from the data past the edge position. It puts the oscillatory portion of the spectrum on the ($y = 1$) axis and the “flattened” data obtained goes from 0 to 1 (Figure 2-13-(b)). The normalization and flattening process allows for direct comparison and improved linear combination fitting of data sets with variations in sample preparation, sample thickness, absorber concentration, detector settings and other aspects of the measurements [240, 254, 260].

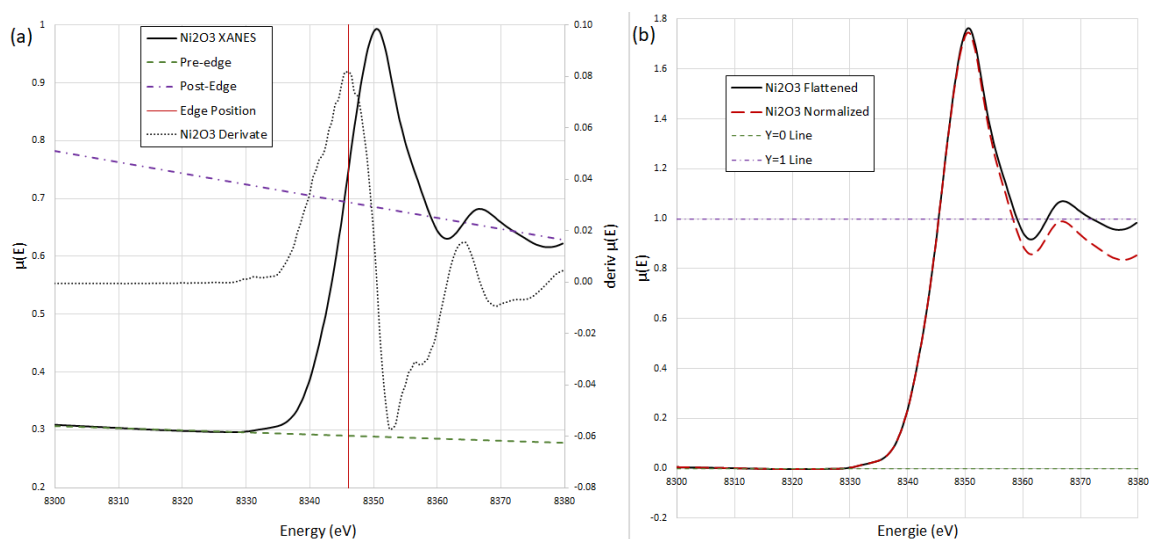


Figure 2-13: Illustration of the Ni XANES data processing prior to linear combination fitting with the example of Ni_2O_3 spectrum (from [261]: (a) Ni XANES data and derivative with pre-edge and post edge functions. The edge energy is defined as the maximum of the derivative the absorption coefficient (red line); (b) Resulting normalized and flattened absorption spectra. A linear combination fit was then applied to the flattened data.

Once pre-processed, *Ni* XANES spectra from the irradiated Zry-2 samples were fit to linear combinations of the *Ni* standards spectra. As mentioned in the previous section, XANES spectra of a mixture of the absorbing atoms are in principle the weighted average of the absorption signal from the different atoms and so the metallic *Ni* weight fraction can be accessed via linear combination fit of the measured data with reference standards [242], as done in previous studies [91, 254, 262, 263]. The metallic fraction of *Ni* across the oxide layer of the material was then calculated by summing the weights of the metallic compounds (*fcc Ni* and *Ni* in Zry-2) resulting from the fit. The linear combination fit analysis is further described in section 3.4.1. Because detectable differences in the metallic *Ni* signal arising from the oxide part were observed between the Zry-2 materials, the *fcc Ni* and *Ni* in Zry-2 weight fractions were investigated as well in this study (section 3.4.2). Finally, the oxidation state of nickel in the oxide layers was analyzed by comparison of the edge energies to that of the XANES spectra (section 3.4.3).

2.4 Microstructure analysis with XRD using synchrotron radiation

2.4.1 Purpose and layout of the XRD measurements at the APS

As described in SECTION 2.1, water rods used in a BWR for 3 to 4 cycles represent a valuable set of materials to study the enhancement of hydrogen pickup at high burnup in Zry-2. In order to better understand the conditions leading up to *H* pickup accelerations at high burnup, it is relevant to study the spatial differences in microstructure of the oxide between the low and high *H* pickup fraction materials - especially in terms of fluence, temperature, and water chemistry. Microbeam X-ray diffraction is available at beamline 34-ID-E at the APS, and so XRD patterns of various locations in the oxide layer were collected concurrently with the second round of

XANES scan on the Zry-2 materials. One XRD scan was collected across the oxide at the XANES location on samples 9-B, 11-B, 12-A, and 14-B and each scan consisted of acquiring a diffraction pattern every $0.25\ \mu\text{m}$ (samples 11-B and 14-B) or $0.5\ \mu\text{m}$ (samples 9-B and 12-A). A lower spatial resolution was applied for samples 9-B and 12-A due to time constraints at the end of the experimental beamtime available (a XRD scan at $0.25\ \mu\text{m}$ across the thick oxide typically requires 2 to 3 hours).

As presented in detail in the next sections, X-ray diffraction experiments provide information on the microstructure of the materials, i.e. their crystal structure and grain size [125, 264]. The different phases composing the materials can be investigated at the submicron level with a high photon flux thanks to synchrotron radiation. Previous examinations of oxide layers formed on *Zr* alloys using microbeam XRD proposed that the mechanism consists in nucleation of small monoclinic (predominant) and tetragonal zirconia particles, followed by grain growth as the oxide advances into the metal [89, 120, 236]. The monoclinic grains elongate in the direction of oxide growth, the tetragonal grains which are properly oriented to minimize stresses undergo a phase transformation to monoclinic particle as the grains grow, while the grains that are not properly oriented do not grow [120, 265-267]. As mentioned in SECTION 1.3.1, *t-ZrO₂* is not stable at the reactor pressure and temperature (and below) but can be stabilized by alloying elements, by small oxide grains and by high stresses [268]. Hence, tetragonal zirconia grains have been observed mainly near the metal/oxide interface where stresses are high, and oxide particles start to nucleate, such that grains are small. Shivprasad [91] observed a higher concentration of tetragonal zirconia near the metal interface in the low hydrogen pickup water rods as has been observed previously with TEM on various *Zr* alloys [144]. In this context, a thorough study of the microstructure of the oxide and of the metal part near the metal/oxide interface was done on all four materials selected (Table 2-1) and the results of these examinations are presented in chapter 4.

2.4.2 Principles of X-Ray diffraction

In this section, we present the principles of microstructure analysis using X-ray Diffraction. The XRD technique is based on the specular scattering of electromagnetic waves by the atoms of a crystalline structure when the wavelength of the incident photons, λ , is comparable to the spacing between atomic planes in the crystal structure. For coherent incident light (such as that from microbeam synchrotron radiation), the scattered waves undergo constructive and destructive interferences so that X-ray are reflected at certain angles of incidence only. This phenomenon is known as Bragg diffraction [269], as illustrated in Figure 2-14. If the diffracted X-rays from the atoms in the lattice planes are in phase because the difference in path length is an integral multiple of the photon wavelength, then constructive interferences form at specific reflection angles so that a diffracted beam with significant intensity is produced and can be collected. This diffraction condition for constructive interferences is a special case of the more general Laue equations and is summarized by Bragg law [264]:

$$2d \sin(\theta) = n\lambda$$

(Eq. 2-2)

where d is the interplanar spacing, θ the diffraction angle, and n the order of reflection.

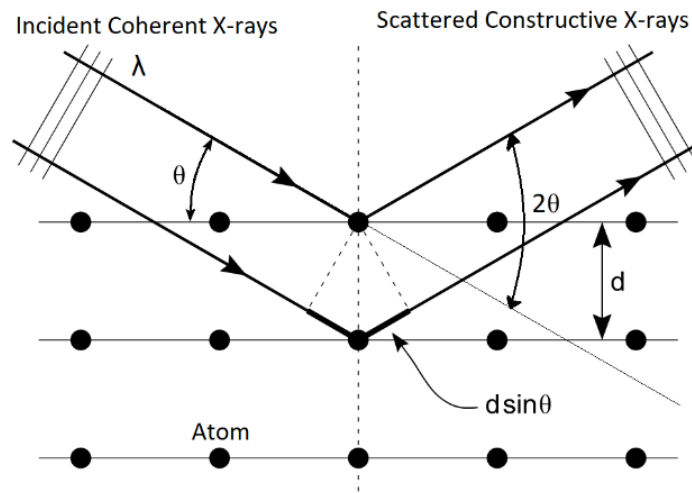


Figure 2-14: Illustration of Bragg diffraction by the atoms of crystallographic planes [270].

The order of reflection n is a positive integer and is equal to the number of wavelengths in the path difference between diffracted X-rays from adjacent planes. The spacing d between the crystallographic planes $(h\ k\ l)$ of a lattice can be expressed as a function of the Miller indices h , k , l and of the unit cell parameters. For example, the interplanar spacing of a $(h\ k\ l)$ plane in a cubic lattice with cell parameter a is determined by [264]:

$$\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2}$$

(Eq. 2-3)

Combining this expression of d with the Bragg law (Eq. 2-2), one can obtain for cubic crystals:

$$\sin^2 \theta = \frac{\lambda^2}{4a^2} (h^2 + k^2 + l^2)$$

(Eq. 2-4)

Therefore, the diffraction angle θ can be determined directly from the plane indices and the unit cell parameters. The structure of materials with specific set of planes and unit cells can then be investigated by measuring the diffraction angle θ . Obtaining a diffraction pattern consists of collecting with a large light detector the intensity of the scattered X-rays as a function of the diffraction angle. The 2θ notation is usually preferred so that the incident beam, rather than the sample surface is set as normal to the detector. The intensity of the scattered beam from a set of planes is given by the structure factor F determined by the position of the atoms in the unit cell $(u_j\ v_j\ w_j)$, their atomic scattering factor f_j and the Miller indices of the planes $(h\ k\ l)$ [264]:

$$F_{h\ k\ l} = \sum_{j=1}^N f_j e^{2\pi i(hu_j + kv_j + lw_j)}$$

(Eq. 2-5)

where N is the total number of atoms in the unit cell.

The structure factor represents both the amplitude and phase of the summation of diffracted waves over all the atoms in the unit cell. The scattering intensity reaching the detector is directly proportional to the squared modulus of F :

$$I_{scattered} \propto |F|^2$$

(Eq. 2-6)

In a perfect single crystal, the diffraction pattern is composed of points of high intensities, each one of them corresponding to a specific $(h\ k\ l)$ plane. On the other hand, in a multigrain single crystal without texture, diffraction can occur in all directions and luminous rings form on the diffraction pattern, each one of them corresponding to a specific diffraction angle 2θ . Examples of diffraction patterns for a single crystal and a powder CeO_2 standard (multigrain single crystal) are shown in Figure 2-15. If grains have preferred crystallographic directions in the sample – due to material fabrication or preferential growth under stress for example - then azimuthal parts of the rings will be more luminous than others (as can be seen in chapter 4 for zirconium alloys bulk samples). The texture of the material is therefore studied by analysis of the diffraction pattern and the “cake” partial integration which plots the intensity as function of the diffraction angle 2θ and of the azimuthal angle on the detector χ (see section 2.4.4).

For further analysis, the diffraction pattern is integrated over the azimuthal range so that the luminous intensity can be plotted as a function of the 2θ angle only. An example of the resulting 2θ -plot is shown in Figure 2-16 for CeO_2 powder. The intensity peaks resulting from the different rings are then identified using materials databases. The Powder Diffraction File (PDF) database, produced and maintained by the International Center for Diffraction Data (ICDD) [271], was used in this study. The PDF of a material provides information on the crystal structure of the phase, the unit cell parameters, the crystal planes (Miller indices), and the corresponding interplanar spacings and scattering intensities. The PDFs for the zirconium, zirconium oxides, and zirconium hydrides phases used in this study are available in APPENDIX

A. The diffraction peak centroids, widths, and intensities of the integrated diffraction pattern are then fitted (section 2.4.4) which yields information on which phases are present and on their volume fraction (section 2.4.5). In the next section, the experimental setup for the X-ray diffraction measurements at beamline 34-ID-E of the APS (ANL) is presented.

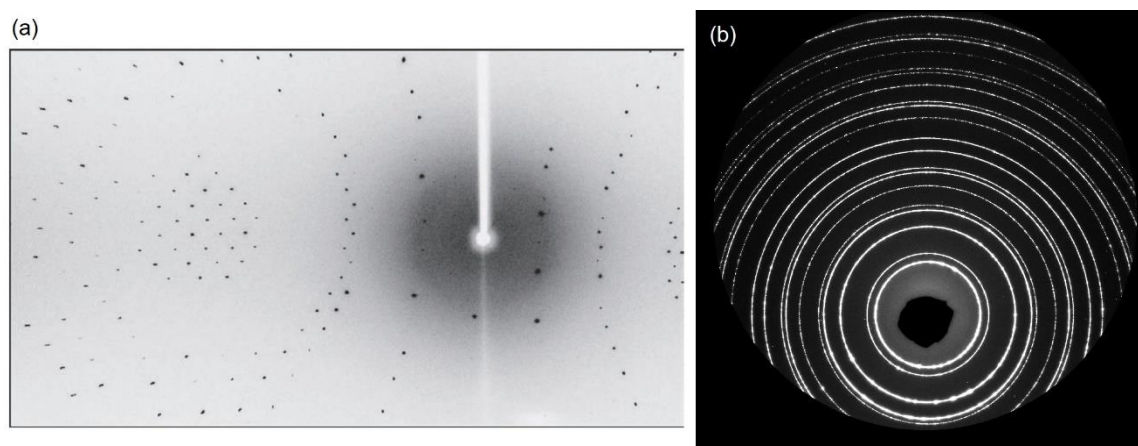


Figure 2-15: X-ray diffraction pattern for (a) a single crystal [272] and (b) CeO_2 powder (data collected at the APS at $E = 22 \text{ keV}$).

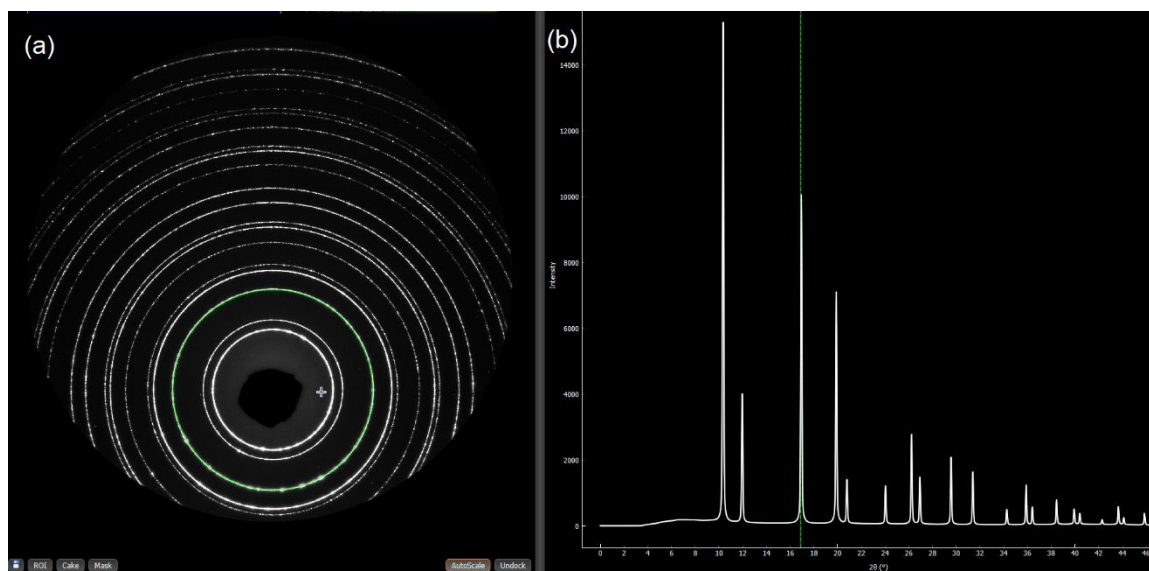


Figure 2-16: X-ray diffraction pattern (a) and integrated 2θ -plot (b) for CeO_2 powder (data collected at the APS at $E = 22 \text{ keV}$). The green ring represents the integrated area for the peak intensity corresponding to $2\theta = 17^\circ$ (green line).

2.4.3 Experimental setup for XRD

The X-ray diffraction measurements on the Zry-2 water rod cross-section samples were conducted concurrently to the XANES experiments at beamline 34-ID-E at the APS (ANL). The cross-section samples were examined in reflection mode because of the low beam energy and the substantial sample thickness. As seen in Figure 2-19 in the next section, only half of the circumference of the diffraction rings can be collected in reflection mode as the light scattered in the other directions is absorbed in the sample. The setup was identical to that previously described in section 2.3.3 (Figure 2-9 and Figure 2-10) but a charge collection device (CCD) surface detector (PI-SCX:4300) was added and placed about 1.1 m past the sample holder to collect the diffracted beams. The XRD setup is illustrated in Figure 2-17. In order to examine the similar volume as that of XANES measurements, the sample was tilted to a 14° angle and the beam energy set to the low energy for typical XRD: $E = 8.5 \text{ keV}$. The sampling volume was therefore of the order of $5 \mu\text{m}^3$ as well because the X-ray penetration depth and the beam size at $E = 8.5 \text{ keV}$ are identical to those obtained at the nickel K-edge energy $E = 8.34 \text{ keV}$. A photon energy of $E = 8.5 \text{ keV}$ implies the wavelength $\lambda = 0.14586 \text{ nm}$, which was used for calibration and calculation of the 2θ angles.

The diffraction patterns were acquired at the location of the *Ni* oxidation state scans on the cross-section samples so that the microstructure information for specific *Ni* oxidation states was acquired. The oxide/metal interface was aligned as closely as possible with the beam and *Zr* fluorescence at the K-edge ($E = 20 \text{ keV}$) enabled to locate the interface on the x axis during the experiments. The sample was moved along the x axis and a XRD pattern was collected at each point (acquisition time was 20 seconds). As mentioned in section 2.4.1, one XRD scan was acquired on one of the samples from each material (9-B, 11-B, 12-A, 14-B) and the results of this examination are presented in chapter 4.

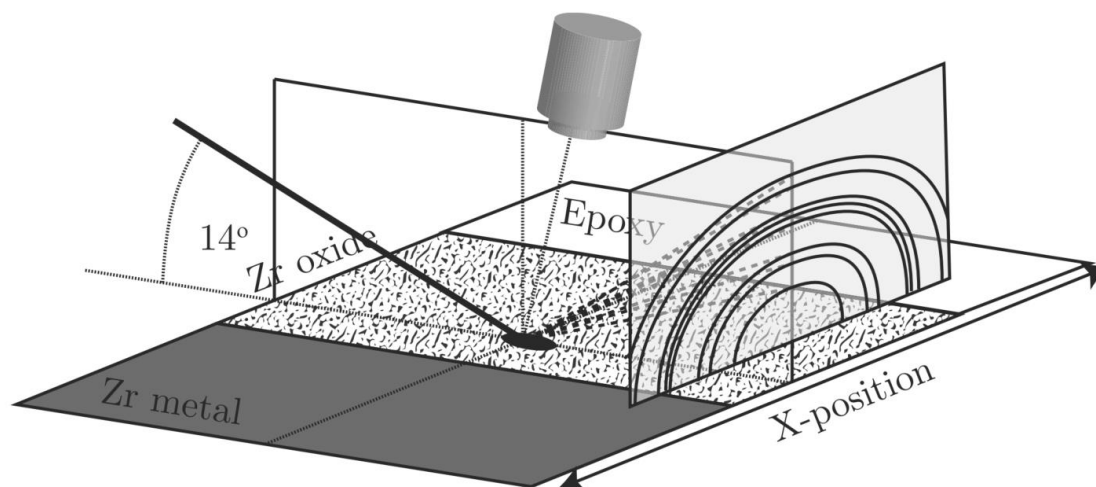


Figure 2-17: Schematic of the experimental geometry for XRD at beamline 34-ID-E at the APS [91]. During the XRD scan across the oxide layer, the sample is moved along the x axis.

2.4.4 Diffraction data processing using DIOPTAS and PEAKFIT

Once the XRD patterns were collected across the oxide, the images were imported into the DIOPTAS program [273] for analysis of the diffraction intensities in terms of azimuthal and diffraction angles (χ and 2θ). The CeO_2 powder standard shown in Figure 2-18 was used for calibration of the XRD patterns by ensuring that the correct 2θ position is used. Note that the pattern in Figure 2-16 only contains the first few reflections of the more complex XRD pattern of CeO_2 standard shown in Figure 2-15 and Figure 2-16 because of the low beam energy ($E = 8.5 \text{ keV}$) compared to standard XRD measurements, which means that many of the higher order reflections are not seen. Lowering the incident photon energy increases the wavelength which in turn increases the 2θ values for Bragg reflection. Thus, as the energy decreases, the diffraction rings are pushed out of the surface detector frame. Only the light scattered by the planes with the highest d -spacing values (i.e. the lower order reflection) is collected. Additionally, the lower energy allows for more interaction of the photons with matter which reduces the signal-to-noise

ratio. However, the CeO_2 pattern at $E = 8.5 \text{ keV}$ still provided the information quality necessary for calibration of the XRD data.

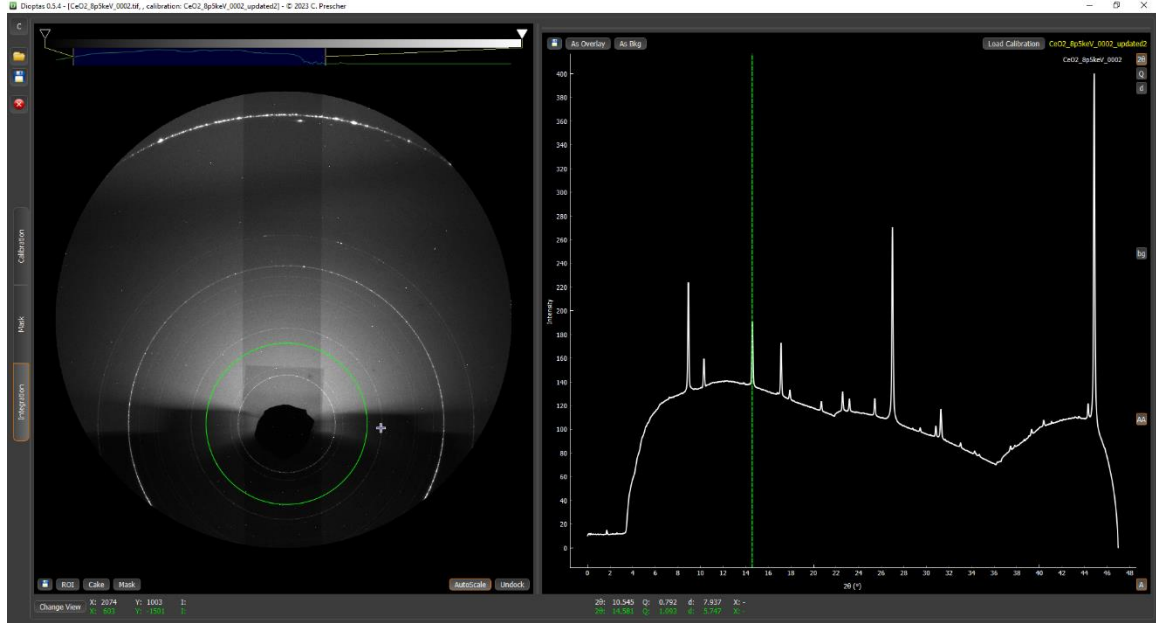


Figure 2-18: XRD pattern of CeO_2 powder standard collected at $E = 8.5 \text{ keV}$ which was used for calibration, and its integrated 2θ -plot. Less diffraction rings and more background signal are observed compared to Figure 2-16 because of the lower photon energy.

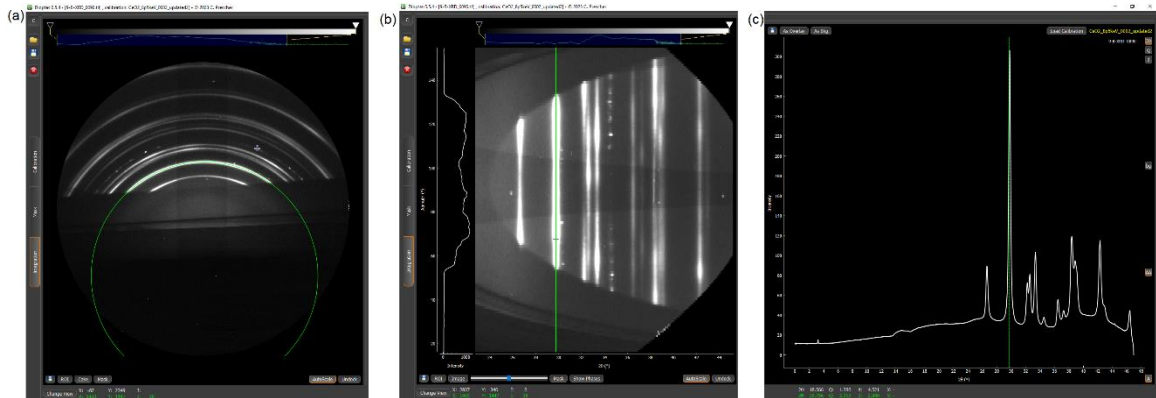


Figure 2-19: (a) XRD Image, (b) “cake” χ - 2θ -plot and (c) corresponding integrated 2θ -plot for sample 9-B (far oxide) using the DIOPTAS [273]. Because the XRD setup was in reflection for the Zry-2 cross section samples, only the upper half-circle of the XRD image was filled. The green lines and circle correspond to $2\theta = 29.75^\circ$, where the main peak for the oxide is located.

The texture of the material is reflected in the variations of intensities along the diffraction rings and is further analyzed with the “cake” or sector-integrated plots. The “cake” integration of the XRD image consists of plotting the intensity of the scattered beam as a function of χ and 2θ .

An example of the XRD pattern and its corresponding χ - 2θ -plot are shown Figure 2-19-(a) and Figure 2-19-(b) (respectively) for sample 9-B. Because the measurements were conducted in reflection mode, the azimuthal range is about half ($\Delta\chi \sim 180^\circ$) of the full detector range available in transmission XRD. Although the 2θ range of the experimental setup was $[0^\circ\text{-}48^\circ]$, the region of interest was set between $[20^\circ\text{-}44^\circ]$ for better fit of the peaks from the bulk and the oxide (see chapter 4).

In order to further investigate the microstructure of the material, the patterns are integrated over the azimuthal range to produce the 2θ -plots presented in Figure 2-19-(c) for a scan in the oxide of sample 9-B. The integrated data is then imported into the PEAKFIT program for peak identification and fit. It can be seen in Figure 2-19-(c) that a significant background is present in the 2θ -plot of the oxide of material 9 but a lower noise signal was seen in the metal part as discussed further in section 4.1.2. This background was removed prior to peak fitting using the “2nd Deriv Zero” algorithm with an N -parameter baseline. The N -parameter baseline is composed of successive linear functions converging at specified 2θ regions. It was manually set for each XRD pattern by ensuring that $I = 0$ between non overlapping peaks. An example of the background fit function for sample 9-B (oxide) is shown in Figure 2-20-(a) and the resulting 2θ -plot is shown in Figure 2-20-(b). The yellow segments correspond to the points of convergence of the linear functions of the background fit (the white line) where the intensity is set to zero.

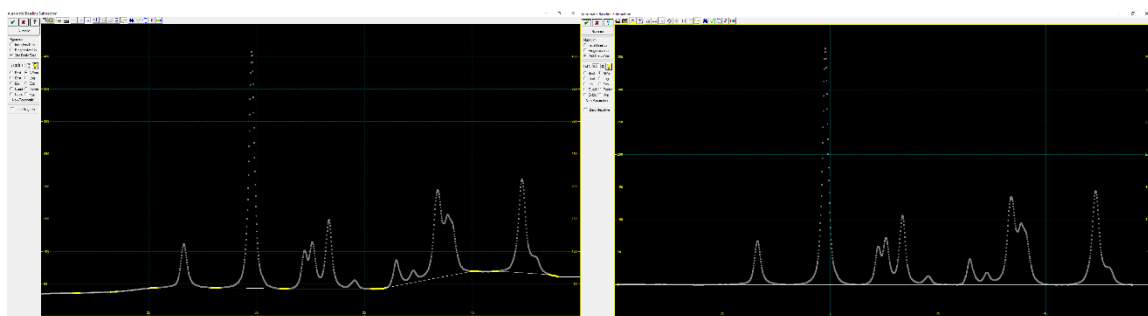


Figure 2-20: (a) Example of background fit function for sample 9-B (far oxide) using the “2nd Deriv Zero” algorithm with the N -parameter function in PEAKFIT, and (b) the 2θ -plot after removal of the background.

Once background was removed, the diffraction peaks were fitted using the Pearson *VII* area peak shape. The Pearson *VII* function is a Lorentzian function raised to a power m which converges to a Gaussian peak shape as m increases [274]. The peaks were manually adjusted for each scan before autofitting the residuals using the “AutoFit Peaks I Residuals” algorithm available in PEAKFIT. An example of the fit review for sample 9-B in the oxide is available in Figure 2-21 with the multiple identified peaks shown in colors. These identified peaks were indexed to their corresponding phases using the Powder Diffraction Files (Appendix A) for zirconium, zirconia, and zirconium hydrides as described in detail in section 4.1.1.

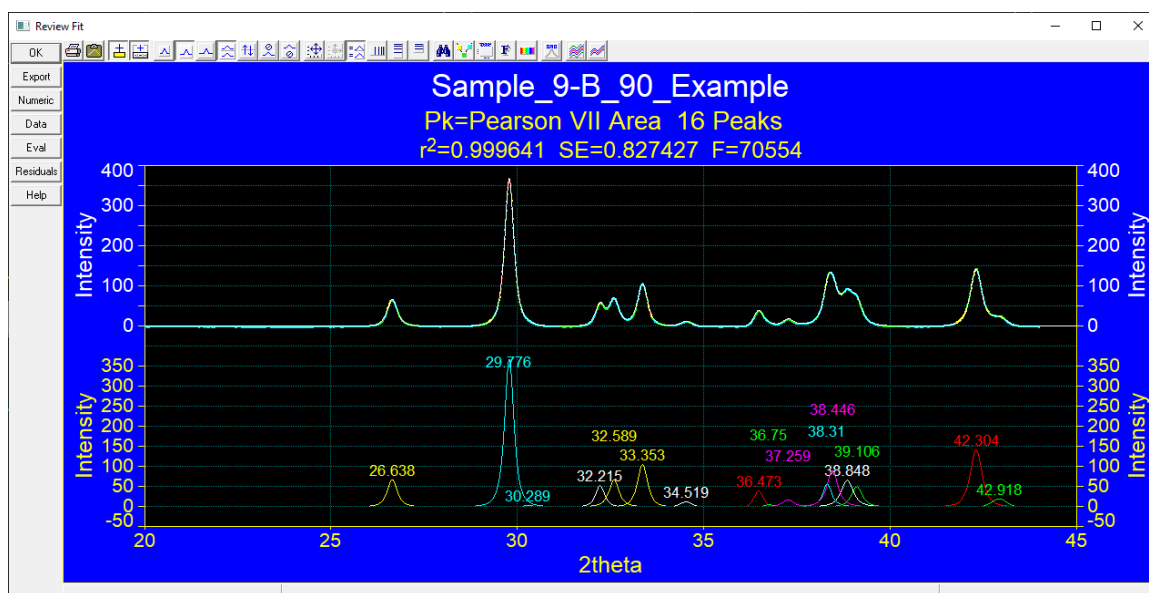


Figure 2-21: Review of the peak fit of the XRD data from sample 9-B (far oxide) using PEAKFIT software and Pearson VII area functions.

2.4.5 Phases and grain analysis

As mentioned in the previous sections, the volume fraction of different crystalline phases in a mixture of materials can be quantitatively assessed from XRD patterns. As described in section 2.4.2, the expected phases of ZrO_2 were the monoclinic and tetragonal phases. From the

PDFs of ZrO_2 phases (Appendix A), the most intense peaks are the $(\bar{1}11)$ and (111) reflections for monoclinic zirconia and (101) for tetragonal zirconia. Considering the integrated areas of the diffraction peaks, the tetragonal phase fraction can be computed using the Garvie-Nicholson formula [275]:

$$f_T = \frac{I_{(101)}^T}{I_{(111)}^M + I_{(\bar{1}11)}^M + I_{(101)}^T} \quad (\text{Eq. 2-7})$$

where $I_{(111)}^M$, $I_{(\bar{1}11)}^M$, and $I_{(101)}^T$ are the areal intensities of the $(111)_M$, $(\bar{1}11)_M$, and $(101)_T$ reflections respectively.

Although not entirely justified theoretically, the Garvie-Nicholson formula has been used for quantitative analysis in many XRD studies because of its accuracy in stabilized zirconia systems [275]. The tetragonal phase fraction f_T was therefore calculated with (Eq. 2-7) as a function of distance from the metal/oxide interface in the oxide layer of all four materials selected. In previous work [236], a correction was applied to the peak intensities to account for texture in the oxide because only a small azimuthal range was available for the experiments. Since a much wider azimuthal range was possible at beamline 34-ID-E at the APS (as was the case at beamline 2-ID-D [91]), no correction was applied in this study at first. However, sample holder shadows were seen in two of the four materials investigated due to their closeness to the edge of the holder which reduced the detector 2θ and azimuthal range and a correction was then introduced for these two samples (as described in chapter 4).

Additionally, the grain size was investigated in the oxide thanks to the increase in peak broadening as crystallite size decreases. Typically, broadening of XRD peaks occurs due to two phenomena: crystal imperfections and instrumental broadening. The latter may be due to beam divergence, sample size, X-ray penetration, monochromatic energy fluctuations, imperfect focusing and others. The former arises from a number of phenomena such as small crystallites or

micro strains and defects in the lattice. Broadening of the zirconia intensity peaks has been observed in previous XRD studies of the oxide as the beam gets closer to the metal interface and is believed to arise from the growth of zirconia grains as the metal is further oxidized. For this reason, the Scherrer equation has been used to estimate the broadening of the diffraction peaks from crystallite size changes [276]:

$$B_c(2\theta) = \frac{0.9 \lambda}{L \cos \theta} \quad (\text{Eq. 2-8})$$

where B_c is the crystallite size broadening, λ is the photon wavelength, and θ is the diffraction angle for the measured reflection, and L the crystallite edge size.

The Scherrer equation was developed for cubic systems but has been used for non-cubic system by interpreting the crystallite edge size L as the average crystallite dimension perpendicular to the reflecting plane. Therefore, grain sizes along the different directions in the oxide have been investigated using different sets of planes. It should be noted that the Scherrer equation is valid for particles smaller than 100 nm – which is the case in the oxide layer – because little to no broadening occurs when particles grow beyond this size [277, 278]. Additionally, it was important to account for the instrumental broadening when computing the grain sizes in the oxide. Instrumental broadening was estimated using the beam divergence (both horizontally and vertically, see section 4.2.3) and the crystallite size broadening was then calculated using the instrumental and total broadenings:

$$B_c(2\theta) = \sqrt{B_t^2 - B_i^2} \quad (\text{Eq. 2-9})$$

where B_t is the total peak broadening (width of a diffraction reflection (peak broadening i.e. the full width half maximum FWHM) and B_i is the instrumental broadening.

Chapter 3

Oxidation state of Ni in the oxide of BWR Zry-2 water rods with XANES

In this chapter, the results of the microbeam X-ray absorption near-edge spectroscopy measurements and analysis of the BWR-corroded water rod samples are presented. The XANES technique using microbeam synchrotron radiation at the APS (ANL) – presented in the previous chapter – allows for the determination of the oxidation state of nickel as a function of depth in the oxide layer (distance from the metal/oxide interface) formed on the Zry-2 water rods. Previous research has found that the metallic nickel present in the last 10 – 15 μm of oxide built on Zry-2 materials that spent an additional fourth cycle in a BWR reactor is correlated with and may be responsible for the high hydrogen pickup observed in these materials [91]. In order to further investigate this hypothesis, four additional materials (9, 11, 12, and 14) were analyzed from low and high elevation cut of the two Zry-2 water rods corroded in Limerick-1 (Pennsylvania, USA) reactor for 3 to 4 cycles (Table 2-1). The first section describes the XANES spectra of the metallic and oxidized nickel standards required for the Linear Combination Fit analysis with ATHENA software. The second section depicts the SEM images of the cross-section samples showing the XANES scan locations and the oxide thickness measurements. In the third section, the plots of the *Ni* K-edge XANES spectra as a function of distance from the metal/oxide interface in the oxide layer formed on irradiated materials are discussed. Then, the oxidation states of nickel across the oxide layers determined by linear combination fit analysis of the XANES spectra using ATHENA and by investigation of the edge energies are detailed before concluding on the XANES examinations of the oxide layers grown on in-reactor corroded Zry-2 water rods.

3.1 XANES spectra of metallic and oxidized nickel standards

As described in section 2.3, reference standards of metallic and oxidized *Ni* are used for the linear combination fit (LCF) analysis of the XANES spectra collected in the cross-section samples. The standards XANES spectra were all acquired in fluorescence at beamline 34-ID-E at the APS (ANL) and normalized with ATHENA [255] following the procedure presented in section 2.3.5 (Figure 2-13). The results are plotted in Figure 3-1 and compared to available spectra collected in transmission and retrieved from the Materials Data Repository (MDR) [279, 280] and the X-ray Absorption Fine Structure (XAFS) data libraries [261, 281].

The oxide powder standard (*NiO*, *Ni₂O₃* and *NiFe₂O₄*) were diluted to 5-10% in *ZrO₂* powder to ensure linearity between the absorption coefficient and the fluorescence yield (section 2.3.4). On the other hand, the XANES spectrum of the metallic *fcc Ni* foil was distorted due to self-absorption effects, which are briefly described further below. The spectrum was corrected using the self-absorption algorithm implemented in ATHENA with inputs of angles in and out of 45° (section 2.3.3). The normalized XANES spectra for the *fcc Ni* foil (as-measured and “self-absorption” – SA – corrected) are compared in figure Figure 3-1-(a) along with a *fcc Ni* foil spectrum from the XAFS database [281]. To account for differences in experimental setup, the *fcc Ni* foil spectrum from database is aligned to that from our measurement (SA corrected) matching the edge energies. The correction algorithm implemented in ATHENA is FLUO and is described in detail in [256]. Once corrected and calibrated, the spectrum from the *fcc Ni* foil is identical in shape to the high quality spectrum from database [281] but contains high levels of noise in the post-edge region due to the self-absorption distortions. For this reason, the calibrated *fcc Ni* standard spectrum from the XAFS database [281] was used for LCF analysis.

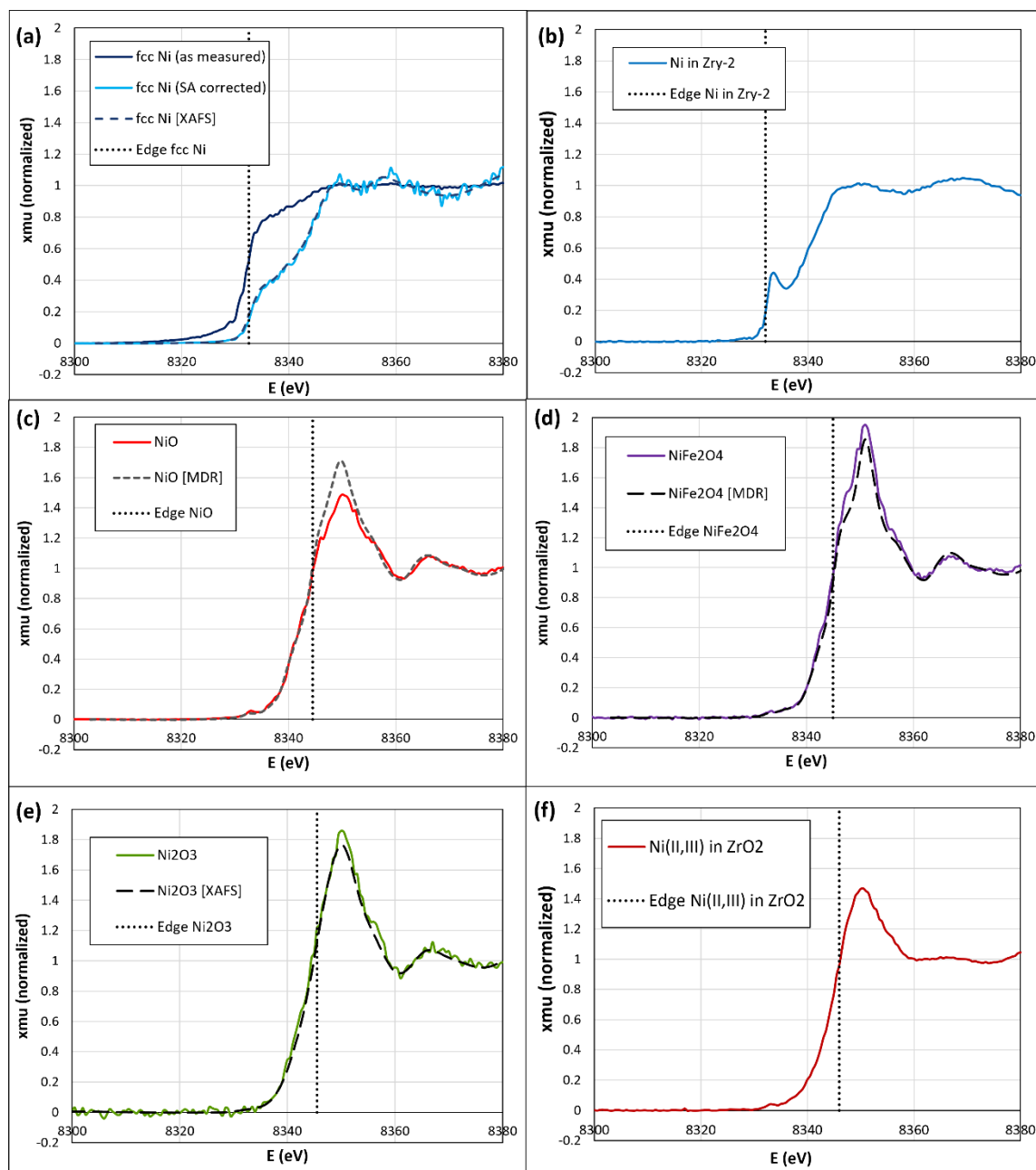


Figure 3-1: XANES spectra of nickel standards collected in fluorescence at beamline 34-ID-E at the APS (ANL) and compared to spectra from databases collected in transmission. The edge energies of the spectra from databases have been aligned to that of the APS measurements to account for differences in experimental setup. (a) as measured fcc Ni foil (dark blue), corrected for “self-absorption” using ATHENA [255] (light blue), and fcc Ni foil from the XAFS database [281]. (b) Ni in Zry-2, average of 10 XANES spectra collected in the metal region of material 9. (c) NiO from experiment and MDR database [279]. (d) NiFe_2O_4 from experiment and MDR database [280]. (e) Ni_2O_3 from experiment and XAFS database [261]. (f) Ni(II,III) in ZrO_2 , average of 10 XANES spectra collected in the far oxide of material 9.

The XANES spectra obtained from the diluted oxide powders (NiO , $NiFe_2O_4$, and Ni_2O_3) are plotted in Figure 3-1-(c), Figure 3-1-(d), and Figure 3-1-(e) respectively and compared with standards spectra collected in transmission from MDR and XAFS database [261, 279, 280]. For all three standards, the measurements from this work agree with XANES signals of transmission standards, confirming that dilution of the oxide powders was successful in limiting self-absorption effects. However, the maximum intensity in the oxide standards (also known as “white line” intensity as described below) is seen lower for NiO and higher for $NiFe_2O_4$ and Ni_2O_3 compared to reference standards. White line intensities depend on many factors and may vary between two runs as seen in transmission at the $Pt\ L_{III}$ -edge [282]. Also, the grain size of the powder samples was observed to play a key role in the white line intensity in fluorescence (due to self-absorption effects occurring if the grain size is comparable to the absorption length [240, 283-285]). Therefore, multiple XANES spectra were collected on each diluted powder sample until reasonable absorption steps were obtained which ensured little self-absorption distortions.

The second metallic standard Ni in Zry-2 (Figure 3-1-(b)), collected in the metal region of material 9 (average of 10 XANES scans), is similar to the $fcc\ Ni$ XANES with a strong rising edge feature and no white line. The clear differences between oxidized and metallic Ni XANES spectra, described in detail further below, allow for the quantitative analysis of the oxidation state of nickel. However, because of the similarity of the XANES spectra from the three nickel oxides considered and the uncertainty of the fit due to differences with the XANES signal arising from oxidized nickel in Zry-2 oxide, it was not possible to clearly distinguish the contributions from each oxide standard during the linear combination fit. Another oxide standard was then considered instead of the three powder standards, $Ni(II,III)$ in ZrO_2 , which was collected in the far oxide of material 9 as the average of 10 XANES spectra from the $[20\ \mu m-25\ \mu m]$ region. Similar in shape to that of reference nickel oxides, the main differences are an edge shift to higher

energy and a lower white line intensity. Identical to that collected from the far oxide of other materials (see section 3.3), it yielded improved fit results in the oxide region as shown in section 3.4. Here we briefly present the origin and implications of the “self-absorption” distortions in fluorescence.

“Self-absorption” distortions (also known as “over-absorption” as it better represents the mechanism) arise from the loss of a linear relationship between the fluorescence intensity reaching the detector and the absorption coefficient of the element of interest when the sample is too thick or the element of interest too dense in the material. The fluorescence functional, a well-known equation that describes the ratio of the X-ray fluorescence intensity $I_f(E)$ to the intensity of the incident beam X-ray $I_0(E)$ is given by [251, 286]:

$$\frac{I_f(E)}{I_0(E)} = \left(\frac{\Omega}{4\pi} \right) \epsilon(E) \frac{\mu_e(E)}{\mu_t(E) + \mu_f \frac{\sin(\theta)}{\sin(\phi)}} g(E) \quad (\text{Eq. 3-1})$$

$$g(E) = 1 - \exp \left(- \left(\mu_e(E) + \mu_b(E) + \mu_f \frac{\sin(\theta)}{\sin(\phi)} \right) \frac{L}{\sin(\theta)} \right) \quad (\text{Eq. 3-2})$$

where Ω is the solid angle of the fluorescent detector above the sample, θ the incident angle, ϕ the fluorescent yield angle, L the sample thickness, $\epsilon(E)$ the fluorescent yield of the atom of interest, $\mu_e(E)$ the absorption coefficient of the element of interest, $\mu_t(E)$ the total absorption coefficient in the sample, $\mu_f = \mu_t(E_f)$ the total absorption coefficient at the fluorescence energy E_f of the target edge, and $\mu_b(E)$ the absorption coefficient from the background so that $\mu_t(E) = \mu_e(E) + \mu_b(E)$.

The fluorescent yield is rather constant around the edge energy i.e. $\epsilon(E) \approx \epsilon_0$ [251], and a linear relationship between the fluorescent intensity and the absorption coefficient $\frac{I_f(E)}{I_0(E)} \propto \mu_e(E)$ can be

obtained by performing a first-order Tayler series approximation of $g(E)$ when the exponential part verifies $\left[\left(\mu_e(E) + \mu_b(E) + \mu_f \frac{\sin(\theta)}{\sin(\phi)} \right) \frac{L}{\sin(\theta)} \right] \ll 1$, which corresponds physically to very thin samples (small L compared to the absorption length) or optically dilute samples (low density of the absorbing element of interest reduces $\mu_t(E)$ and $\mu_t(E_f)$ compared to the oxide thickness L) [240, 251, 287]. Under this condition, $g(E)$ is approximated by [251]:

$$g(E) \approx 1 - \left(1 - \left(\mu_e(E) + \mu_b(E) + \mu_f \frac{\sin(\theta)}{\sin(\phi)} \right) \frac{L}{\sin(\theta)} \right) \quad (\text{Eq. 3-3})$$

$$g(E) \approx \left(\mu_t(E) + \mu_f \frac{\sin(\theta)}{\sin(\phi)} \right) \frac{L}{\sin(\theta)} \quad (\text{Eq. 3-4})$$

Then incorporating $g(E)$ into (Eq. 3-1) provides:

$$\frac{I_f(E)}{I_0(E)} = \left(\frac{\Omega}{4\pi} \right) \epsilon_0 \frac{L}{\sin(\theta)} \mu_e(E) \propto \mu_e(E) \quad (\text{Eq. 3-5})$$

Therefore, the fluorescent intensity corresponds to the absorption coefficient in the case of dilute alloys or very thin samples. However, when the element of interest is not diluted in the material and the sample is rather thick compared to the absorption length, the fluorescence intensity is no longer directly proportional to the absorption coefficient μ_e . This is the case for the *fcc Ni* foil standard considering the absorption length of *Ni* is of the order of μm at the K-edge, resulting in higher counts in the pre-edge region and lower post-edge oscillations [288] as observed in the normalized spectra of Figure 3-1-(a). This signal compression generates additional noise in the post-edge range when corrected for self-absorption. As mentioned previously, a high-quality *fcc Ni* standard collected in transmission with synchrotron radiation [281] was used as the

reference standard for the LCF analysis (Figure 3-2) after calibration of the edge energy with the SA corrected measurement of the *fcc Ni* foil (Figure 3-1-(a)).

The main differences between the XANES signal from metallic and oxidized nickel are now discussed in detail. Figure 3-2 gathers the three standards spectra (*fcc Ni*, *Ni* in Zry-2 and *Ni(II,III)* in ZrO_2) used in this study for the final LCF analysis, alongside the XANES spectrum of *NiO* (calibrated, MDR database [279]) for illustration of the oxidized nickel features.

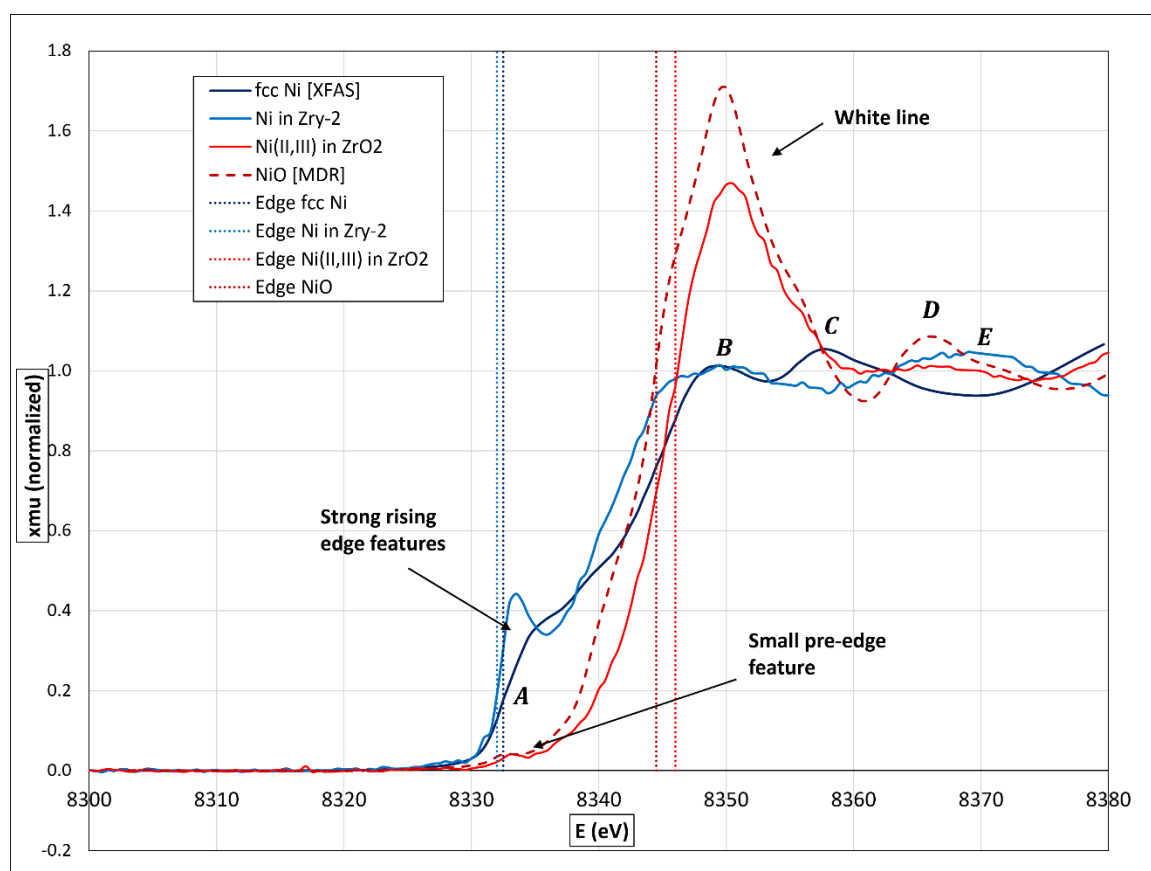


Figure 3-2: XANES spectra of the 3 nickel standards used for LCF analysis with ATHENA: *fcc Ni* (dark blue), *Ni* in Zry-2 (light blue), and *Ni(II,III)* in ZrO_2 (red). *NiO* XANES (dotted spectra, calibrated from MDR database [279]) is added to the plot for discussion of the characteristic features between metallic and oxidized nickel.

As mentioned in chapter 2, the X-ray absorption K-edge arises from the excitation of an electron from the 1s orbitals of the atoms and the photoelectron transitions to the continuum band (EXAFS region). Near the edge, the photoelectron may transition to empty or partially filled

electron shells. For *Ni* and other *3d* transition metals (such as *Fe* and *Cr*), the edge represents the dipole allowed *1s* to *4p* transition [254, 283, 289]. In centrosymmetric systems such as for most transition metals and oxides, dipole transitions correspond to high probability transitions where the parity is change, i.e. with a change in quantum number for atomic orbital $\Delta l = \pm 1$ [290]. In nickel, these transitions correspond to *1s* $\rightarrow$ *4p* at the K-edge and *2s* $\rightarrow$ *4p* or *2p* $\rightarrow$ *3d* at the L-edge. On the other hand, Laporte selection rule derived from Fermi's golden rule predicts low probability (about 10^{-2} smaller) for quadrupole transition where parity is maintained i.e. $\Delta l = \pm 2$ [254]. At the K-edge, it corresponds to the *1s* $\rightarrow$ *3d* transition and is usually not visible in the pre-edge region.

However, high density of empty state for *3d* levels, hybridization of the orbitals via atomic bonding, and loss of centrosymmetry in the crystal structure can significantly increase the transition probability [291-295]. It has been observed for many transition metal compounds that a lower coordination of the atoms of interest maximizes quadrupole transition, as shown in Figure 3-3-(a) for *Cr* oxide compounds with different crystal structures where intense pre-edge features are seen for the tetragonal calcium chromates [293]. In contrast, the pre-edge peak is absent in *CrO₃* and metallic *Cr* because of the octahedral coordination of the *Cr* atoms, putting *Cr* at the center of an inversion in both structures. For metallic *Cr*, the rising-edge feature is reflective of the conduction band with hybridization of the *3d* and *4p* orbitals as shown in Figure 3-4-(a) where band energies of transition metals and of oxygen are illustrated [283]. The edge energy of the spectra is shifted to higher energies as the oxidation state increases due to the lower electronic charge of the oxidized atoms (as seen for *Fe* in Figure 2-7 and *Cr* in Figure 3-3-(a)).

Past the edge energy, the XANES features are determined by the local environment of the atoms of interest i.e. the bonds atoms, length, and coordination [240, 254, 296]. The constructive and destructive interferences of the emitted photoelectron wave with the scattered waves on the nearby atoms modify the absorption intensity in the post-edge region as described in section 2.3.2

(Figure 2-6) and illustrated again in Figure 3-3-(b) below [296]. Considering the diverse origin of the XANES features, the spectra from the *Ni* compounds used in this study are now discussed in detail.

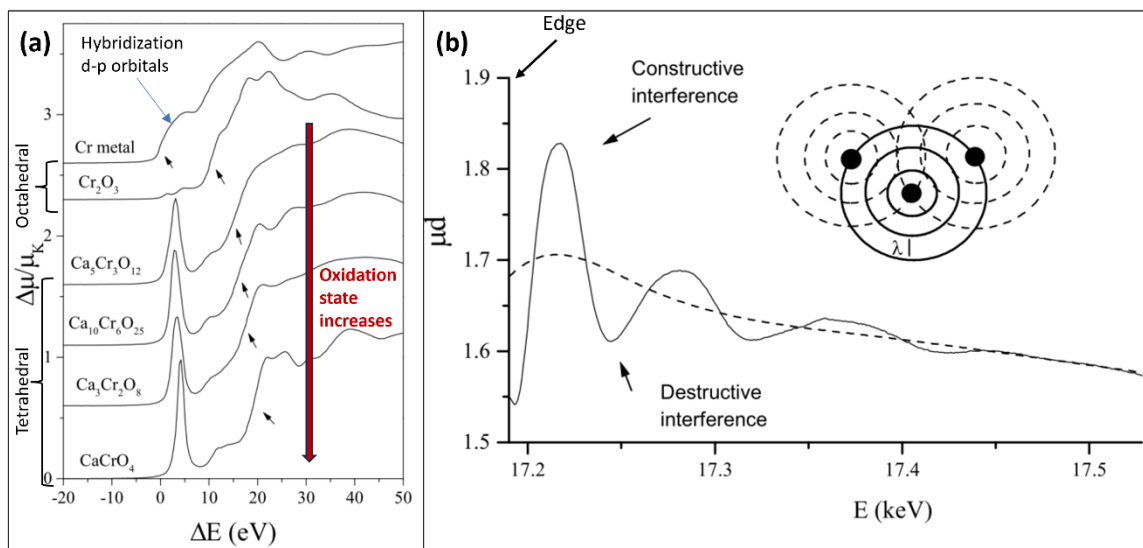


Figure 3-3: (a) Normalized Cr K-edge XANES profiles, displaced vertically, for chromium metal, chromium oxide and calcium chromate compounds, adapted from [293] (b) Schematics of the post-edge oscillations in XANES and EXAFS due to the interference of outgoing and backscattered photoelectron wave [296]

In metallic *fcc Ni* (dark blue line in Figure 3-2), the rising-edge feature (A) originates from the structure of the conduction band formed by the hybridization of the 3*d* and 4*p* orbitals of the bonded nickel atoms, alike *Fe*, *Cr* and other transition metals [283, 297]. The 4*p* character of the hybrid orbitals increases the probability of the quadrupole transition (extinguished due to Laporte selection rule – see above – as *Ni* are located in centrosymmetric sites $m\bar{3}m$ in *fcc Ni* [298]), allowing absorption of X-ray at a lower energy than the high intensity dipole transition. The edge energy (inflection point) was measured at 8332.5 eV with our experimental setup. Past the edge, the two dumps (B and C) and later valley (E) arise from scattering of the photoelectrons on the neighboring *Ni* atoms, as described previously [240, 254, 263, 296, 299]. The second metallic nickel standard considered for this study, *Ni* in Zry-2, consists of the average of 10 *Ni* XANES spectra collected in the metal region of material 9 (light blue line in Figure 3-2). It

leads to the conduction band in the intermetallic precipitates contributes to the rising-edge feature, overlapping with the quadrupole transition peak (whereas a clear distinct peak is seen for *Cr* oxides in Figure 3-3-(a)).

The post-edge bumps result from single and multiple scattering of the photoelectrons on the neighboring *Zr* and *Ni* (or *Fe*) atoms. Because of the similarity between nickel and iron, Kuri *et al.* [220] observed no changes in his modeled XANES signal when substituting *Ni* atoms with *Fe* in Zr_2Ni clusters. The *Zr* atoms are believed to contribute mostly to the XANES features due to their high coordination at the *Ni* sites (8) compared to that of *Ni* (2) [245, 259]. Lastly, the edge shift to lower energy was attributed to a charge transfer from the *Zr* atoms to the *Ni* atoms [245, 259, 300] and the effective charge for the nickel atoms in $NiZr_2$ was estimated at -1.31 (0.65 for the *Zr* atoms) [300] which lowers the binding energy of the electrons and in turn allows photo absorption to occur at a lower energy. Additionally, the stronger shift seen for the edge first maximum (at 8347 eV for *Ni* in $Zr_{1-y}Ni_y$ and at 8349 eV for *fcc Ni* in Figure 3-2) may result from the increased bond length in the $NiZr_2$ *bct* structure compared to the *fcc Ni* crystal structure. This bond length effect is described in the extensive review of XANES and EXAFS analysis of oxides by Kuzmin and Chaboy [301] and is further detailed later in this section with the examination of the *Ni(II,III)* in ZrO_2 standard.

The nickel oxide standard *Ni(II,III)* in ZrO_2 (red line in Figure 3-2) is similar to the nickel oxide phases considered in this study, as illustrated with *NiO* spectrum (red dotted line in Figure 3-2, calibrated, from MDR database [279]). The bonding of the nickel atoms with the oxygen atoms significantly changes the XANES spectra with a loss of the rising-edge feature (small pre-edge bump only), a small shift to higher energy and a significant edge maximum intensity at 8350 eV (white line, *B*) followed by a second bump (*D*) at 8366 eV. The small pre-edge (*A*), seen as well in *NiO* and $NiFe_2O_4$ (Figure 3-1-(d)) and absent in Ni_2O_3 (Figure 3-1-(e)),

reflects the extinction of $1s \rightarrow 3d$ transition due to the centrosymmetry of the *Ni* sites in these structures [291, 292, 294, 302-305]. The standard *Ni(II,III)* in ZrO_2 correspond to the signal arising from the oxidized nickel atoms in the far oxide formed on Zry-2. The oxidized nickel atoms in the far oxide are either precipitating into nickel oxide phases, or present as defect in the ZrO_2 matrix. Based on EXAFS examinations and DFT calculations, Kuri *et al.* [151] suggests that the latter is dominant with *Ni* atoms substituting with *Zr* atoms in the monoclinic oxide layer. For charge balance due to the difference in oxidation state between *Ni* and *Zr*, the nickel atoms are located next to an oxygen vacancy forming $Ni^{2+} - V_o$ defects in the oxide layer. Additionally, Than [153] predicted with DFT calculations the formation of this defect in tetragonal ZrO_2 at various partial oxide pressures believed to represent the bulk oxide. Because the *Zr* atoms are at centrosymmetric sites in the monoclinic and tetragonal phases, the XANES signal arising from the substituted nickel atoms follow the electron transition selection rule with minimization of the $1s \rightarrow 3d$ transition. As for *NiO* and $NiFe_2O_4$, the small measurable signal is due to the high density of available *d* states and the small hybridization of the $3d$ orbitals with the $2p$ orbitals of the oxygen atoms, as illustrated for *TiO* in Figure 3-4-(b) [295].

The edge energy for *Ni(II,III)* in ZrO_2 is measured at 8346 eV, or 1.5 eV higher than that in *NiO* (8344.5 eV in our study), and 0.5 eV higher than that of Ni_2O_3 (8345.5 eV in our study). This edge shift to higher energy has been attributed to higher oxidation [99, 220] of the nickel atoms in the oxide layer. However, the oxidized nickel atoms in the oxide layer are suspected to substitute at zirconium site in zirconia as either Ni^{2+} with a nearby oxygen vacancy [151, 153] or as Ni^{3+} at high oxygen partial pressure in tetragonal ZrO_2 [153], rather than precipitate in nickel oxides as mentioned above. In an extensive review of XANES and EXAFS analysis of oxides, Kuzmin [301] argues that the structural modifications induced by the substitution of *Mn* into *ZnO* strongly affect the edge energy and shape of the XANES spectrum at

the *Mn* K-edge. By increasing the interatomic distances between the larger dopant and the oxygen atoms compared to the matrix during XANES computations, a significant shift to lower energies and modifications to the white line and post-edge peaks were observed (Figure 3-5(b)).

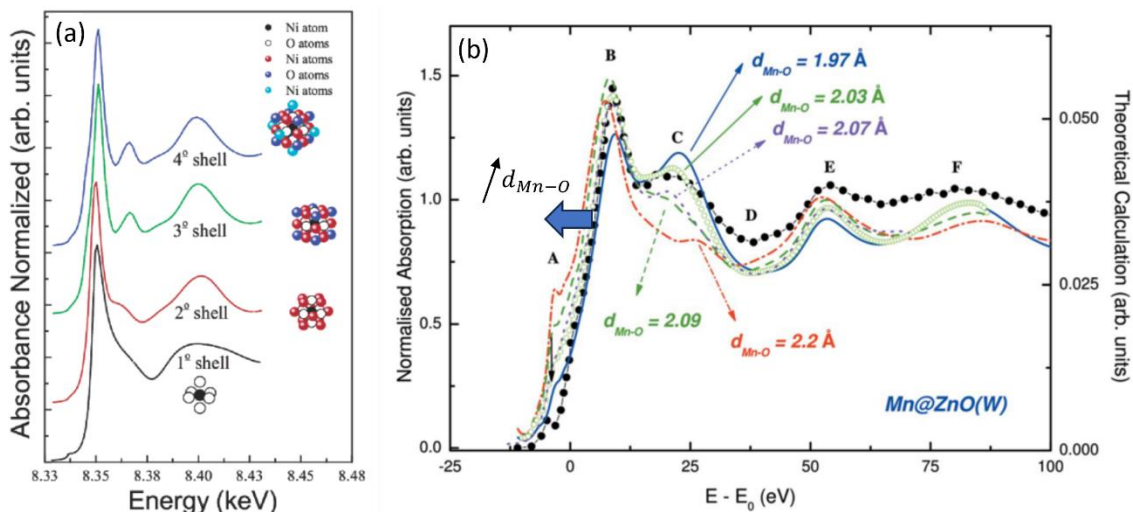


Figure 3-5: (a) NiO XANES spectra at the Ni K-edge calculated with the FEFF8 program considering an increasing number of atomic shells around the nickel atom (taken from [306]). (b) XANES spectra at the Mn K-edge of Mn atoms substituting in ZnO calculated with CONTINUUM [307] multi-scattering program for different Mn-O bond lengths. The edge is shifted to lower energy (blue arrow) as the bond length increases (from [301]).

Considering this effect in the case of nickel atoms doped in zirconia, the interatomic distance between the *Ni(II)* atoms and the first shell of oxygen atoms is 2.070 Å in powder *NiO* [308] and 1.97 Å in *m-ZrO₂* [151] so that the shorter *Ni-O* bonds in *ZrO₂* may shift the absorption edge to higher energy and alter the absorption peaks. This shift of the XANES spectra to higher energy due to contraction of the interatomic distances was observed at the *Ni* K-edge by Pandya *et. al* [309] during the investigation of nickel oxide electrodes by X-ray absorption. The higher edge energy in *Ni(II,III)* in *ZrO₂* would then reflect differences in structural configuration rather than in oxidation state. As mentioned before, this effect is coherent with the strong shift to lower energy of the first edge maximum when metallic *Ni* are located in the *NiZr₂* structure (*Ni* in Zry-2 standard in Figure 3-2) rather than in *fcc Ni* (*fcc Ni* standard in Figure 3-2). With EXAFS examinations of Zry-2 materials, the *Ni-Ni* and *Ni-Zr* first shells bond lengths

were measured at 2.67 Å and 2.75 Å by Kuri *et al.* [259], whereas the *Ni-Ni* bond in *fcc Ni* is estimated at 2.49 Å. The longer interatomic distance in *NiZr₂* would then shift the edge maximum to lower energy as seen for *Mn* in *ZnO* [301].

The white line intensity and the post-edge oscillations arise from the scattering of the photoelectrons on the neighboring oxygen atoms, as illustrated in Figure 3-3-(b) [296]. Specifically, the edge intense peak (*B*) is mostly due to the first shell of atoms (oxygen) while the post-edge peak (*D*) is attributed to the second (nickel) and third (oxygen) shell of atoms (Figure 3-5-(a)) [306, 310, 311]. Therefore, the dumping of the post-edge oscillations in *Ni(II,III)* in *ZrO₂* would originate from the lack of long-range order for the *Ni* atoms in the oxide layer. Considering the local distortions of the matrix around the substitute *Ni* atoms, the spread of the first shell interatomic distances in *ZrO₂* and the irradiation effects in the oxide of the reactor-corroded water rods [220], the scattered photoelectron waves from the second (*Zr*) and third (*O*) shells of atoms may not be in phase so that the constructive and destructive interferences are limited. Additionally, the change in *Ni-O* bond length when present as a defect in *ZrO₂* might alter the white line and post-edge oscillations compared to *NiO* XANES as mentioned above [301, 309]. The differences in edge energy, in white line intensity and in post-edge oscillations between *Ni(II,III)* in *ZrO₂* and *NiO* are further discussed in section 3.3 and section 3.4 where the XANES spectra and the edge energy across the oxide layers are presented.

Lastly, the edge energies (inflection point of the XANES spectrum) of the nickel standards measured in this study (Figure 3-1) are compared in Table 3-1 to database nickel spectra [261, 279-281, 312, 313] and to previous work on Zry-2 materials [91, 220]. The edge energy for *NiO* from Shivprasad's work [91] differs from that reported (8339.6 eV) as it has been calculated again from the analysis of the raw XANES data. The derivative contained two maxima at 8339.6 eV and 8344 eV and comparison with reference spectra suggest that the peak at 8344 eV

corresponds to the edge energy while the peak at 8339.6 eV is artificially amplified due to powder thickness and energy resolution effects [283]. Edge energy variations can be seen between the different experimental and database data with a range of 1 to 4 eV for all compounds. The source of these offsets is diverse (experimental setup, detector energy resolution, sample preparation and others [254]) but calibrating the energy with reference standards allows for investigation of the oxidation state as discussed in section 3.4. The edge energies from the three studies investigating Zry-2 materials are coherent with consistent energy shifts for the different compounds when calibrated with the *fcc Ni* foil (Ni^0). A jump of about 12 eV in edge energy is seen for *NiO* (Ni^{2+}) and of about 13.5 eV for the signal arising from the far oxide of Zry-2 materials. In our study, the second Ni^{2+} oxide $NiFe_2O_4$ had an energy slightly higher than that of *NiO* at 8345 eV (+12.5 eV) and the Ni^{3+} oxide Ni_2O_3 showed a slightly higher energy at 8345.5 eV (+13 eV). The highest energy observed for *Ni(II,III)* in ZrO_2 suggest a higher oxidation state and/or a shorter bond length as mentioned above and further discussed later in this chapter. It is worth mentioning that even though the edge energies are plotted in the same column for the XANES databases (MDR and XAFS), each of spectra was collected individually at different beamlines, preventing direct edge shift comparison for those data.

Table 3-1: Edge energy (eV) of the standards measured in this present study and compared to previous work [91, 220] and databases data [261, 279-281, 312, 313]. The edge energies were determined with ATHENA software [255] as the maximum of the absorption spectrum derivate.

Standard Edges (eV)	Oxidation State	Present Study	Shivprasad [1]	Kuri [2]	MDR [3,4,5,6]	XAFS [7,8]
<i>fcc Ni</i>	0	8332.5	8332	8333	8329.6	8331.5
<i>Ni</i> in Zry-2	0	8332	8332	8333	-	-
<i>NiO</i>	2	8344.5	8344	8345.2	8341.1	-
$NiFe_2O_4$	2	8345	-	-	8341.8	-
Ni_2O_3	3	8345.5	-	-	8343.3	8346
<i>Ni(II,III)</i> in ZrO_2	≥ 2	8346	8345.5	8346.2	-	-

The XANES signal for the reference standards (metallic and oxidized) used in the XANES analysis of the oxidation state of *Ni* across the oxide layer formed on Zry-2 water rods were presented and coherent with the XANES measurements from previous work and database. The main features of the XANES region at the *Ni* K-edge were described in detail and are essential for the quantitative analysis of the oxidation state as seen later in this chapter. In the next section, we present the SEM images of the cross-section samples analyzed with XANES and XRD at the APS.

3.2 SEM imaging of irradiated Zry-2 cross-section samples

As described in chapter 2, cross-section samples of BWR-corroded Zry-2 water rod materials were prepared at Pacific Northwest National Laboratory (PNNL) for XANES examinations at the APS (ANL). In order to locate the bulk and the oxide at the beamline, SEM images of the samples were acquired at PNNL prior to the first round of experiments, and at the Material Characterization Lab (MCL) at Penn State University (PSU) post-experiment. SEM images of the inner and outer oxides at representative locations are shown in Figure 3-7 for materials 9 and 11 and Figure 3-8 for materials 12 and 14 while the whole sample SEM images are presented in Figures 3-9-(a), 3-10-(a), 3-11-(a), 3-12-(a), 3-13-(a), 3-14-(a) and 3-15-(a) for samples 9-A, 9-B, 11-A, 11-B, 14-A, 14-B, and 12-A respectively. As a reminder, materials 9 and 11 correspond to the low hydrogen pickup water rod (3 cycles in BWR) at low and high elevation while materials 12 and 14 were taken from the high hydrogen pickup water rod (4 cycles in BWR) at low and high elevation. The average thickness of the oxides has been measured from the SEM images of the prepared samples using the ImageJ program [314] and the results are presented in Table 3-2 along with the total oxide thickness and hydrogen content measured at GE VNC hot cell facility.

Table 3-2: Thickness measurements with SEM images (analysis with ImageJ [314]) of the inner and outer oxides formed on the Zry-2 water rods. Total oxide thicknesses are derived and compared to measurements done at GE VNC hot cell facility.

Sample	Oxide thickness					Hydrogen Content [GE] (wt. ppm)
	Inner (μm)	Outer (μm)	Total (μm)	Total [GE] (μm)	$\Delta\delta$ (μm)	
9-A	13 (± 9)	25 (± 6)	38 (± 11)	40	-2	250
9-B	15 (± 11)	32 (± 3)	47 (± 11)		+7	
11-A	25 (± 10)	20 (± 5)	45 (± 11)	50	-5	329
11-B	29 (± 7)	23 (± 5)	52 (± 8)		+2	
12-A	15 (± 3)	35 (± 2)	50 (± 4)	40	+10	600
14-A	39 (± 6)	31 (± 2)	70 (± 6)	82	-12	1721
14-B	40 (± 6)	29 (± 2)	69 (± 6)		-13	

The total oxide thicknesses measured in this study (Table 3-2) are consistent with the measurements at Vallecitos Hot Cell facility with material 14 displaying the thickest oxides (up to $50\ \mu\text{m}$ in the inner oxide as seen in Figure 3-8-(d)). However, the oxides were seen significantly larger ($+10\ \mu\text{m}$ total) for material 12 and thinner ($-13\ \mu\text{m}$ total) for material 14. This observation suggests that important oxide thickness variations occur between regions along the water rod perimeter, which is coherent with the lower uniformity observed in Zry-2 materials corroded in BWRs as mentioned in section 1.3.3 and attributed to the boiling conditions of the reactors [137]. The outer and inner oxide present on the prepared samples are rather uniform as seen with SEM in Figures 3-7 to 3-15, but significant variations can be observed between regions for all materials, especially in the inner oxide layers. The high standard deviations for the inner oxide measurements in Table 3-2 illustrates these fluctuations in the inner oxide growth, especially in the 3-cycle water rod materials (9 and 11). Additionally, the circumferential variations of oxide thickness at two locations (low/high elevation) in each of the two GNF water rods (data provided by EPRI) are plotted in Figure 3-6 and confirm that both the inner and outer

oxide growths were significantly varying between different regions of the water rods during exposure in the BWR. As mentioned above, the boiling conditions are thought mainly responsible for the lower uniformity of the oxide layer formed in BWR, where local differences in coolant flow and steam quality may affect corrosion kinetics. Additionally, oxide thickness variations may result from local disparity in SPP distributions, especially under irradiation which induces amorphization and dissolution of the second phase particles (section 1.4.5), as the SPPs are essential to the corrosion resistance of Zr alloys.

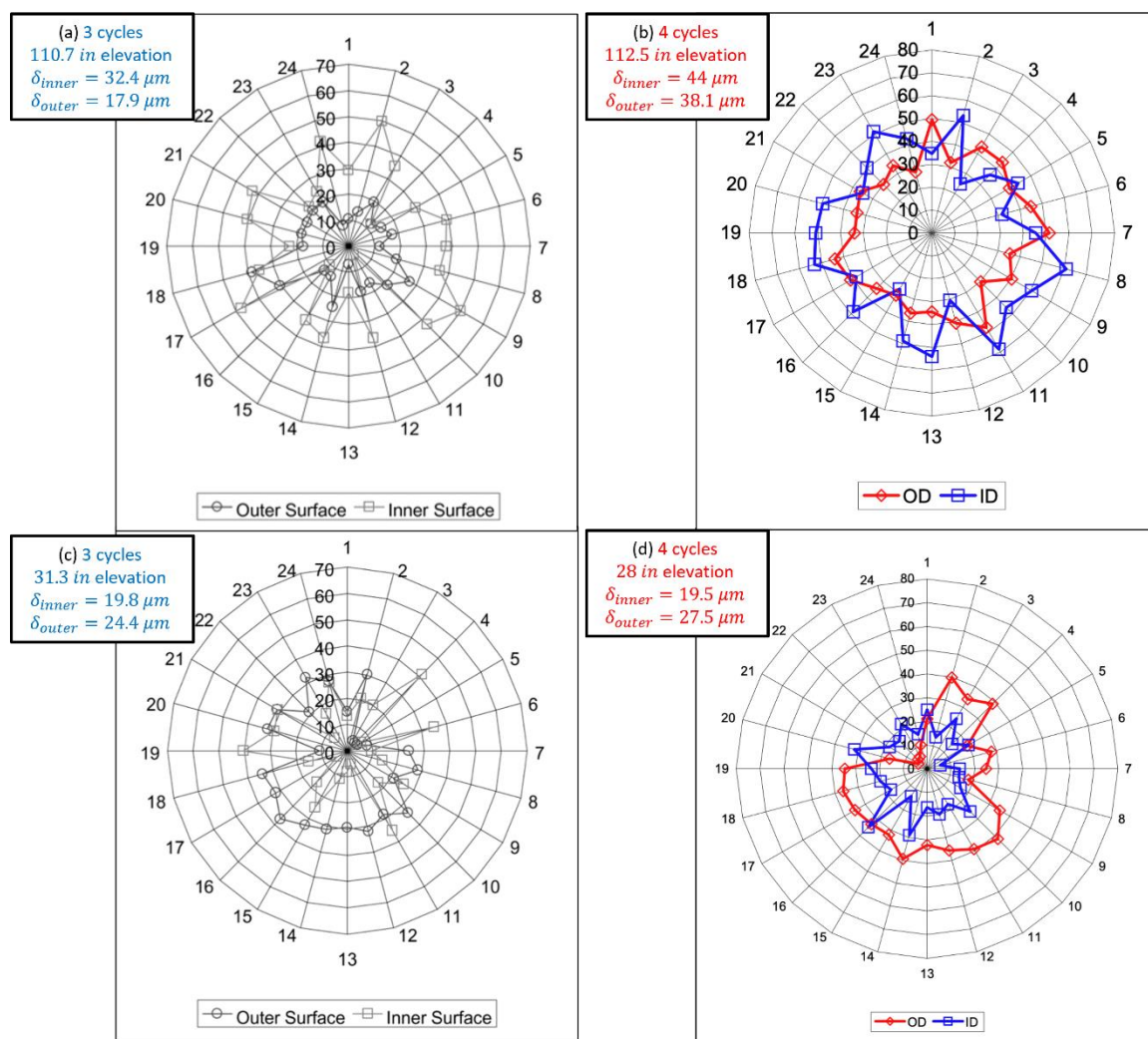


Figure 3-6: Oxide thickness (in μm) circumferential variations at two locations close to that of the materials selected for each of two Zry-2 water rods (3 and 4 cycles). Data provided by EPRI (GNF water rods).

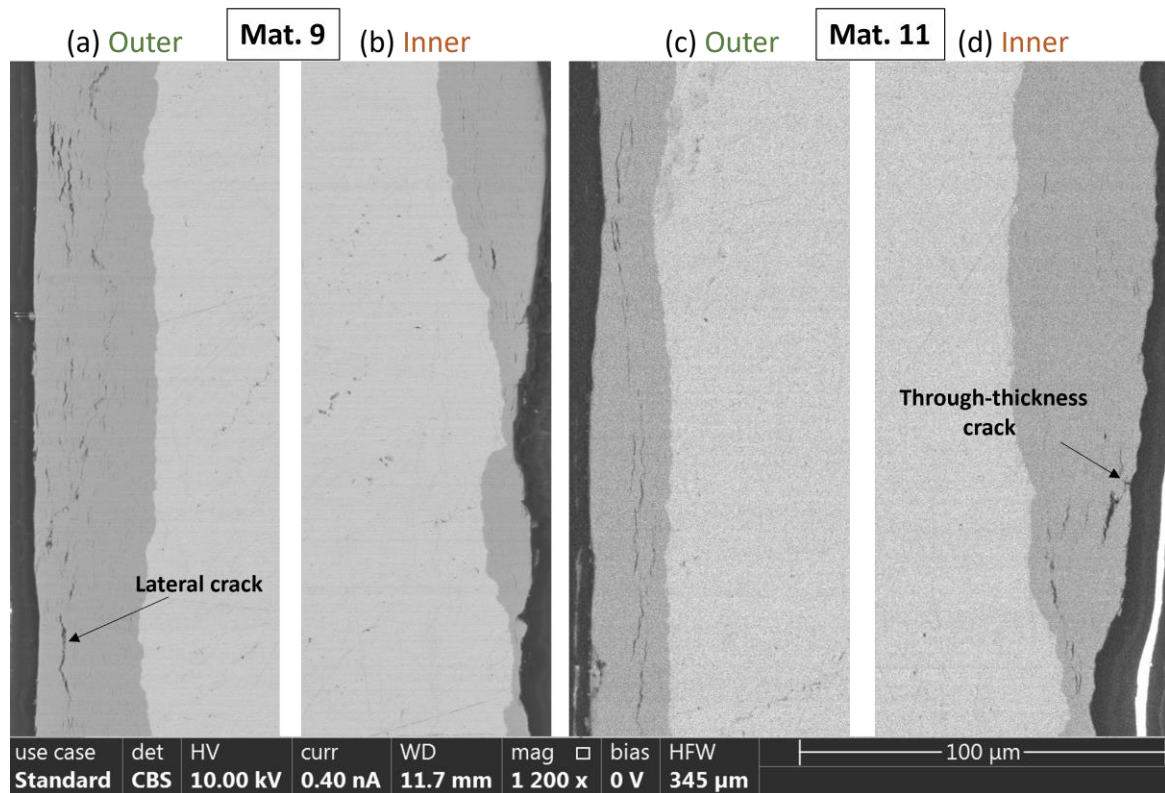


Figure 3-7: SEM images (PSU) of the oxides formed on the low hydrogen pickup materials (3 cycles). (a) Mat. 9 outer (b) Mat. 9 inner (c) Mat. 11 outer (d) Mat. 11 inner.

Comparing the oxide thickness of material 12 ($40\ \mu\text{m}$) to material 9 ($40\ \mu\text{m}$), no acceleration of oxidation can be observed during the last cycle in the reactor at low elevation. At high elevation, the total oxide thickness after 4 cycles ($82\ \mu\text{m}$, material 14) is much larger than after 3 cycles ($50\ \mu\text{m}$, material 11) suggesting that accelerated corrosion has occurred during the additional cycle. These observations are further discussed in chapter 5 where oxide thickness measurements provided by EPRI at multiple elevations in the two water rods are presented.

In general, the oxides of the Zry-2 water rods examined in this study are characterized by a significant number of lateral (or circumferential) cracks and some through-thickness (or radial) cracks as seen in Figure 3-7 and Figure 3-8. Lateral and through-thickness cracks are present in the oxide of *Zr* alloys and may lead to accelerated corrosion and hydrogen pickup when interconnected through the oxide layer [315]. Additionally, large lateral and/or through-thickness

cracks were observed in all materials, but in higher number for the 4-cycle materials (12 and 14). Oxide spallation is seen in the inner oxide of sample 14-B (Figure 3-14-(a)) but likely results from the cutting of the materials near a vast lateral crack during the cross-section sample preparation. Therefore, large lateral cracks may have developed more frequently during the last cycle exposure, especially at high elevation. This observation corroborates the microstructural characterization of a 9-cycle Zry-2 cladding by Baris [316] where the oxide near the metal oxide interface (produced during the last cycles) contained large cracks in higher densities resulting in a high volume fraction of the cracks compared to the outermost layer (produced during the first cycles). When interconnected via through-thickness cracks and porosity, the large cracks may bring the coolant closer to the metal/oxide interface and in turn increase oxidation rate and hydrogen pickup [315]. This hypothesis is further discussed in chapter 5.

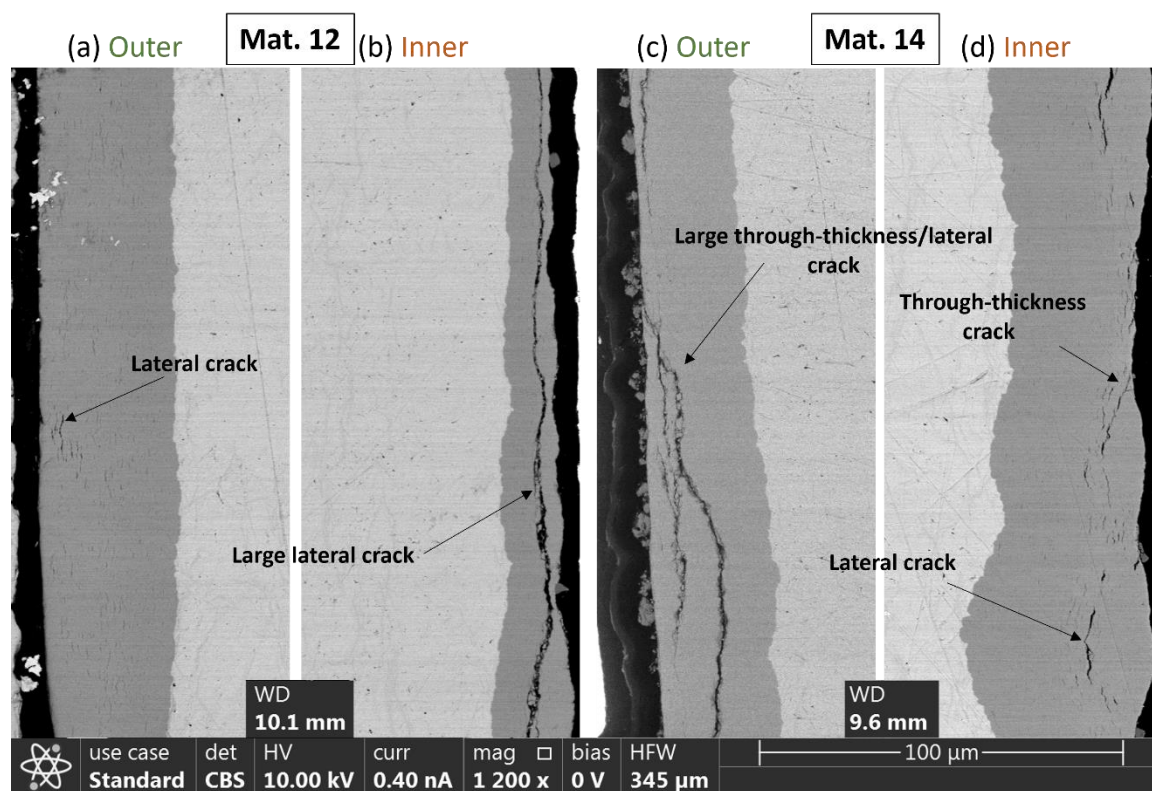


Figure 3-8: SEM images (PSU) of the oxides formed on the high hydrogen pickup materials (4 cycles). (a) Mat. 12 outer (b) Mat. 12 inner (c) Mat. 14 outer (d) Mat. 14 inner.

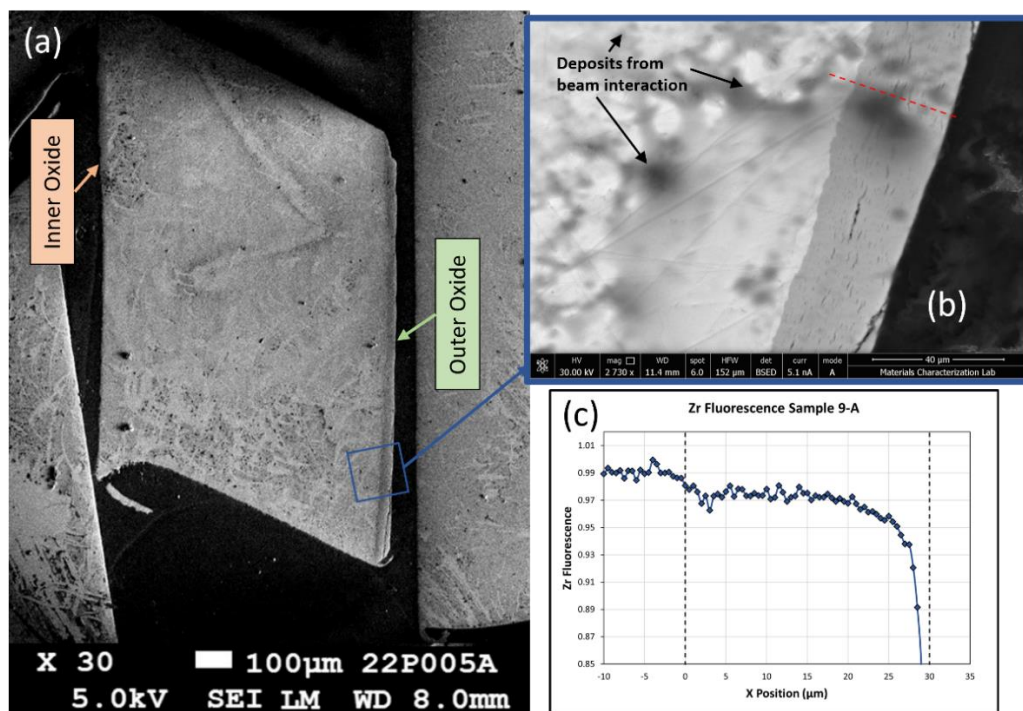


Figure 3-9: SEM imaging of sample 9-A (a) (PNNL) with a zoom at the location of the XANES scan shown by the red dotted line (b) (PSU), and the corresponding Zr K-edge fluorescence (c).

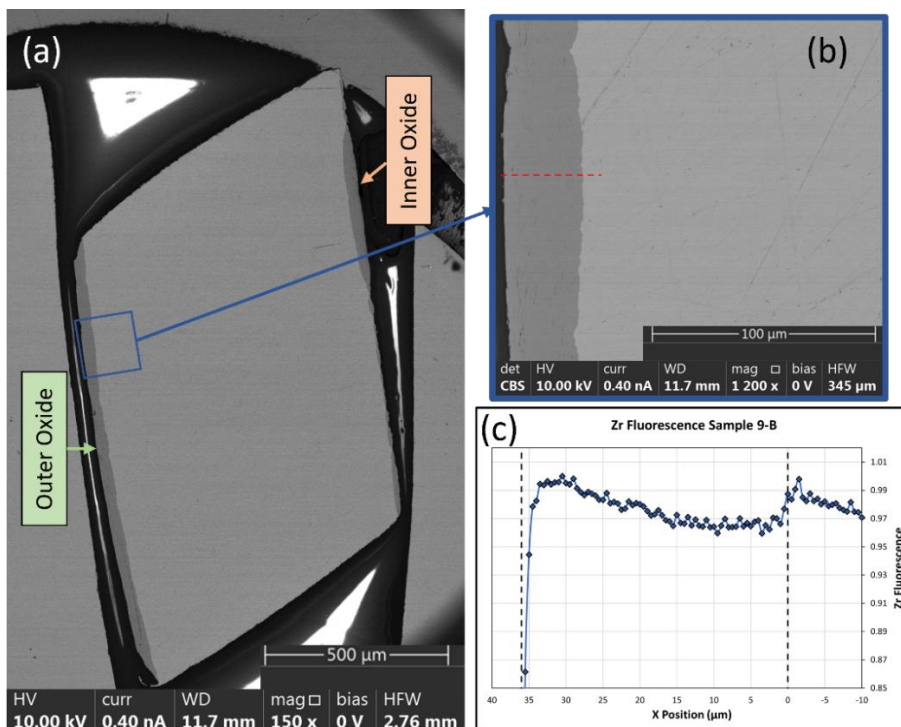


Figure 3-10: SEM imaging of sample 9-B (a) (PSU) with a zoom at the location of the XANES scan shown by the red dotted line (b) (PSU), and the corresponding Zr K-edge fluorescence (c).

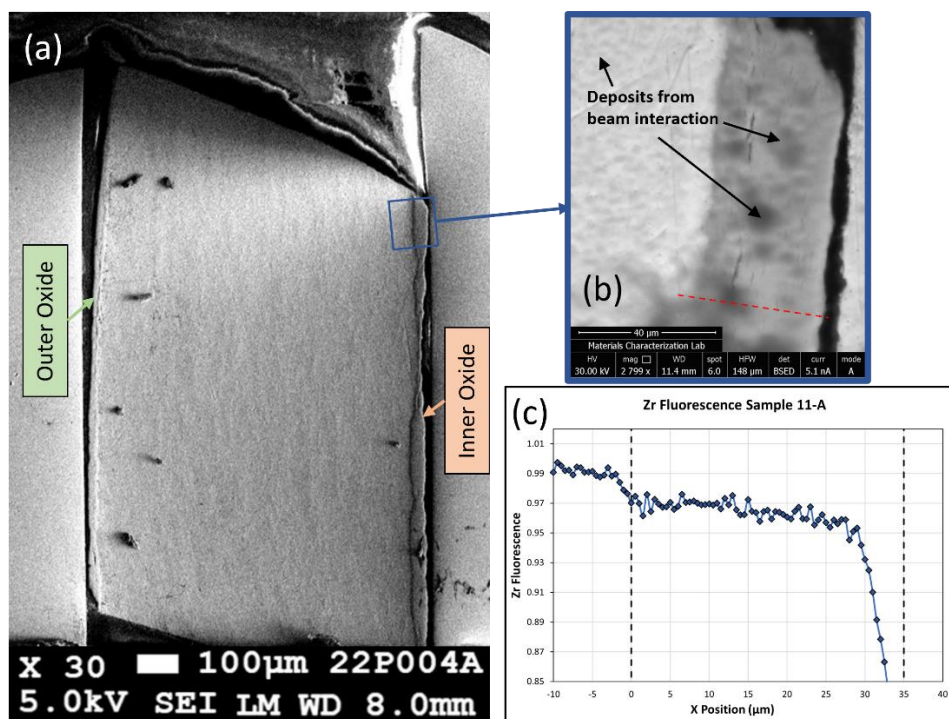


Figure 3-11: SEM imaging of sample 11-A (a) (PNNL) with a zoom at the location of the XANES scan shown by the red dotted line (b) (PSU), and the corresponding Zr K-edge fluorescence (c).

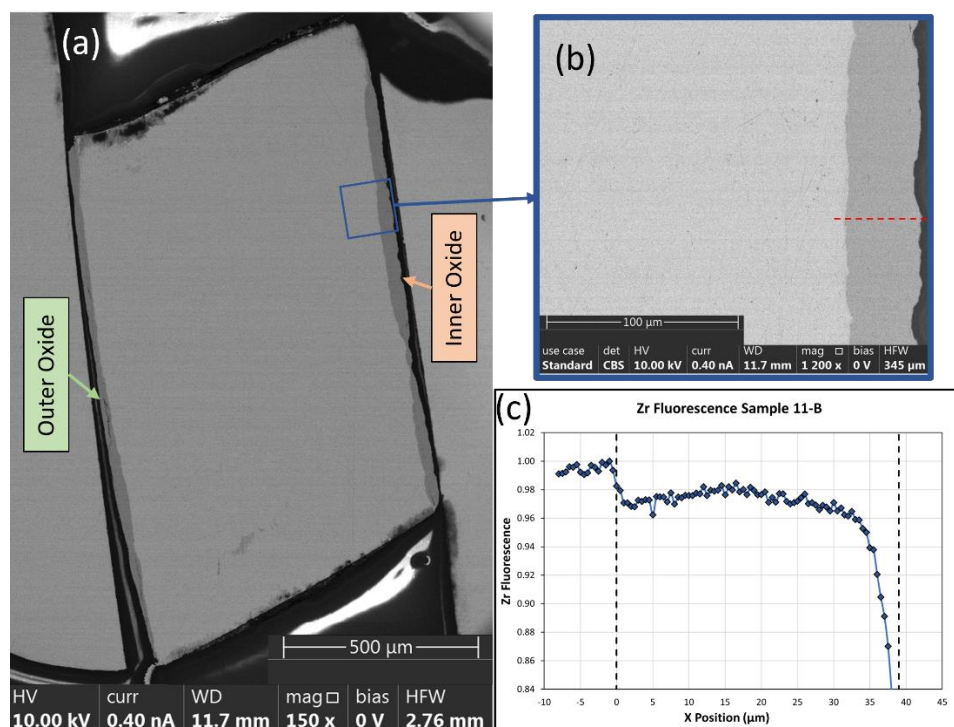


Figure 3-12: SEM imaging of sample 11-B (a) (PSU) with a zoom at the location of the XANES scan shown by the red dotted line (b) (PSU), and the corresponding Zr K-edge fluorescence (c).

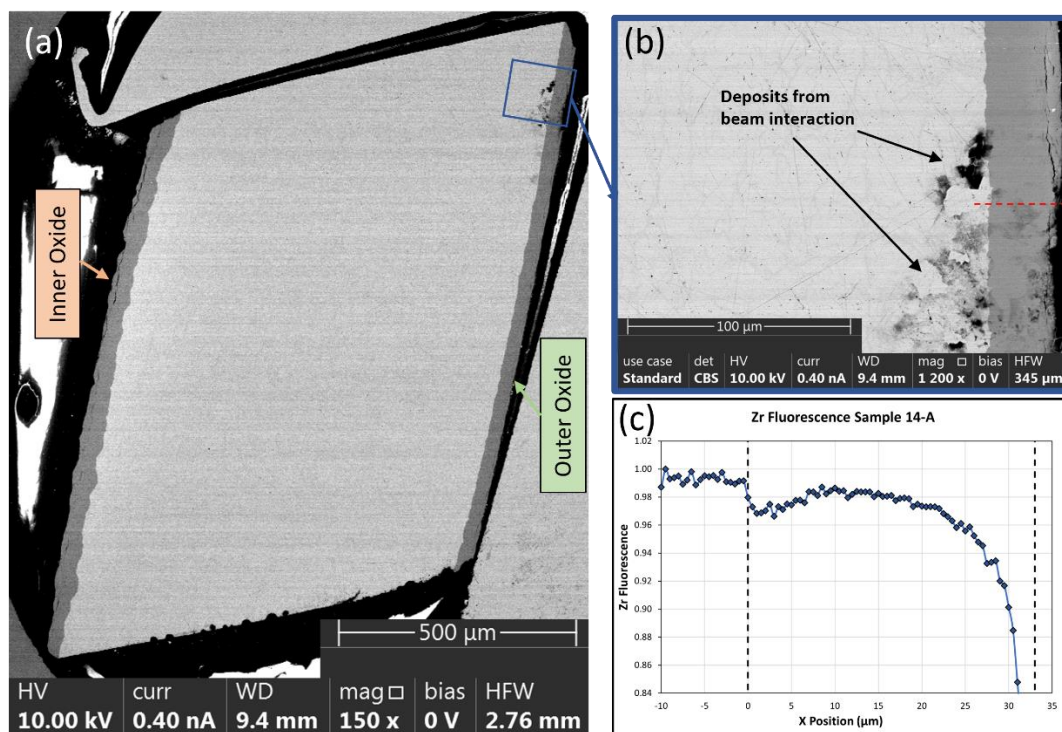


Figure 3-13: SEM imaging of sample 14-A (a) (PSU) with a zoom at the location of the XANES scan shown by the red dotted line (b) (PSU), and the corresponding Zr K-edge fluorescence (c).

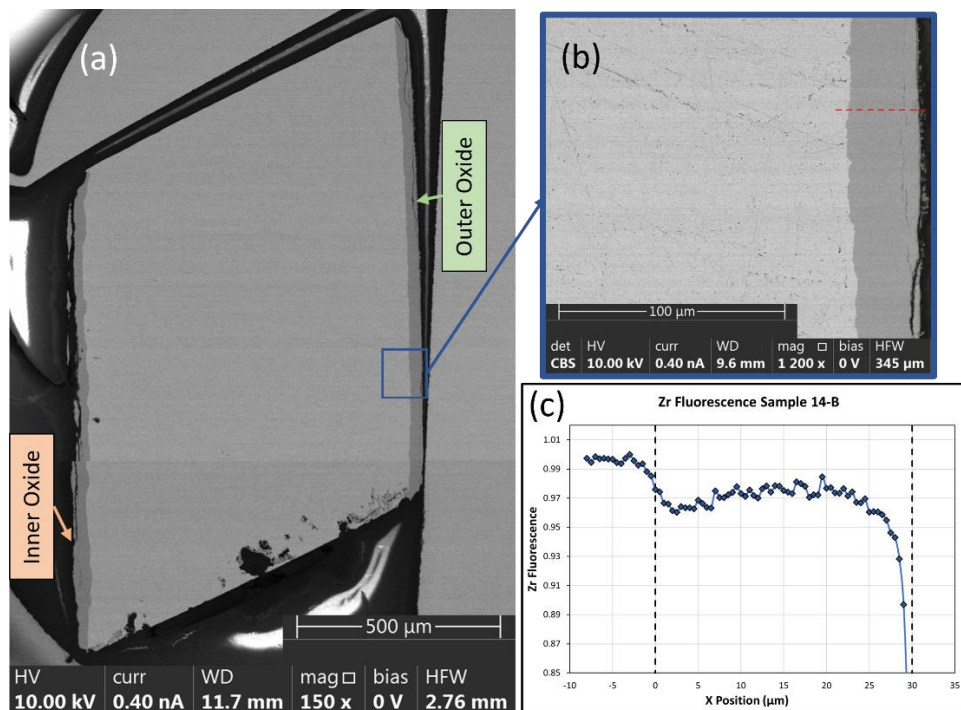


Figure 3-14: SEM imaging of sample 14-B (a) (PSU) with a zoom at the location of the XANES scan shown by the red dotted line (b) (PSU), and the corresponding Zr K-edge fluorescence (c).

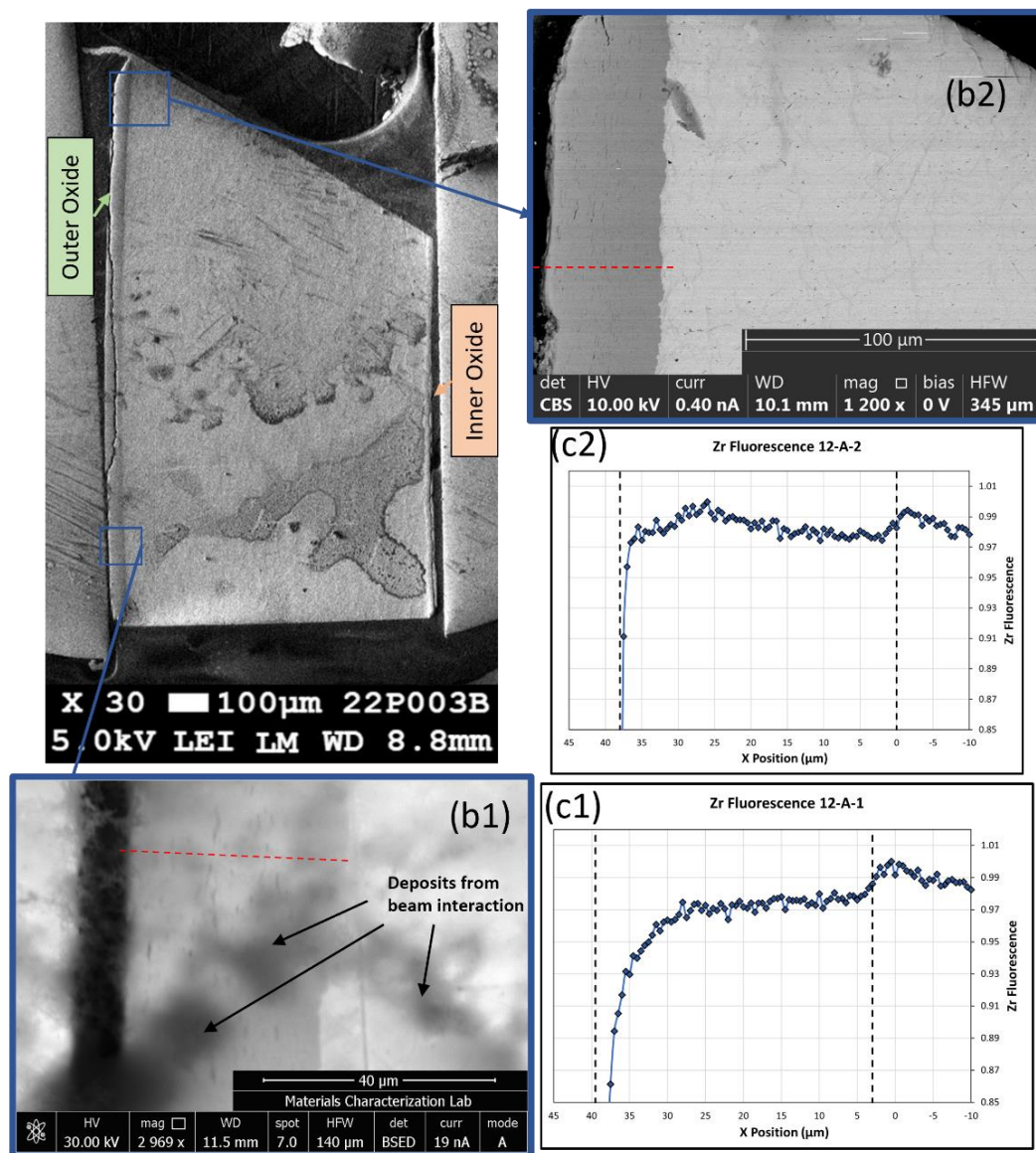


Figure 3-15: SEM imaging of sample 12-A (a) (PNNL) with a zoom at the location of the XANES scan (b1 and b2) shown by the red dotted line (PSU), and the corresponding Zr K-edge fluorescence (c1 and c2).

For the materials examined post-experiment at the APS (sample holder 1 i.e. 9-A, 11-A, 12-A-1, and 14-A), deposits from the beam interaction were observed at the location of the *Ni* XANES scan (as seen in Figures 3-9, 3-11, 3-13 and 3-15). These deposits are believed to arise from the Kapton encapsulation; in spite of some difficulty they were removed after successive cleaning of the sample with ethanol and acetone. Because time was limited at the electron

microscope and all the deposits were not removed after the 10th cleaning and measurement of sample 14-A (Figure 3-13), it was not possible to completely clean the samples for better SEM images at the XANES locations in those samples.

Last but not least, the location of the *Ni* XANES scan was selected based on the following criteria for each cross-section sample: (1) thick uniform oxide regions are preferred (more hydrogen available for pickup); (2) no oxide spallation; (3) clear identification of sample features (edge, cracks, oxide, nearby epoxy or molybdenum) and alignment of the metal/oxide interface with the CCD camera available at the beamline (which proved to be difficult because of the 14° angle of the sample rather than the usual 45° for which the camera was set up); (4) good *Zr* fluorescence signal with an oxide thickness similar to that observed via SEM; (5) adjustment to available beam time (sample drifts, beam shutdown, oxide location search and more). Considering all these criteria, the locations for the *Ni* XANES scan are represented by the red dashed line in each of the high magnification SEM images ((b) of Figure 3-9 to Figure 3-15) and the corresponding *Zr* K-edge fluorescence ((c) of Figure 3-9 to Figure 3-15). The metal and water interfaces were determined at first using the *Zr* K-edge fluorescence features but were later readjusted (0.5 to 3 μm) using the onset of nickel oxidation ($f_m = 0.7$) as the interface location, corroborating the interface determined by X-ray diffraction for samples 9-B, 11-B, and 14-B. The higher energy of the *Zr* K-edge (beam energy at $E = 20\text{ keV}$) was thought to induce a larger sampling volume error in the determination of the metal/oxide interface (see section 2.3.3) than in previous examinations performed at lower energy which led in some cases to oxidized nickel being located in the metal part. Nonetheless, the *Zr* fluorescence signal at the K-edge provided the users with a reasonable approximation of the interface location in limited amount of time (a *Zr* K-edge scan across 50 μm of material only takes a few min) during the experiments at the synchrotron. In the next sections, the *Ni* XANES scans and the resulting *Ni* oxidation state measurements are presented.

3.3 XANES spectra shape analysis of in-reactor corroded Zry-2

Prior to the linear combination fit analysis (presented in section 3.4), the XANES spectra collected in the metal (about 5 μm from interface) and oxide (about 25 μm from metal/oxide interface) of the BWR-corroded Zry-2 samples are plotted along with the metallic and oxidized nickel standards (presented in section 3.1) in Figure 3-16-(a) (metal) and Figure 3-16-(b) (oxide) for examination of the effects of corrosion temperature (elevation) and irradiation (neutron fluence) on the local environment and oxidation state of *Ni*. These XANES spectra collected at a specific point in the metal or in the far oxide are representative of the XANES signal tendencies in these regions as seen in the in-depth *Ni* XANES plots further below (Figure 3-17 and Figure 3-18).

Exploring the metal spectra in Figure 3-16-(a), there is no clear difference between the *Ni* XANES spectra collected in the different materials and all sample spectra are quite similar to that of the *Ni* in Zry-2 standard (which is the average of 10 XANES in the metal region of material 9), as was previously observed by Shivprasad with irradiated and unirradiated Zry-2 [91]. This is consistent with the observations by Kuri [259] that the XANES part of the nickel XAS spectrum was not affected by the amorphization of the precipitates in Zry-2 due to irradiation, whereas EXAFS post-edge oscillations were greatly diminished because of the loss of long range order. This agrees with the observation that although the long range order is lost as the material undergoes the crystal to amorphous transformation in intermetallic compounds, the nearest neighbors do not appreciably change [317]. Similarly, the corrosion temperature does not seem to impact the signal from the SPPs in the metal as the spectra collected in materials at low elevation (9 and 12) and high elevation (11 and 14) are essentially interchangeable. Therefore, no irradiation or elevation effects can be deduced from the analysis of the XANES spectra collected in the metal of the BWR-corroded Zry-2 water rods.

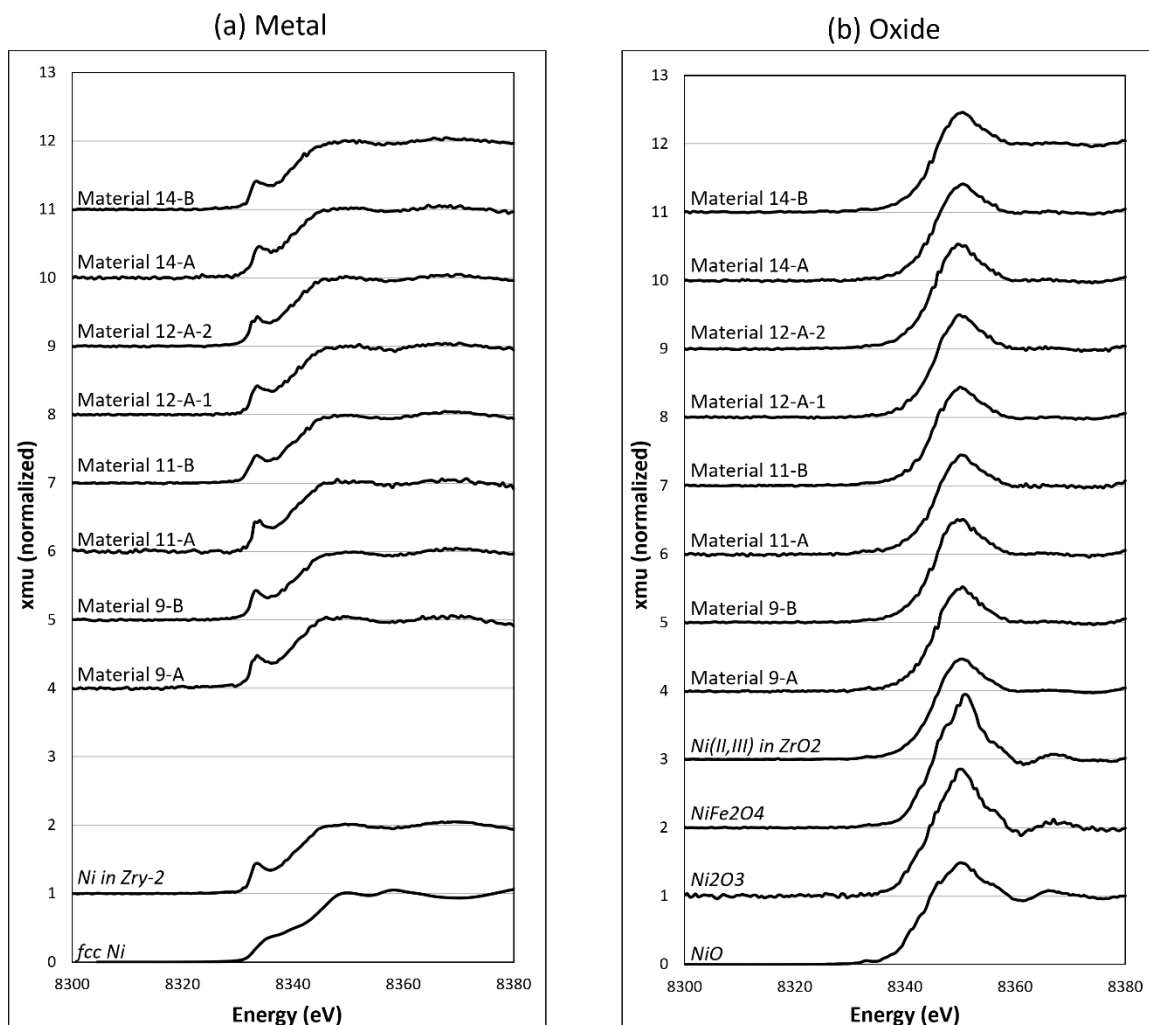


Figure 3-16: Nickel XANES spectra acquired from the standards and the Zry-2 cross-section samples. (a) Ni XANES spectra of the metallic standards and of the Zry-2 materials in the metal 2-5 μm from the interface. (b) Ni XANES spectra of the oxide standards and of the Zry-2 materials in the far oxide about 25 μm from the metal/oxide interface.

During XANES examinations combined with fluorescence mapping of thin samples of the Zry-2 water rods prepared with focused ion beam (FIB), Shivprasad [91] isolated the signal from *Ni* in solid solution and from *Ni* in precipitates in the metal. Both spectra were similar but lower post-edge oscillations were seen for *Ni* in solid solution (Figure 4.15 in [91]). This is coherent with the non-centrosymmetric sites for *Ni* in both structures (422 point group in *bct* NiZr_2 [71] and $\bar{6}m2$ for *Ni* in $\alpha\text{-Zr}$ [318]) which allows $1s \rightarrow 3d$ transitions to occur (rising-edge feature). The disappearance of the post-edge oscillations when *Ni* is in solid solution

suggests a lower order in the neighboring shells of the *Ni* atoms. The dopant atoms in solid solution may deform locally the *Zr* matrix due to the differences in atomic size, resulting in diminished constructive and destructive interferences of the scattered photoelectrons.

In the far oxide of the materials in Figure 3-16-(b), the *Ni* XANES signal is similar to that obtained from the nickel oxides with hardly detectable pre-edge features, a higher edge energy compared to metallic *Ni*, a white line peak, and post-edge oscillations. Specifically, the far oxide XANES signal in all Zry-2 materials are identical (within noise error) to the standard *Ni(II,III)* in ZrO_2 (which is the average of 10 XANES from the far oxide of material 9) such that a standard from any of the four Zry-2 materials investigated yielded the same LCF results. As previously discussed in section 3.1, the edge energy is higher than that of the nickel oxides, the white line intensity is lower, and the post-edge oscillation amplitudes are significantly damped. The edge energy is defined by the oxidation state of the element and by the oxygen bond length in the material [240, 254, 301] and the edge shift to higher energy is attributed to the shorter *Ni-O* bond and/or a higher oxidation state for *Ni* when *Ni* atoms substitute for *Zr* in zirconia. Lower oscillation amplitudes in the post-edge region of the XAFS signal reflect less constructive and destructive interferences of the photoelectron wave scattered on the neighboring atoms (Figure 3-2-(b)). The post-edge oscillations in nickel oxides were identified with the 2nd and 3rd shells of atoms surrounding the *Ni* atoms while the white line intensity was correlated to the first oxygen shell [306, 311]. This would signify that the local environment of the oxidized *Ni* atoms in the water rods is significantly disturbed compared to the powder samples. Disorder in the shell of atoms reduces the white line intensity and disorder in the 2nd and 3rd shells damp post-edge oscillations. Additionally, FEFF simulations by Shivprasad (Figure 4.10 in [91]) suggested that the XANES signal for oxidized *Ni* in *m-ZrO₂* is similar to that of *NiO* with smaller post-edge oscillations. Therefore, it is believed that the oxidized *Ni* atoms in the far oxide of the BWR-corroded Zry-2 water rods are located as substitution defects in the zirconia matrix of the Zry-2

materials investigated in this study. These observations contrast with the XANES measurements by Kuri [220] in the far oxide of a fuel Zry-2 water (high burnup, high hydrogen content). In his paper, Kuri observed a similar shift to higher energy for the edge (compared to the nickel oxides) but a sharper white line intensity and clear post-edge oscillations when examining the XANES signal taken from a point in the far oxide, about $40\ \mu\text{m}$ away from the metal interface. This suggests that the first 3 shells surrounding the oxidized *Ni* atoms incorporated in zirconia are more ordered than in the water rod materials analyzed in this work. As this difference is present for all water rod materials independently of the elevation, fluence and time in the reactor, it may arise from the presence of radial heat flux in the Zry-2 cladding materials. The higher temperature would allow for improved ordering of the first 3 shells during oxide growth. On the other hand, the shorter oxygen bond still and/or higher *Ni* oxidation state shifts the edge energy of the spectrum compared to *NiO* and *Ni₂O₃*. Lastly, as it was the case for the metal part, no clear effect of irradiation or elevation is observed in the *Ni* XANES spectra in the far oxide of these materials.

To investigate the shape of the *Ni* XANES signal across the near oxide, the normalized spectra are plotted as a function of distance from the metal/oxide interface in Figure 3-17 and Figure 3-18. For each material, the metal and the oxide regions are represented by the negative and positive (respectively) x values and the oxide/water interface is located at the last plotted x point. As described in section 2.3.3 and section 3.2, the metal/oxide interface was determined at first using the K-edge *Zr* fluorescence but was then readjusted (0.5 to $2\ \mu\text{m}$) to the onset of the nickel oxidation represented by the x value at which the metallic fraction falls below 0.7 (or 70%). It allows for better comparison between the materials and is believed to adequately represent the metal/oxide interface, as corroborated with X-ray diffraction measurements (see chapter 4). The *Ni* XANES spectra across the oxide layer of the low hydrogen pickup materials (samples 9-A, 9-B, 11-A, 11-B) and of the high hydrogen pickup materials (samples 12-A-1, 12-

A-2, 14-A, 14-B) are shown in Figure 3-17 and Figure 3-18 respectively. The two main features representative of the *Ni* oxidation state (strong/weak pre-edge and white line intensity) are marked in each of the plots and discussed below.

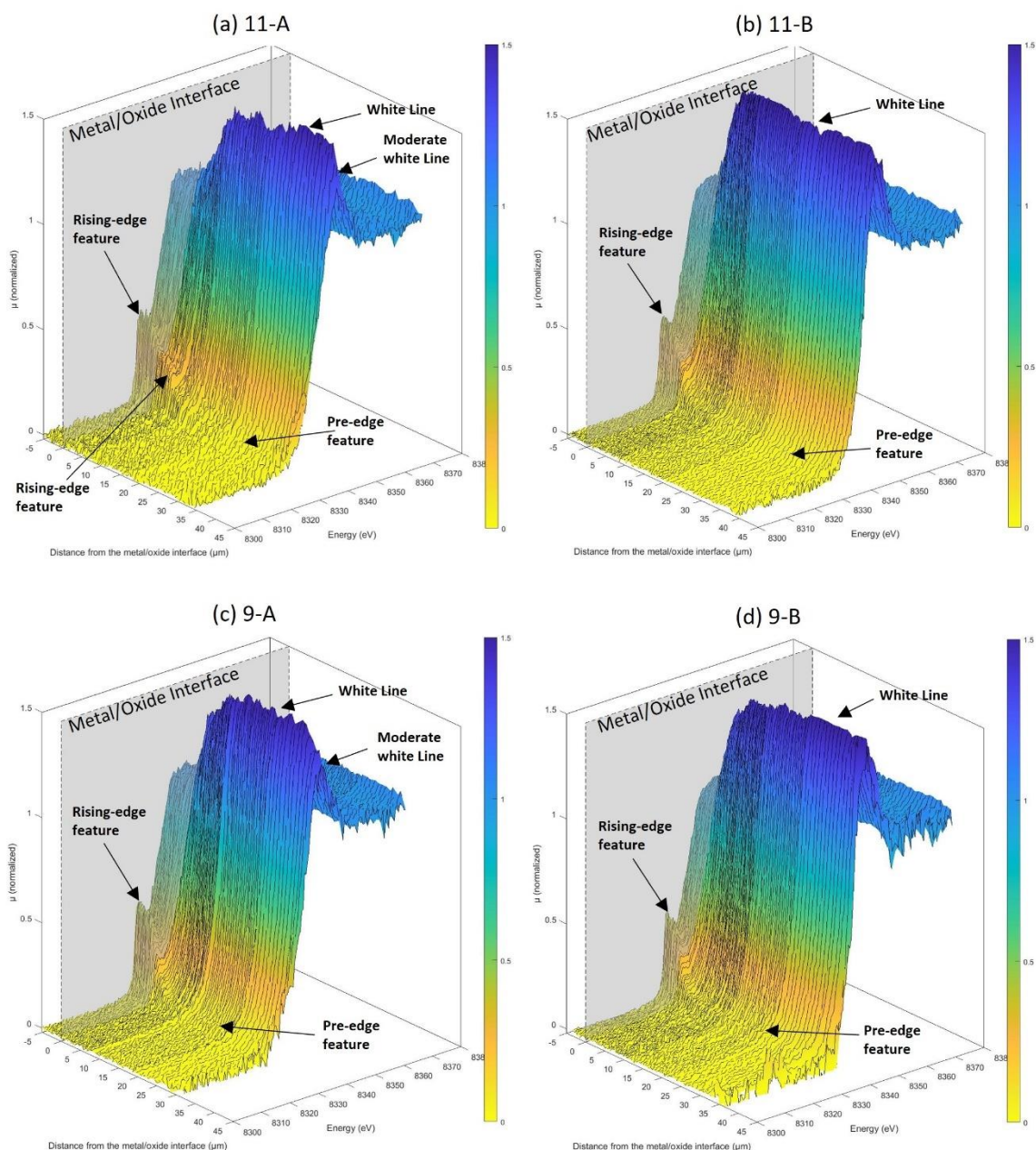


Figure 3-17: Plots of nickel XANES spectra as a function of distance from the oxide/metal interface for the low hydrogen pickup Zry-2 materials (3 cycles): Material 11 (high elevation,) (a) sample 11-A (b) sample 11-B; Material 9 (low elevation) (c) sample 9-A, (d) sample 9-B.

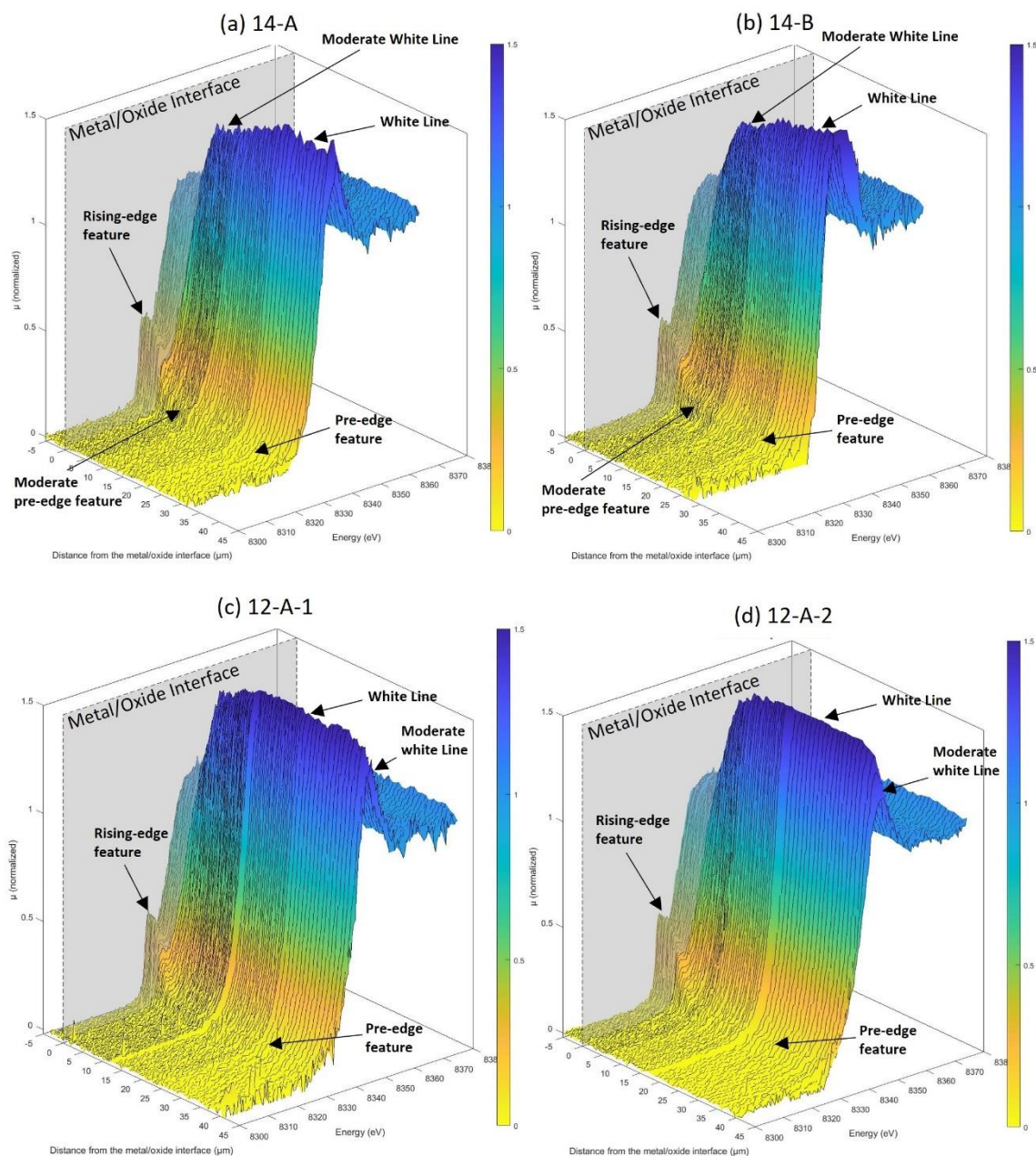


Figure 3-18: Plots of nickel XANES spectra as a function of distance from the oxide/metal interface for the **high** hydrogen pickup Zry-2 materials (3 cycles): Material 14 (high elevation,) (a) sample 14-A (b) sample 14-B; Material 12 (low elevation) (c) 12-A-1, (d) 12-A-2.

Starting at low elevation in the low HPUF water rod, the two scans from material 9 (Figure 3-17-(c) and Figure 3-17-(d)) are identical: a strong rising-edge with no white line in the metal, followed by an acute decrease of the rising-edge features and increase of the white line

intensity within the first 5 μm in the oxide. Ultimately, oxidized *Ni* spectra with a weak pre-edge and a clear white line are obtained when scanning the rest of the oxide layer. It is also observed that the absorption edge (the inflection point) is moved to higher energy once the strong rising-edge has disappeared in the oxide. It is clear that not all *Ni* atoms are readily oxidized as soon as they are incorporated in the oxide layer, but rather get all oxidized over 5 μm of oxide. This had previously been observed by Shivprasad [91] and Kuri [151]. This delayed oxidation is explained by the higher noble quality of the alloying elements compared to the *Zr* host and was seen to a lesser extent with *Fe* and *Cr* [13, 99-101, 145, 147, 148, 151] as detailed in section 1.3.4. Then, the 3D XANES plot of material 9 suggest no metallic nickel is observed in the oxide layer past a distance of 5 μm from the metal/oxide interface. This is further confirmed by the linear combination fit analysis presented in the next section.

Continuing with the high elevation material from the low HPUF water rod, the scan across the oxide layer of sample 11-B (Figure 3-17-(b)) is similar to that obtained from material 9 exhibiting a strong rising-edge and no white line in the metal, as well as an acute decrease of the rising-edge and increase of the white line intensity and of the edge energy within the first 5 μm into the oxide, and oxidized *Ni* spectra showing a weak pre-edge and a clear white line throughout the rest of the layer. On the other hand, scans collected in sample 11-A (Figure 3-17-(a)) differ from the three previous spectra in that these scans reveal a strong rising-edge shoulder feature, about 3-5 μm wide, in the oxide region near the metal/oxide interface. Past the shoulder, the rising-edge decreases further (until about 10 μm into the oxide) and a weak pre-edge remains in the scans taken from the rest of the oxide. Similarly, the white line (edge maximum intensity) slightly until the shoulder ends, then quickly reaches its maximum for the rest of the oxide layer. This observation may suggest the presence of non-oxidized precipitates far in the oxide layer, as the strong rising-edge feature are associated with *Ni* surrounded bonded to metallic *Zr* atoms. Considering the host matrix is now zirconia in the oxide layer, the metallic *Ni* atoms can only be

bonded to metallic *Zr* within remaining precipitates. However, this observation is unique to all materials and may instead result from the presence of a metal region underneath the oxide as further discussed in section 3.4.

For both scans in the oxide of sample 12-A (Figure 3-17-(c) and Figure 3-17-(d)) which was cut from the high HPUF Zry-2 water rod at low elevation, the *Ni* XANES spectra across the layer follow the trends observed in the low HPUF materials 9-A, 9-B, and 11-B: a strong rising-edge and no white line in the metal; also an acute decrease of the rising-edge and increase of the white line intensity and of the edge energy within the first 5 μm of oxide; and oxidized *Ni* spectra with a weak pre-edge and a strong white line for the rest of the layer. The overall shape of the 3D plot is clearly similar to that obtained from the low hydrogen pickup materials and no remaining metallic nickel is apparent past 5 μm into the oxide as confirmed by LCF analysis in the next section. This observation challenges the hypothesis of remaining metallic nickel in the oxide layer increasing hydrogen uptake [99] and is further discussed in CHAPTER 5.

Lastly, material 14 was taken from the high elevation of the high HPUF water and contained the most hydrogen content. The *Ni* XANES are plotted in Figure 3-18-(a) for sample 14-A and Figure 3-18-(b) for sample 14-B. For both scans, the features are similar to those observed in materials 13 and 21 by Shivprasad (Figure 4.3 of [91]): strong rising-edge and no white line in the metal; a sharp decrease of the rising-edge and increase of the white line intensity and of the edge energy to reach a moderate pre-edge feature and white line intensity within 5 μm past the metal/oxide interface; these moderate features remain for about 10 μm further in the oxide until the spectra eventually transition to weak pre-edge and high white line intensity. This plateau has been identified with the presence of metallic nickel in the oxide and is confirmed by the oxidation state analysis in the next section. The presence of metallic *Ni* in the oxide is thought to be responsible for the high hydrogen content of the material and is further discussed in chapter 5.

The shape of the *Ni* K-edge XANES spectra collected across the different materials of this study have been presented. Each individual spectrum was then fitted to a linear combination of the standards spectra to obtain the metallic fraction of nickel as a function of depth in the oxide. The results are presented in the next section.

3.4 Oxidation state of nickel in the oxide of in-reactor corroded Zry-2

3.4.1 Metallic fraction via linear combination fit

The XANES spectra across the oxide layers of the BWR-corroded Zry-2 water rods were presented in the previous section. As mentioned in section 2.3.4 and section 2.3.5, XANES spectra of a mixture of the absorbing atoms are in principle the weighted average of the absorption signal from the different atoms and so the metallic *Ni* weight fraction can be accessed via linear combination fit of the measured data with reference standards [242], as done in previous studies [99, 100, 145, 262, 263]. Each individual spectrum was then fitted to a linear combination of the *Ni* reference standards (section 3-1) and the metallic fraction was computed at each location by summing the LCF weights of the metallic compounds (*fcc Ni* and *Ni* in Zry-2).

Examples of the linear combination fit at 3 different locations (metal, oxide near interface, far oxide) in sample 9-A using the 3 nickel oxide powders (*NiO*, *NiFe₂O₄*, and *Ni₂O₃*, selection 1) are shown in Figure 3-19-(a), -(b) and -(c); and using *Ni(II,III)* in *ZrO₂* (selection 2) in Figure 3-19-(d), -(e), and -(f). The oxide standard *Ni(II,III)* in *ZrO₂* was used for the final as it more accurately represents the XANES signal arising from oxidized *Ni* atoms in Zry-2 oxide. As mentioned before, the standard consists of an average of 10 XANES spectra collected in the metal region of material 9. The linear combination fit was significantly improved in the

oxide layer with the use of $Ni(II,III)$ in ZrO_2 as illustrated below. The accuracy of the LCF is measured with the R -factor which is defined by:

$$R = \frac{\sum (\mu(E) - \mu_{fit}(E))^2}{\sum \mu^2(E)}$$

(Eq. 3-6)

where $\mu(E)$ represent the X-ray absorption data and $\mu_{fit}(E)$ the LCF result.

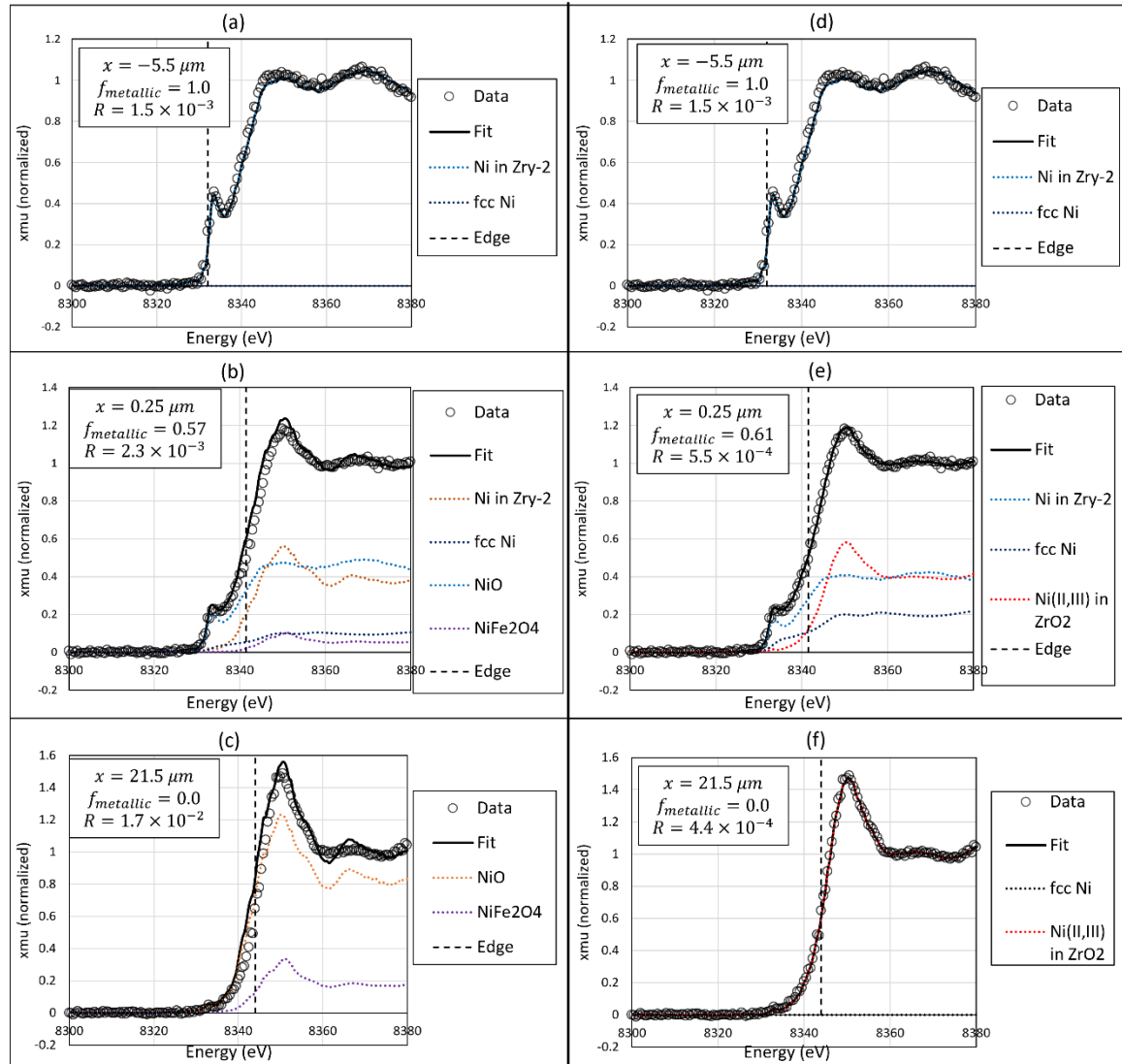


Figure 3-19: Nickel XANES linear combination fitting results for several points in material 9-A using the two metallic standards ($fcc\ Ni$, $Ni\ in\ ZrY-2$) and either the three nickel powder oxides (selection 1, NiO , $NiFe_2O_4$, Ni_2O_3 , left side plots) or $Ni(II,III)$ in ZrO_2 (selection 2, right side plots). (a) $5.5\ \mu m$ into the metal, selection 1. (b) $0.25\ \mu m$ into the oxide, selection 1. (c) $21.5\ \mu m$ into the oxide, selection 1. (d) $5.5\ \mu m$ into the metal, selection 2. (e) $0.25\ \mu m$ into the oxide, selection 2. (f) $21.5\ \mu m$ into the oxide, selection 2.

For all LCF plots in Figure 3-19, the XANES normalized data is represented by the black circles, the linear combination fit by the black line, and the weighted contributions from the nickel standards by the colored dotted lines. In the metal region ($x = -4 \mu m$), both selection of standards yielded the same LCF results (Figure 3-19-(a) and Figure 3-19-(d)) the XANES spectrum is better fitted with the standard *Ni* in Zry-2 with a very small input from *fcc Ni*, attributed to fitting error. This provides a metallic fraction of 1.0 at this location with a *R*-factor of 1.5×10^{-3} .

In the oxide near the metal interface ($x = 1.75 \mu m$), the XANES spectrum using the first selection of standards (Figure 3-19-(b)) is fitted with primary contributions from *Ni* in Zry-2 and *NiO* and secondary contributions from *fcc Ni* and *NiFe₂O₄*. The resulting metallic fraction is 0.57 and nickel is seen partially oxidized and the associated *R*-factor is 2.3×10^{-3} . Using the second selection of standards (Figure 3-19-(e)), the XANES spectrum in the oxide near the metal interface is fitted with contributions from all three standards: *fcc Ni*, *Ni* in Zry-2, and *Ni(II, III)* in *ZrO₂*. The resulting metallic fraction is 0.61, slightly higher than the fraction obtained with the first selection of standards, but with reduced fitting error as $R = 5.5 \times 10^{-4}$. In the far oxide ($x = 23 \mu m$), the XANES spectrum fit with the first selection (Figure 3-19-(c)) gives contributions from the oxide standards *NiO* and *NiFe₂O₄* only, leading to the metallic fraction of 0.0 and so all the nickels atoms are oxidized. However, the accuracy of the fit is lower than in other regions ($R = 1.7 \times 10^{-2}$) as measurable errors are seen at the edge and post-edge energies due to the differences between the XANES signal from the powder samples and from the oxidized *Ni* in Zry-2 oxide which were discussed in the previous sections. Using the second selection of standards (Figure 3-19-(f)), the accuracy of the fit is significantly improved to $R = 4.4 \times 10^{-4}$ with contribution from *Ni(II, III)* in *ZrO₂* only, resulting in the same metallic fraction $f_{metallic} = 0.0$ as the one determine with the first selection of standards. It is worth

mentioning that the results with the first selection of standards were unchanged when replacing the contribution from $NiFe_2O_4$ with the same contribution from Ni_2O_3 . For these reasons, the final LCF analysis was conducted using the second selection of standards: $fcc\ Ni$, Ni in Zry-2, and $Ni(II,III)$ in ZrO_2 .

The presented fitting method allows for quantitative analysis of the oxidation state of Ni . Each fit had a R -factor of less than 2.0×10^{-3} , except in the outer region of the oxide where noisy spectra led to higher R -factors. The metallic fraction error associated with the LCF analysis was estimated considering two inputs:

$$e_f = \pm(e_0 + kR)$$

(Eq. 3-7)

where e_0 is a fixed value determined by accuracy of the pre-edge fit, and k an arbitrary constant multiplied by the R -factor of the fit to account for the edge and post-edge errors.

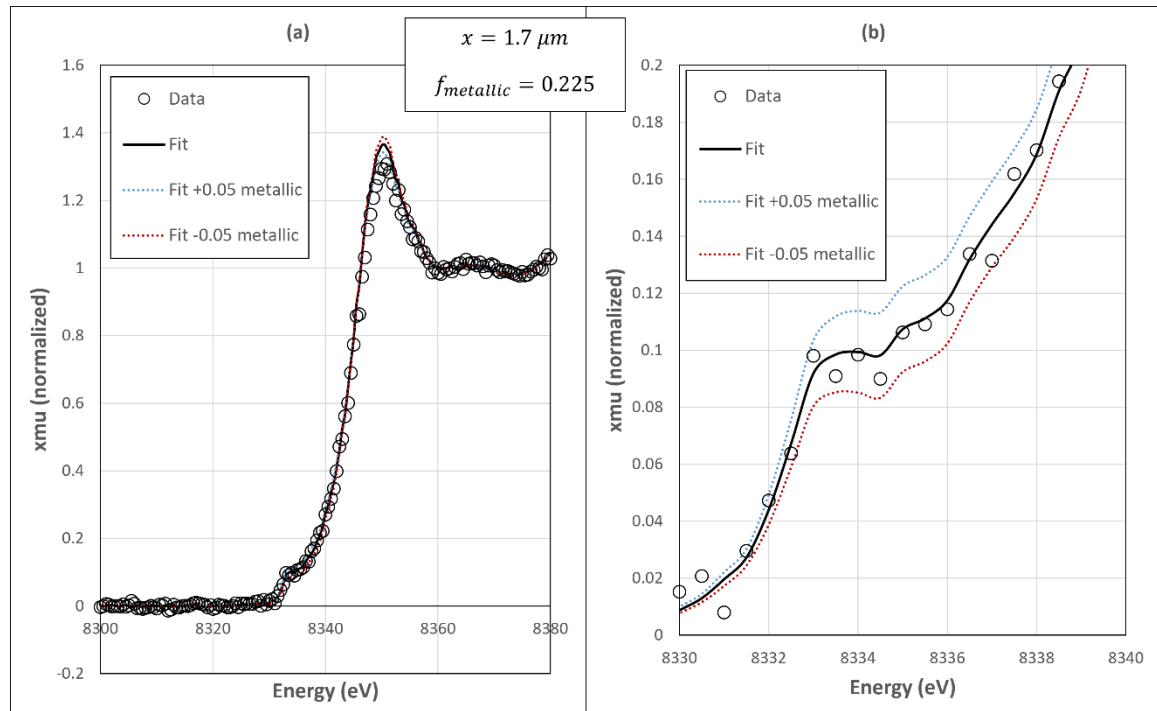


Figure 3-20: Metallic fraction error estimation with the example of Ni K-edge XANES spectra in the oxide of sample 9-A ($x = 1.7\ \mu m$, $f_{metallic} = 0.225$). The linear combination fit (black line) of the XANES data (circle markers) is shown with the linear combination spectra of the standards where 0.05 metallic weight is added (blue dotted line) or subtracted (red dotted line) to the LCF results: (a) whole spectra; (b) region around the rising-edge feature.

A value of 2 for the constant k was determined by the author after analysis the spectra with large R -factors while the e_0 was estimated by varying the metallic fraction around the fit value as illustrated in Figure 3-20-(a) (whole energy range) and in Figure 3-20-(b) (pre-edge range) at a location in the oxide of material 9 near the metal interface. The data points are shown as black circles, the fit result as a black line, the over fit (increased metallic fraction) as a blue dotted line, and the under fit (decreased metallic fraction) as a red dotted line. It can be seen in Figure 3-20-(b) that a value of 0.05 (or 5%) for e_0 allows for all the data points to be in between the over and under fit in the pre-edge region. This observation was valid for all the XANES scan collected in this study, except in the outer region of the oxide where high levels of noise were present in the XANES data. Therefore, the metallic fraction error was estimated in this study by:

$$e_f = \pm(0.05 + 2R)$$

(Eq. 3-8)

The metallic fractions as a function of distance from the oxide interface in the four materials are presented in Figure 3-21 and Figure 3-22. The metallic fraction obtained from the first round of *Ni* XANES scans (samples 9-A, 11-A, 12-A-1, and 14-A) are plotted across the entire oxide layer in Figure 3-21-(a) and across the near interface region of interest $[-5 \mu\text{m}; 15 \mu\text{m}]$ (ROI) in Figure 3-21-(b). Similarly, the metallic fraction for the second round of *Ni* XANES scans (samples 9-B, 11-B, 12-A-2, and 14-B) are plotted across the whole oxide layer and across the ROI $[-5 \mu\text{m}; 15 \mu\text{m}]$ in Figure 3-22-(a) and Figure 3-22-(b). The errors bars are shown on the different plots and were estimated as detailed previously in this section. The different features of the plots are described below.

Firstly, partial oxidation of nickel is observed for at least $3\text{-}5 \mu\text{m}$ in all materials for all scans. This delayed oxidation compared to the *Zr* host has been observed previously for nickel and iron [13, 99-101, 145, 147, 148, 151] and was attributed to *Ni* and *Fe* being more noble than the *Zr* host as detailed in section 1.3.4. Secondly, metallic nickel has been observed near the

oxide/water interface for some of the samples, though the XANES *Ni* scans are significantly noisy at these locations. Some metallic *Ni* is seen in the outmost region of the oxide layer for at least one of the two scans performed in each material (Figure 3-21-(a) and Figure 3-22-(a)), reaching values as high 0.75 in material 11 (high elevation, low high hydrogen pickup) but at most 0.15 in material 14 (high elevation, high hydrogen pickup). Therefore, this metallic nickel at the oxide/water interface does not seem to play a role in accelerating hydrogen pickup at high burnup and is attributed to CRUD deposits of *Ni* and *Fe* atoms from the corrosion of other structural materials in the reactor as further discussed later in this section.

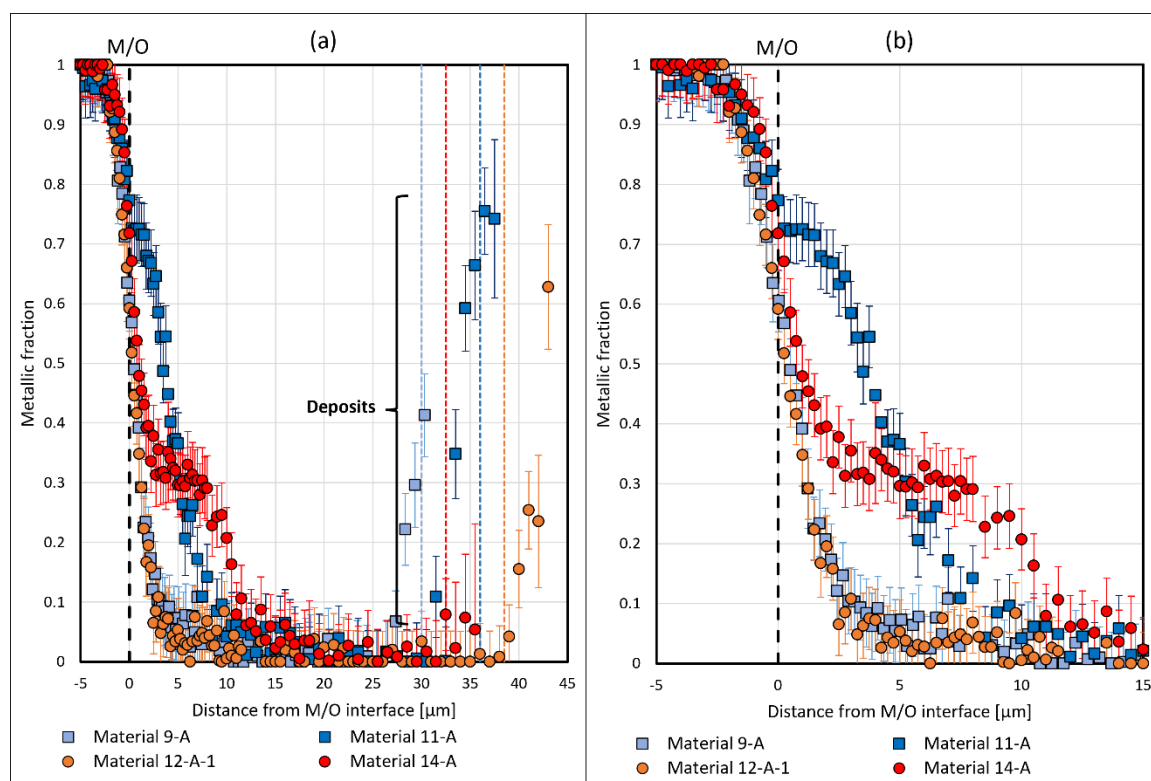
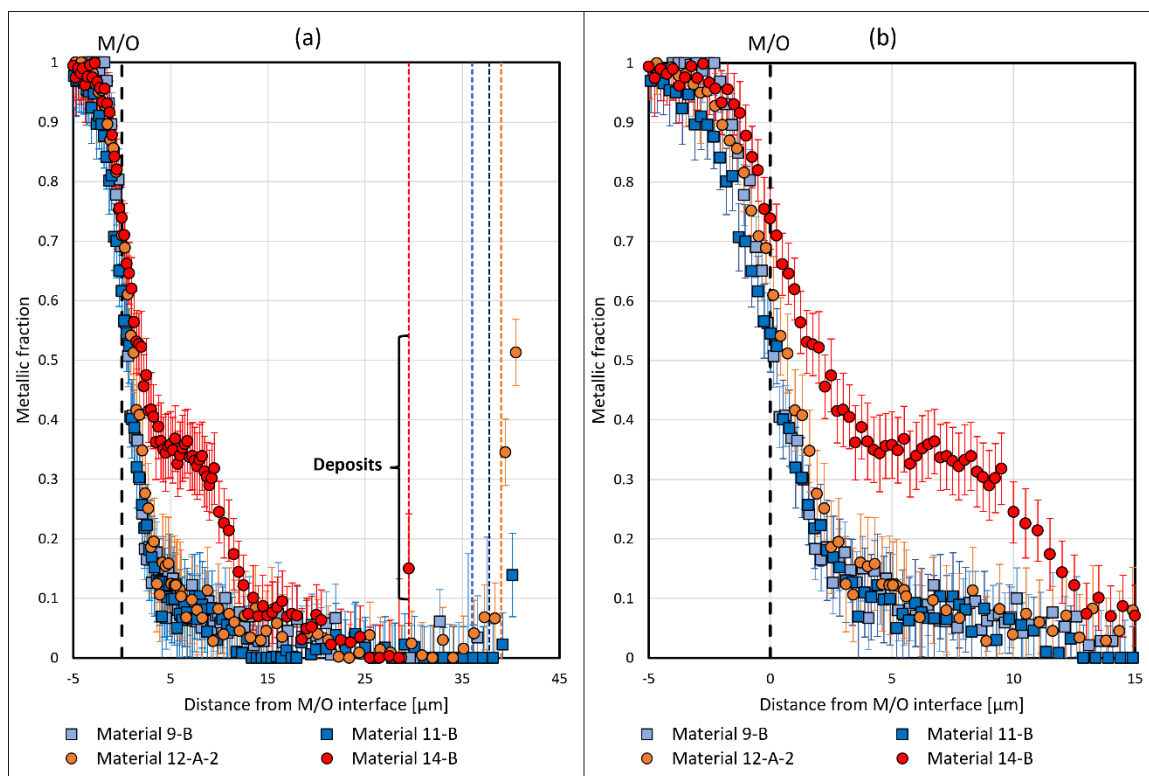


Figure 3-21: Metallic *Ni* weight fraction as a function of distance from the metal/oxide interface for the **first** scan in each of the materials (9-A, 11-A, 12-A-1, 14-A): (a) over the whole oxide thickness range; (b) over the ROI $[-5\mu\text{m}; 15\mu\text{m}]$ near the interface.



*Figure 3-22: Metallic Ni weight fraction as a function of distance from the metal/oxide interface for the **second** scan in each of the materials (9-B, 11-B, 12-A-2, 14-B): (a) over the whole oxide thickness range; (b) over the ROI $[-5\mu\text{m}; 15\mu\text{m}]$ near the interface.*

For material 9 (low elevation, low hydrogen pickup, light blue square markers) and material 12 (low elevation, high hydrogen pickup, orange circle markers) as well as for the second scan in material 11 (high elevation, low hydrogen pickup, dark blue square markers), nickel atoms are fully oxidized after a continuous decrease for $3\text{--}5\ \mu\text{m}$ in the oxide past the metal/oxide interface. Then, nickel atoms remain fully oxidized for the rest of the oxide layer. Results from these materials are identical to those obtained by Shivprasad in the low hydrogen pickup Zry-2 water rods (materials 10 and 17 in [91]).

For material 14 (high elevation, high hydrogen pickup, red circle markers), a plateau at about 0.3-0.4 metallic fraction is present in the oxide regions $[2\ \mu\text{m}; 9\ \mu\text{m}]$ and $[3\ \mu\text{m}; 11\ \mu\text{m}]$ past the metal/oxide interface in sample 14-A and 14-B respectively. This remaining metallic fraction was observed for the high hydrogen pickup Zry-2 water rods in the previous study

(materials 13 and 21 in [91]). This remaining metallic fraction was hypothesized to cause the increase of H pickup in these materials. This interpretation is further discussed in chapter 5.

Surprisingly, in the first scan collected in material 11 (high elevation, low hydrogen pickup, dark blue square markers) shown in Figure 3-21-(a) (sample 11-A), a plateau at about 0.6-0.7 metallic fraction is seen in the near oxide region $[0\ \mu m; 3\ \mu m]$ just past the metal/oxide interface. This observation is unique to the Ni XANES scans collected in the BWR-corroded Zry-2 materials in this study and in Shivprasad's work [91]. This plateau of metallic nickel differs from that of high hydrogen pickup materials by its metallic fraction value (0.6-0.7 compared to 0.3-0.4) and shorter range (about $4\ \mu m$ compared to $7-10\ \mu m$). Because the hydrogen pickup fraction of this materials was low ($HPUF = 13.4\%$, Table 2-1), this remaining metallic nickel atoms in the oxide layer of sample 11-A did not influence the hydrogen uptake in this material ($HPUF = 13.4\%$, Table 2-1). This observation is further discussed in the next section where the XANES metallic nickel signal arising from the oxide of the different materials is further investigated. and in chapter 5.

Lastly, high Ni metallic fractions were observed at the oxide/water interface of some of the Zry-2 samples examined (9-A, 11-A, 12-A in Figure 3-21-(a) and Figure 3-22-(a). As mentioned above, because the observation was seen to a much lesser extent in material 14 (red circles in FIGURE 3-21-(a) and Figure 3-22-(a)) which had the highest content of hydrogen, these metallic Ni atoms at the oxide/water interface are not believed to affect the hydrogen pickup of the material. Examinations of the fluorescence signal of Fe , Ni and Zr (at $E = 20\ keV$) revealed higher counts for Fe and to a lesser extent for Ni at the oxide/water interface as seen in Figure 3-23 at the XANES locations in samples 9-A, 11-A, 12-A-1, and 14-A. The higher counts for Fe and Ni were identified as resulting from CRUD (Chalk River Unknown Deposits) released in the water by the oxidation of the stainless steel and absorbed at the oxide surfaces of the water rods. CRUD have been seen extensively on cladding layers as seen in [220, 316] where a CRUD

layer a few μm thick is distinctively observed at the oxide/water interface of the high burnup Zry-2 cladding materials. Because the deposition rate increases with heat flux in the material [319], thick CRUD layers are seen on Zry-2 cladding whereas on Zry-2 water rod, the deposition results in increased alloying element (*Fe*, *Ni* and others) concentrations at the oxide/water interface after long exposure in the reactor environment. Similarly, increased concentrations of *Fe* were observed near the oxide surface of ZIRLO and *Zr-Nb* alloys corroded in stainless steel autoclave [89].

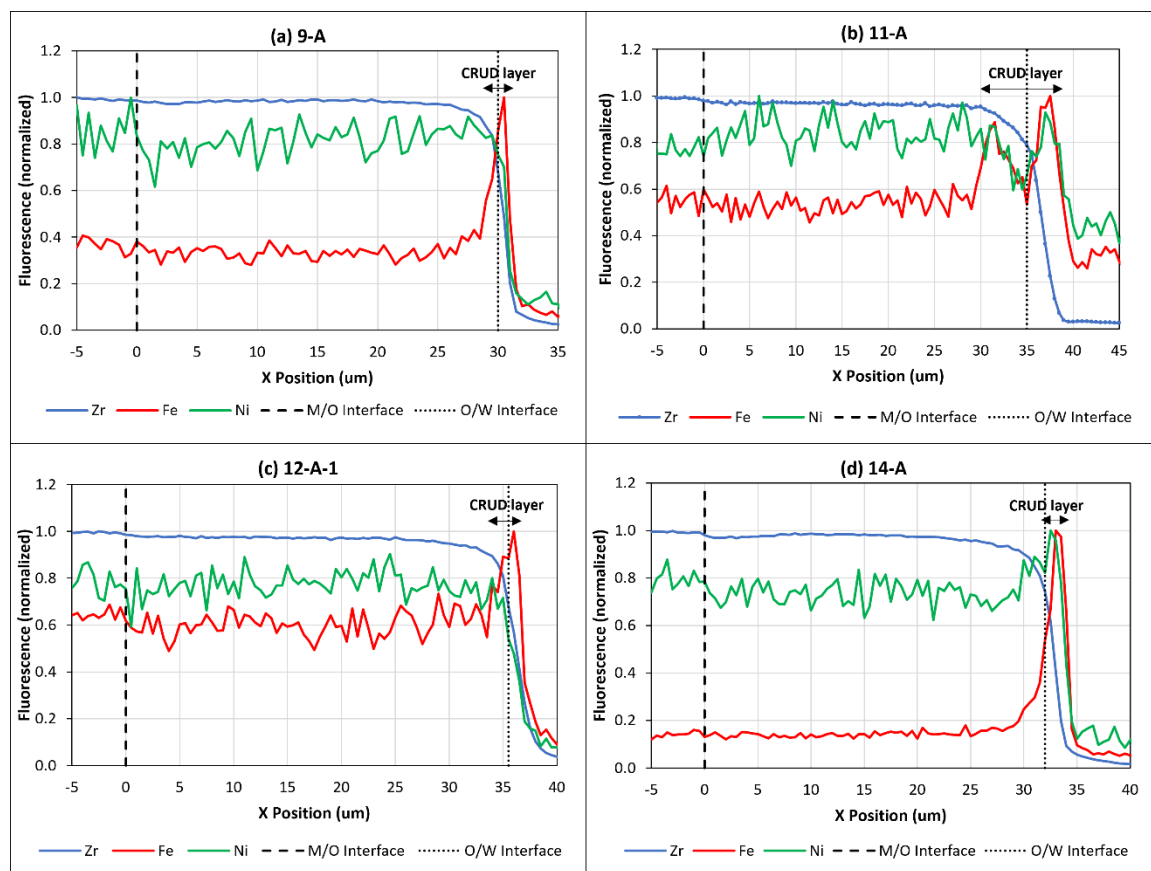


Figure 3-23: Fluorescence counts of Zr (blue), Fe (red) and Ni (green) as a function of distance from the M/O interface at the location of the XANES measurements for samples (a) 9-A, (b) 11-A, (c) 12-A-1, (d) 14-A.

3.4.2 Metallic Ni features in low and high hydrogen pickup samples

In this section, we investigate the metallic nickel signal observed in the near oxide of samples 11-A, 14-A, and 14-B. In Figure 3-24, the metallic fraction and metallic standards (*fcc Ni* and *Ni* in Zry-2) weight fractions from the LCF analysis are plotted across the region $[-5\ \mu\text{m}; 15\ \mu\text{m}]$ of oxide for materials 11-A, 14-A, 14-B, and 9-A. The metallic fractions across the oxide of sample 9-A are representative of the samples where no metallic nickel was observed past 3-5 μm of oxide (the metallic weight fractions in the oxide of samples 9-B, 11-B, and 12-A followed the trends seen across the oxide of sample 9-A in Figure 3-24(b)).

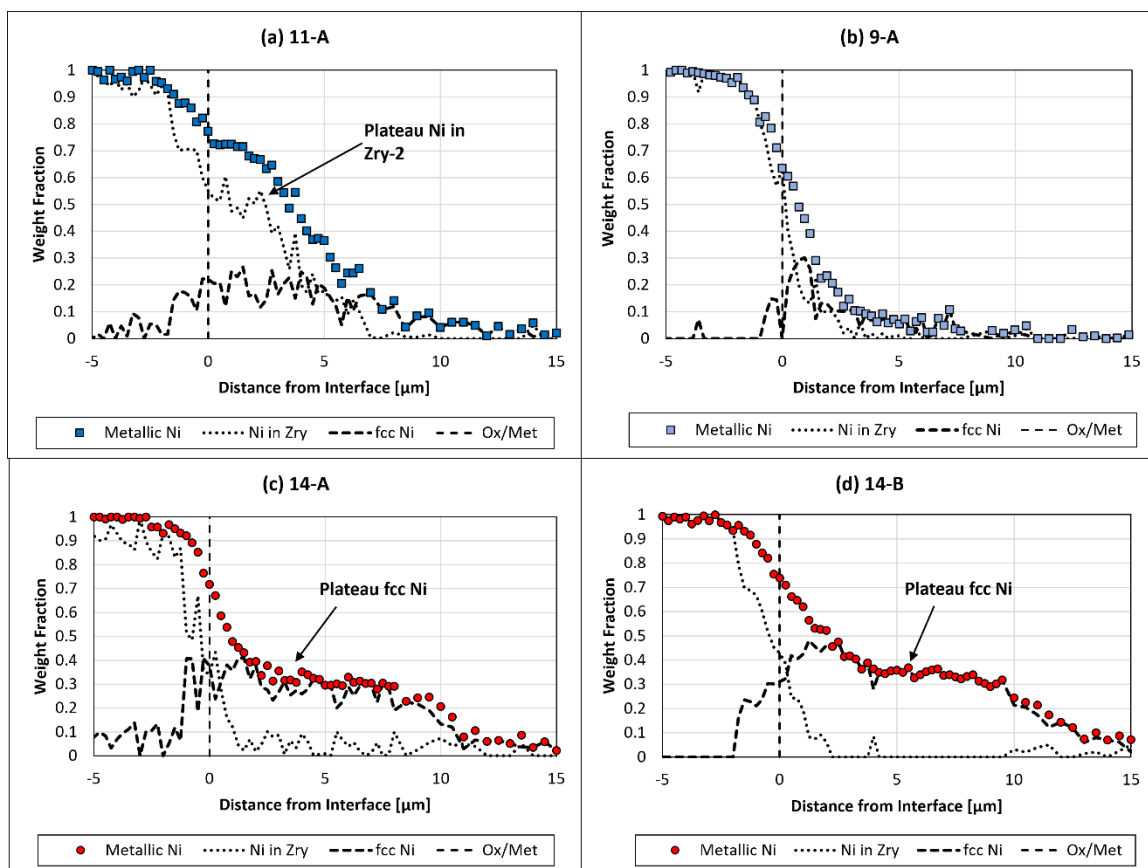


Figure 3-24: Metallic Ni (markers) and metallic Ni standards (*fcc Ni*, dashed line; *Ni* in Zry-2, dotted line) weight fractions in the near oxide region $[-5\ \mu\text{m}; 15\ \mu\text{m}]$ resulting from the linear combination of the XANES spectra. (a) Sample 11-A; (b) 9-A; (c) 14-A; (d) 14-B.

For all materials, the metallic fraction in the metal region is fitted with the standard *Ni* in Zry-2 as detailed in section 3.3 (and seen in Figure 3-19). Once entering the oxide layer, the weight fraction of *Ni* in Zry-2 sharply decreases. At about $3\ \mu\text{m}$ past the metal/oxide interface in the oxide of sample 9-A, 14-A, and 14-B ((b), (c) and (d) in Figure 3-24), there is no more contributions from the metallic standard *Ni* in Zry-2. For sample 9-A, some *fcc Ni* contributions are seen in the near oxide layer ($[-1\ \mu\text{m}; 3\ \mu\text{m}]$). Interestingly, in the high hydrogen pickup material (samples 14-A and 14-B in Figure 3-24-(c) and Figure 3-24-(d) respectively), the weight fraction of *fcc Ni* increases strongly past the interface to reach a plateau at about 0.3 which is maintained until full oxide of the *Ni* atoms is seen at about $14\ \mu\text{m}$ of oxide. As such, the XANES signal attributed to metallic nickel in the oxide layer of material 14 correspond to that of the *fcc Ni* standard, rather the *Ni* in Zry-2 standard. In contrast, the metallic fraction plateau seen at 0.6-0.7 in the near oxide of sample 11-A (Figure 3-24-(a)) correspond to a plateau of *Ni* in Zry-2 weight fraction at about 0.5 while the *fcc Ni* contributions are similar to that in the oxide of sample 9-A but extended over a larger oxide region $[-1.5\ \mu\text{m}; 9\ \mu\text{m}]$.

These observations can be interpreted in terms of nickel atoms bonded to zirconium atoms. In sample 11-A (low hydrogen pickup), the significant metallic fraction in the near oxide is thought to represent mainly metallic nickel atoms still bonded to metallic zirconium atoms (*Ni* in Zry-2) whereas in material 14 (high hydrogen pickup), the remaining metallic fraction corresponds to metallic nickel atoms no longer bonded to metallic *Zr* atoms but rather *Ni* atoms. Indeed, the rising-edge feature typical of the *Ni-Zr* bonds is a sharp rising-edge feature as seen in the XANES K-edge spectrum of *Ni* in Zry-2 (Figure 3-5), distinct from the diffuse rising-edge of *fcc Ni*. Therefore, the metallic *Ni* XANES signal in the oxide layer of sample 11-A is not originating from metallic nickel in the oxide, but rather from metallic nickel still bonded to metallic *Zr* atoms, suggesting the presence of a metal region. This metal region would reflect the

non-uniformity of the oxide and of the metal/oxide interface as described in section 3.2. On the other hand, the metallic signal in the oxide layer of the high hydrogen pickup material – material 14 in Figure 3-24-(c) and Figure 3-24-(d) – corresponds to *fcc Ni*, indicating that the metallic *Ni* atoms are no longer bonded to *Zr* atoms. In a study of the XANES signal of the short-range of *Ni* nanoparticles embedded in carbonaceous matrix, Nietubyc [310] was able to measure XANES spectra of the dopant (*Ni*) nanoclusters which were similar to that of *fcc Ni* foil (Figure 3-5) with lower post-edge oscillations. The remaining metallic fraction in the oxide layer of material 14 would then correspond to nanoclusters of metallic *Ni* embedded in the zirconia matrix. The metallic nickel atoms in the near oxide layer affecting hydrogen uptake are then located in solid solution or in small clusters in the oxide layer, rather than in second phase precipitates. Though not shown here, the remaining metallic *Ni* XANES signal in the oxide of materials 13 and 21 studied by Shivprasad [91] also featured the *fcc Ni* standard, corroborating the observations in the oxide of material 14. These interpretations of the metallic XANES signal in the oxide layer of the Zry-2 water rods and the implications in terms of hydrogen pickup are further discussed in chapter 5. In the next section, the edge energies as a function of distance from the metal/oxide interface are investigated.

3.4.3 Oxidation state calculation using edge energy

As illustrated in Figure 2-7 and Figure 3-2-(a) with the examples of iron and chromium, the oxidation state of the element of interest (nickel) may be assessed by the position of the edge energies (inflection point) of the XANES. This approach has been used by researchers in the past [99, 254, 320-322] to determine the oxidation state of the element of interest in different compounds using reference metallic and oxidized standards. As the atom gets more oxidized, it loses electrons in its inner shells resulting in less shielding of the nucleus. The binding energy for

the remaining electrons is slightly increased and in turn the energy needed for the photons to eject the core-electrons is raised (as described in section 2.3.2) [240, 242, 254, 293]. However, it was discussed in section 3.1 that the XANES edge energy may be influenced by the structural configuration around the element of interest, namely the interatomic distances in the crystal structures as illustrated in Kuzmin's work [301] with *Mn* substituting in *ZnO*. The edge energy for the *Ni(III)* oxide considered in this study (Ni_2O_3) was seen only 0.5 eV and 1.0 eV higher than that of the other two *Ni(II)* oxides (*NiO* and $NiFe_2O_4$) as seen in Table 3-1. This slight shift in edge energy for *Ni* as the oxidation state increases from 2 + to 3 + close to the energy resolution (0.5 eV at beamline 34-ID-E) limits the possibility to accurately measure the oxidation state of the *Ni* atoms in the oxide. Mansour *et al.* [323] was able to correlate the edge energy (determined as the edge half maximum energy instead of the inflection point) to the oxidation state (from 0 to 4 +) in different nickel oxycompounds. However, this approach did not yield the same correlation with the nickel oxides considered in this study as the half edge maximum for $NiFe_2O_4$ (Ni^{2+}) was seen 1.0 eV higher than that of Ni_2O_3 . Therefore, the inflection point method was maintained for the edge energy analysis. Shifts in edge energy are then attributed to a combined effect of the shielding of the nucleus due to oxidation and of the local environment (namely the bond length and coordination) in the different nickel compounds. Considering both effects, we now investigate the evolution of the edge energy (inflection point) across the oxide layers of the Zry-2 water rods.

The edge energies measured as the maximum of the spectra derivative (the inflection point) and calibrated to the edge energy $E_0 = 8333$ eV for metallic nickel (*fcc Ni* foil in section 3.1) are presented for all BWR Zry-2 water rod samples in Figure 3-25-(a) for the first round of scans and Figure 3-25-(b) for the second round of scans in the materials. The edge energy range of the nickel standards (± 0.5 eV in Table 3-1) for the different oxidation states considered (0, 2 + and 3 +) are also plotted for comparison.

It can be seen in Figure 3-25 for all samples except 11-A that within $1\ \mu\text{m}$ in the oxide, the edge energy jumps from the metallic nickel (Ni^0) range (around $E - E_0 = 0\ \text{eV}$) to the nickel (*II*, or $2+$) and nickel (*III*, or $3+$) range to reach the average value of $E - E_0 = 13.5\ \text{eV} \pm 1.5\ \text{eV}$ for the first round of scan (a) and $E - E_0 = 13.5\ \text{eV} \pm 1\ \text{eV}$ for the second round of scan.

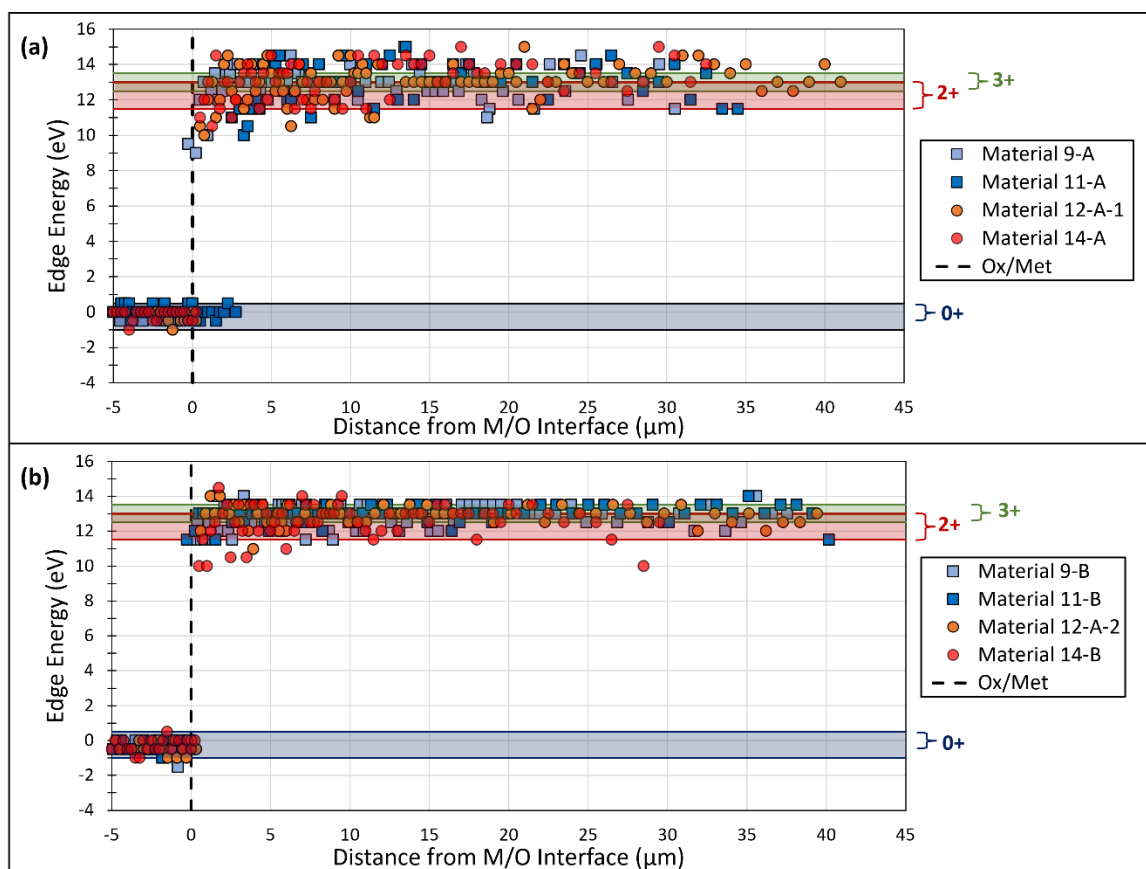


Figure 3-25: Ni XANES edge energies across the oxide layers of: (a) 9-A, 11-A, 12-A-1 and 14-A; (b) 9-B, 11-B, 12-A-2, 14-B. Boxed regions show the edge position $\pm 0.5\ \text{eV}$ of the standard materials with their corresponding valence (TABLE 3-1).

The lower edge energy variations seen for all samples during the second round of scan (Figure 3-25-(b)) were attributed to improved experimental setup (mainly by bringing the X-ray detector closer to the samples) which slightly reduced noise in the XANES spectra compared to the data collected during the first round of experiment. Shivprasad, who observed similar edge

energy trends on Zry-2 irradiated and unirradiated materials [91], suggested that the oxidation state of nickel increases at first in the few μm of oxide (closer to 2 + right after the jump) and quickly converges to a higher oxidation state (between 2 + and 3 +). Considering the discussions mentioned above and detailed in section 3.1, the author believes that the initial jump is due to the oxidation of *Ni* to a 2 + state in solid solution in zirconia [151], then as oxygen partial pressure increases in the oxide layer, nickel atoms may oxidize further to Ni^{3+} as suggested by DFT calculations [153]. The later shift to higher edge (on average 0.5 eV above the Ni_2O_3 edge) is attributed to the shorter interatomic distances (measured with EXAFS by Kuri *et al.* [151]), between the oxidized *Ni* atoms and the *O* atoms in ZrO_2 compared to the bond lengths in the nickel oxides, modifying the XANES shape as seen for *Mn* in *ZnO* by Kuzmin *et al.* [301]. Because of the combined effect of the oxidation state and of the bond length on the edge energy, and the similarities between the XANES spectra of the nickel oxide powder standards considered in this study, it was not possible to quantify the fraction of Ni^{2+} and of Ni^{3+} the oxide but only the fraction of oxidized nickel atoms.

Lastly, it can be seen in Figure 3-25-(a) that the jump only occurs at about 3 μm in the oxide of sample 11-A before it follows the trend of the other materials for the rest of the oxide. This delayed jump is consistent with the high metallic fraction observed in Figure 3-21 and the jump position corroborates the depth at which the fraction of metallic nickel in the oxide decreases below 0.5 ($\pm 0.5 \mu m$), a correlation seen as well in the other materials. The edge jump position is then a good indicator of the depth at which oxidized nickels become dominant in the mixture of nickel atoms. Coherently to this observation, the edge energy is not affected when the metallic is at about 0.3 – 0.4 for samples 14-A and 14-B (Figure 3-21 and 3-22). Therefore, LCF analysis was necessary to detect the lower fraction of metallic nickel remaining in the oxide of material 14.

3.5 Conclusions on XANES examinations of in-reactor corroded Zry-2

In this chapter, we presented the results of the in-depth oxidation state analysis of nickel across the oxide layers of BWR-corroded Zry-2 water rod materials with low and high hydrogen pickup using K-edge XANES with synchrotron radiation. Additionally, SEM images of the cross-section samples were acquired at PNNL and at Penn State. In previous work [91], high hydrogen content in the water rod was correlated to the presence of metallic nickel up to 10-15 μm oxide past the metal/oxide interface and a focused set of high and low hydrogen materials was then selected for characterization at the APS (ANL) to further investigate this relationship. While this hypothesis is discussed in detail in chapter 5, the main observations of the XANES and SEM experiments are gathered below:

- (1) Many cracks were seen in the oxide layers of the Zry-2 water rods selected, with slightly more cracking observed in the high HPUF/high elevation samples. The oxide layers were rather uniform but extensive oxide thickness variations could be observed between different regions for all the materials, especially regions in the inner oxide layers of the samples prepared for this study. Examinations of the GNF water rods by EPRI confirmed circumferential variations of the oxide thickness in both the inner and outer parts of the two rods. These variations may result from the differences in coolant flow, steam quality, irradiation flux and SPP distributions in the water rods, as well as the proximity to other structural materials in the reactor. These observations are coherent with previous examinations of Zry-2 oxide layers formed in BWRs.
- (2) Full oxidation of nickel is reached within the first 3-5 μm and continues throughout the oxide layers of the low HPUF materials (both scans in material 9 – low elevation - and the second scan in material 11 – high elevation) and of the high HPUF and low

elevation material (material 12, both scans). This delayed oxidation compared to the *Zr* host is attributed to the higher noble property of the *Ni* atoms compared to the *Zr* host, as reported in previous work.

- (3) In the oxide of material 14 (high elevation and high HPUF), after initial oxidation of nickel in the first few μm of oxide, a plateau at about 0.3-0.4 metallic fraction is present in the regions $[2\ \mu\text{m}; 9\ \mu\text{m}]$ and $[3\ \mu\text{m}; 11\ \mu\text{m}]$ past the metal/oxide interface (samples 14-A and 14-B respectively), followed by full oxidation throughout the rest of the oxide layer; as measured in previous work in the oxide layers of high hydrogen pickup Zry-2 materials.
- (4) The first scan across the oxide of material 11 (low HPUF, high elevation) contained a plateau at about 0.6-0.7 metallic fraction in the region $[0\ \mu\text{m}; 3\ \mu\text{m}]$ past the metal/oxide interface. Oxidation of the nickel atoms ensues until full oxidation is reached at about $8 - 10\ \mu\text{m}$ and unchanged up to the oxide/water interface. Examining the standard weight fractions resulting from the LCF, the metallic nickel XANES signal in the near oxide region corresponded to that of *Ni* in Zry-2, rather than that of *fcc Ni*. This observation suggests that the nickel atoms are still bonded to the zirconium host while in high percentage metallic, hence the metallic plateau was attributed to an underneath metal region.
- (5) On the other hand, the metallic signal measured in the oxide layers of the high HPUF samples at high elevation (Mat. 14) corresponded to that of *fcc Ni*, indicating that the metallic nickel atoms are no longer bonded to zirconium atoms, i.e. in solid solution or small clusters in the oxide layer, rather than in precipitates.
- (6) Analysis of the edge energies – defined as the inflation point of the XANES spectrum – across the oxide layer formed on the Zry-2 water rods exposed no clear differences in terms of elevation, hydrogen pickup or time in the reactor. A jump of about 11 eV

is observed at about $0.5 \mu m (\pm 0.5 \mu m)$ in all materials, except for sample 11-A where the jump occurred at $3 \mu m$. These jump locations were corroborated to the points at which oxidized nickels become dominant ($f_{metallic} < 0.5$). The edge energies then quickly shift to higher energies at about $13 eV$ above the metallic nickel edge energy for the rest of the oxide layer. This edge shift is slightly higher than that observed for the $Ni(II)$ and $Ni(III)$ oxides standard considered in this study but may reflect differences in local environment rather than a higher oxidation state ($> 2+$) of the nickel atoms in the oxide layer of Zry-2.

- (7) Metallic nickel atoms have been observed in the oxide layer near the oxide/water interface for some of the samples examined. A significant metallic fraction was seen at the oxide/water interface in at least one of the two XANES scans of materials 9, 11 and 12, with the highest metallic fraction (0.75 or 75%) measured in the low HPUF/high elevation material (Mat. 11), but only a small metallic fraction was seen at the oxide/water interface of material 14 (highest hydrogen content material). This observation indicates that metallic nickel atoms at the oxide/water interface do not seem to have played a determinant role in the enhancement of hydrogen uptake in the Zry-2 examined. This metallic nickel is attributed to deposits of Ni and Fe atoms from the corrosion of other structural materials in the reactor, as observed in previous studies. This hypothesis is confirmed by the increased fluorescence counts of the elements (especially Fe) near the outmost region of the oxide.

Chapter 4

Microstructure of the oxides of BWR Zry-2 water rods with XRD

Zircaloy-2 water rods corroded in BWR for 3 to 4 cycles were analyzed using microbeam X-ray diffraction at beamline 34-ID-E at the APS (ANL), as described in section 2.4. The examinations were performed across the oxide layers of samples 9-B, 11-B, 12-A, and 14-B at the location of the XANES scans presented in the previous chapter (Figures 3-9, 3-11, 3-13, 3-14) during the second round of measurements. The *Ni* metallic fraction as a function of oxide depth corresponding to these locations were presented in Figure 3-21. In turn, the microstructure of the oxide layer and of the metal near interface was investigated for each of the materials in Table 2-1 and compared to the measured *Ni* metallic fraction. The phase content, texture, and grain sizes in the Zry-2 oxides were examined in terms of hydrogen pickup, fluence, elevation, and *Ni* oxidation state in the oxide. Previous work by Shivprasad [91] suggested a lower tetragonal fraction in the near oxide of high hydrogen pickup materials. Additionally, the size and the crystallographic orientation of oxide grains that form on zirconium alloys have been observed to affect the diffusion of species through the oxides [93, 144, 324]. All four XRD patterns were collected in reflection as detailed in section 2.4.3 and the results are presented in this chapter. Section 4.1 gathers information on diffraction pattern indexing, on background levels in oxide and metal, and on the general observations of the XRD patterns across the oxide layers of the materials. In section 4.2, we present the results of the PEAKFIT analysis of the integrated XRD patterns as a function of distance from the metal/oxide interface, including the peak intensities of crystal planes in the different phases identified in the samples, and the resulting volume fraction of *t*- ZrO_2 and oxide grain sizes. Section 4.3 contains the analysis of the preferred orientation in the metal and in the oxide layers, and section 4.4 concludes the microstructure observations with XRD in low and high HPUF Zry-2 materials corroded in BWR.

4.1 Analysis of diffraction patterns from Zry-2 water rods

4.1.1 Indexing of X-ray diffraction patterns from metal and oxide regions

The four water rod materials with low (9, 11) and high (12, 14) hydrogen pickup were investigated using microbeam XRD at the location of the XANES scan presented in the previous chapter (samples 9-B, 11-B, 12-A-2 and 14-B with the resulting metallic fraction shown in Figure 3-21 as a function of distance from the metal/oxide interface). The X-ray diffraction patterns were obtained across the oxide layer of the cross-section samples (Figures 2-1, 2-2, 2-3) as illustrated in Figure 2-17. The XRD patterns in the metal, in the oxide near interface, and in the far oxide of sample 11-B are shown in Figure 3-1, Figure 3-2 and Figure 3-3 respectively. The reflections at various diffraction angles (θ) were successfully attributed to crystal planes of hexagonal close compact α -Zr (shown with dark blue arrows in Figures 3-1 and 3-2), cubic δ -ZrH_{1.66} (light blue arrows in Figure 3-1), monoclinic ZrO₂ (red arrows in Figures 3-2 and 3-3), and tetragonal ZrO₂ (light red arrow in Figure 3-2) using the powder diffraction files (PDFs) available in Appendix A. These four phases are typical of Zr alloys and oxides and were previously observed in many XRD studies of Zr alloys [52, 91, 125, 325, 326].

No reflections associated with sub-oxide phases or oxygen bearing Zr (i.e. ZrO_x-type or ω -Zr observed in autoclave Zr-alloys [77, 327]) were detected in the in-reactor corroded Zry-2 (3 to 4 cycles) water rods, coherent with previous XRD of irradiated Zry-2 materials [91, 325] where no suboxide was seen using a synchrotron microbeam. APT measurements by Sundell *et al.* [233] revealed only a very thin suboxide layer of about 50 nm in a high burnup Zry-2 material which suggests that the oxide layer is too thin in the in-pile materials to be detected with microbeam XRD. Chollet *et al.* suggested that the diffusion of O in Zr alloys is enhanced by irradiation, supported by traces of suboxide phases in non-irradiated Zry-2 channel material

[325]. However the thickness of this non-stoichiometric oxide layer is highly dependent on the *Zr* alloy composition as suboxides as thick as 3-4 μm were seen near the metal/oxide interface of in-reactor corroded *Zr*-2.5%*Nb* alloys [328].

While investigating the near oxide layer of material 14 where metallic nickel was seen in the oxide up to 12 μm from the metal/oxide interface (Figure 3-21, sample 14-B), it was not possible to detect *fcc Ni* peaks in the XRD patterns at these locations. The main peak of *fcc Ni*, (111), overlaps with the peaks (211) and ($\bar{2}$ 02) of *m-ZrO₂*, which makes it challenging to detect due to the low concentration of *Ni* in *Zry*-2. Additionally, APT results [329] indicated no significant clustering of *Ni* in the oxide layer of high HPUF *Zry*-2 materials, suggesting no formation of *fcc Ni*. The location of the remaining metallic nickel atoms in the oxide layer of material 14 is further discussed in the next chapter.

The experiment setup at beamline 34-ID-E of the APS (ANL) allowed a 2θ range of [15-50°] with an azimuthal range of about 100° at low 2θ , and up to 120° at high 2θ . The energy of the beamline was set at 8.5 *keV* to scan a similar volume at each point across the metal and oxide layers than during the XANES measurements ($E \sim 8.4$ *keV*). At this energy, the 2θ angles corresponding to the high intensity diffraction peaks of the phases of interest (α -*Zr*, δ -*ZrH*, *m-ZrO₂*, and *t-ZrO₂*) are located between 25° and 35°. The large azimuthal range allowed for an analysis of the tetragonal fraction without correction, except for materials 9 and 12 who suffered from being too close to the sample holder edge during the experiment. This issue reduced the azimuthal of the XRD pattern when examining these samples, especially at low diffraction angles and a correction factor was estimated to input the tetragonal fraction for these materials as further discussed in the next sections. However, the azimuthal range was wide enough for analysis of the texture and of the grain sizes in all of the samples. Additionally, a rectangular shadow near the vertical azimuthal angle was observed in all the XRD patterns collected from the different

materials and is attributed to the XRD experimental setup, without clear identification of its origin. It was observed to slightly lower the intensity in this region for all patterns and therefore was overlooked during the XRD analysis.

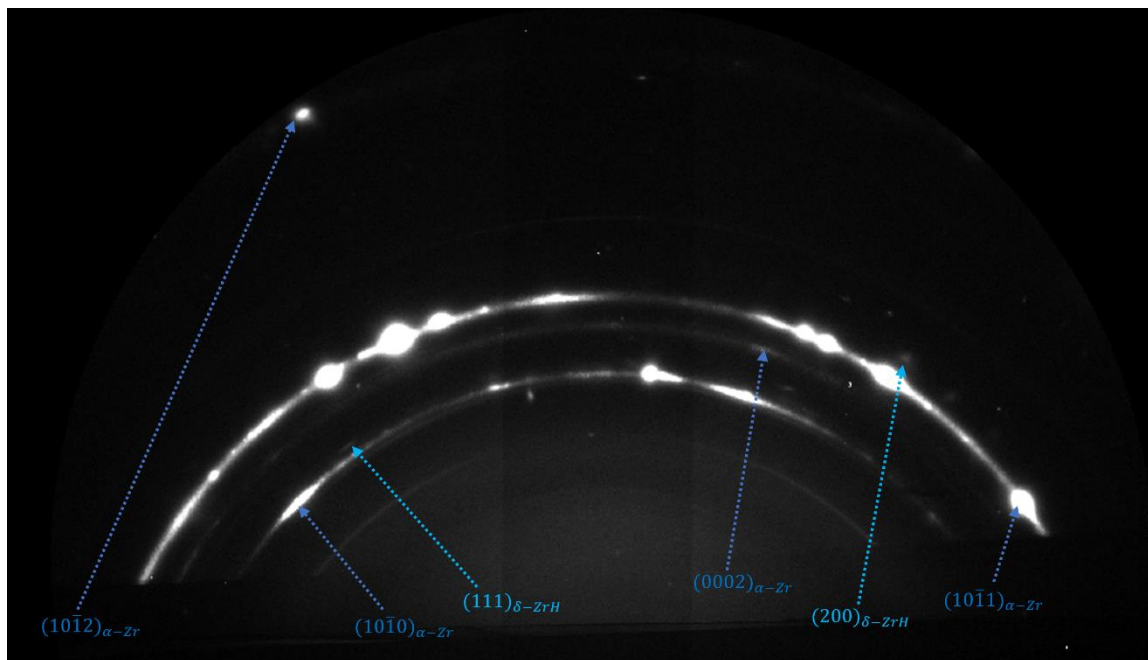


Figure 4-1: X-ray diffraction pattern in the metal region of material 11 (10 μm from the metal/oxide interface).

As mentioned above, four phases were identified using the XRD patterns in the metal and oxide of the Zry-2 water rods: $\alpha\text{-Zr}$, $\delta\text{-ZrH}$, $m\text{-ZrO}_2$ and $t\text{-ZrO}_2$. Clear differences can be seen in the 2D patterns in Figures 4-1, 4-2, 4-3 between the metallic and oxide regions and these differences highlight the main characteristics of the metallic and oxide grains. Starting with the metallic phase, the main reflections for $\alpha\text{-Zr}$ correspond to the $(10\bar{1}0)$ and $(10\bar{1}1)$ crystal planes in the hexagonal crystal structures – also labeled as (100) and (101) reflections in other studies – and are defined by incomplete low intensity arcs and high intensity diffraction spots. The diffraction spots originate from the micrometric grains of the bulk which are larger than the beam size as observed in many studies before [52, 89, 91, 325, 330].

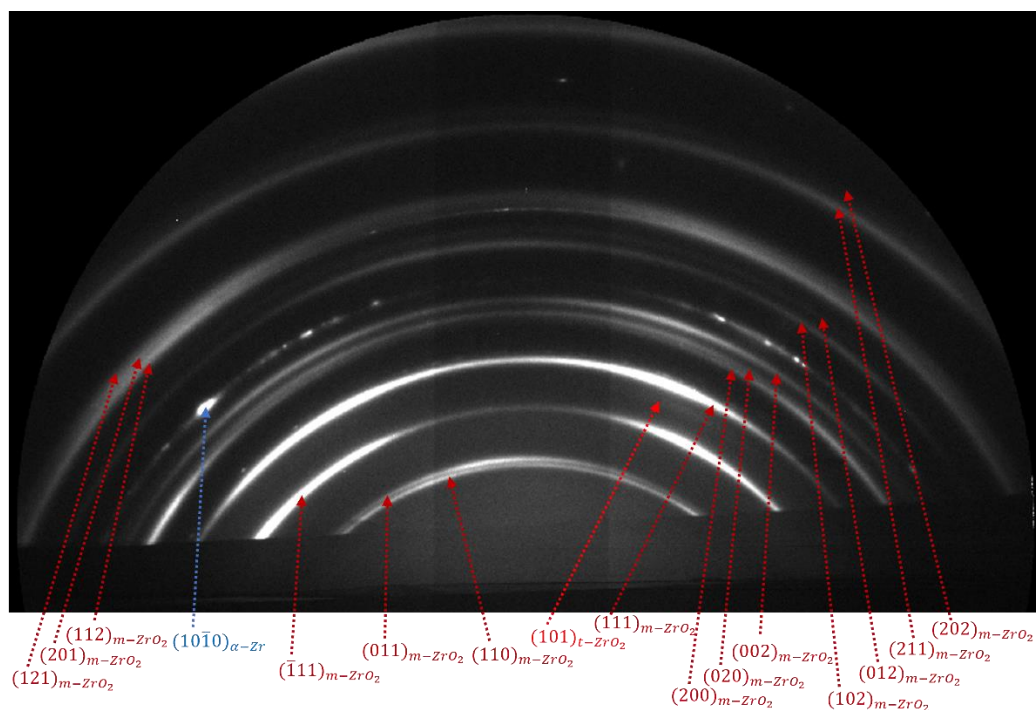


Figure 4-2: X-ray diffraction pattern in the near oxide region of material 11 (2.25 μm from the metal/oxide interface).

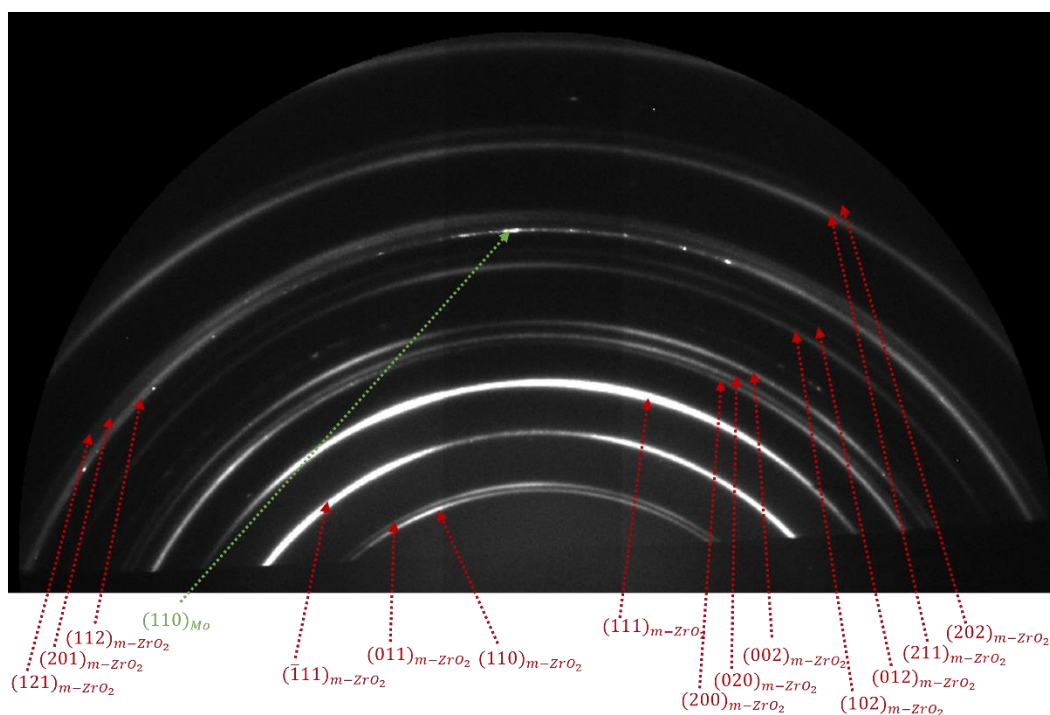


Figure 4-3: X-ray diffraction pattern in the far oxide region of material 11 (25.75 μm from the metal/oxide interface).

For the hydride phase ($\delta\text{-ZrH}_{1.66}$), the main XRD peak corresponds to the (111) set of planes, and a secondary peak (200) was seen at some locations in the metal regions of the samples (as seen in Figure 4-1). Hydrides in Zry-2 and Zry-4 at concentrations 300 – 600 *wt.ppm* are dominantly in the non-stoichiometric *fcc* $\delta\text{-ZrH}_2$ phase with a typical ratio of 1.66 [331]. For simplicity, $\delta\text{-ZrH}_{1.66}$ is labeled as $\delta\text{-ZrH}$ in this study and was observed in the metal region of all materials, with significant spatial variations. The reflections are typically localized, even point like for the (200) signal in Figure 4-1, suggesting micrometric hydrides with preferred orientation in the metal region. The presence of hydride in these materials is coherent with their hydrogen concentration (200 – 1700 *wt.ppm*), orders of magnitude higher than the terminal solid solubility for precipitation (TSSp) of *H* in *Zr* at room temperature (0.13 *wt.ppm*) [164]. No other hydride phases ($\gamma\text{-}$ or $\epsilon\text{-ZrH}$) were detected in the 2D XRD patterns collected in both the low *H* pickup (250 *wt.ppm* and 329 *wt.ppm*) and high *H* pickup (600 *wt.ppm* and 1721 *wt.ppm*) materials, which suggests that at high *H* content (above 600 *wt.ppm* to 1800 *wt.ppm*), hydrides in *Zr* alloys are still mostly the $\delta\text{-ZrH}$ types, as predicted by the *Zr-H* phase diagram (Figure 1-16). Shivprasad [91] had observed traces of $\epsilon\text{-ZrH}$ in some of the Zry-2 water rod materials but this could not be confirmed in this study. However, local variations in hydride concentrations and the overlap of $\delta\text{-ZrH}$ and $\epsilon\text{-ZrH}$ reflections complicate the detection of $\epsilon\text{-ZrH}$ in these materials.

On the other hand, the oxide layer is composed mainly of fine (nanometric) monoclinic oxide grains identified by the limited circles or arcs at the diffraction angles of the crystal planes (Figure 4-2 and Figure 4-3). Fine oxide grains between 20-50 *nm* in size have been observed in many TEM and XRD studies of the oxide layers of *Zr* alloys [52, 89, 91, 325]. The high intensity reflections for *m-ZrO*₂ are from the ($\bar{1}11$) and (111) crystal planes and reveal preferred orientation of the oxide grains as the arc intensity varies along the azimuthal range of the 2-D

patterns. These two reflections are used for calculation of the tetragonal fraction in the oxide using the Garvie-Nicholson formula (Eq. 2-7). Additionally, preferred orientation is further investigated with the intensities of the main diffraction peaks of the metal and oxide phases, with as special focus on the (200) family of monoclinic crystal planes – (200), (020), and (002) *m-ZrO₂* – and is the topic of section 4.3 later in this chapter. Lastly, small fraction of tetragonal *ZrO₂* near the metal oxide interface have been identified with the maximum intensity (101) peak in all of the materials (shown in Figure 4-2 for material 11) and was used to compute the tetragonal volume fraction in these locations. The tetragonal fraction has been related to oxidation kinetics and hydrogen pickup [91, 332] and is further investigated in section 4.2.2. (002) reflection for *t-ZrO₂* has been observed in other studies but it overlaps with the (200) *m-ZrO₂* reflections. Because the (101) intensity was so low in our materials already, it was not possible to deconvolute (200) *t-ZrO₂* peak from the (200) *m-ZrO₂*. Preferred orientations of the tetragonal grains are reported in literature [52, 89, 91, 325] but could not be investigated in this study as the signal was too low, and only the tetragonal volume fraction using the (101) *t-ZrO₂* reflection was investigated. As mentioned in chapter 1, the tetragonal phase is not expected at the temperatures and pressures of the reactor based on the *Zr-O* phase diagram (Figure 1-9) but is stabilized in the oxide layers of *Zr* alloys by small crystallite sizes, alloying elements, oxygen vacancies and compressive stresses [86-89, 333]. Hence it is mostly located near the metal/oxide interface where the oxide crystallites start nucleating and the compressive stresses are maximized.

The 2D XRD patterns shown in Figures 4-1, 4-2, and 4-3 were then integrated along the azimuthal range with DIOPTAS software and further processed with PEAKFIT program as presented in section 2.4.4. For all four samples, background was fitted and removed, and all peaks were identified and fitted to obtain the centroids, areas, and widths of the crystal planes reflections. The indexed 2θ plots (normalized to the maximum intensity) corresponding to the 2D patterns in the metal, in the near oxide and in the far oxide of material 11 (shown in Figure 4-1, 4-

2 and 4-3 respectively) are compared in Figure 4-4. The diffraction peaks correspond to four phases identified in the oxide - α -Zr, δ -ZrH, m -ZrO₂, and t -ZrO₂ – as described above. The crystal plane indices, the PDFs d -spacings and intensities, and the peak centroids from the XRD patterns (average over the full metal and oxide regions) are shown for all materials in Table 4-1, while the 2θ differences with the PDF values at $E = 8.5$ keV are gathered in Table 4-2.

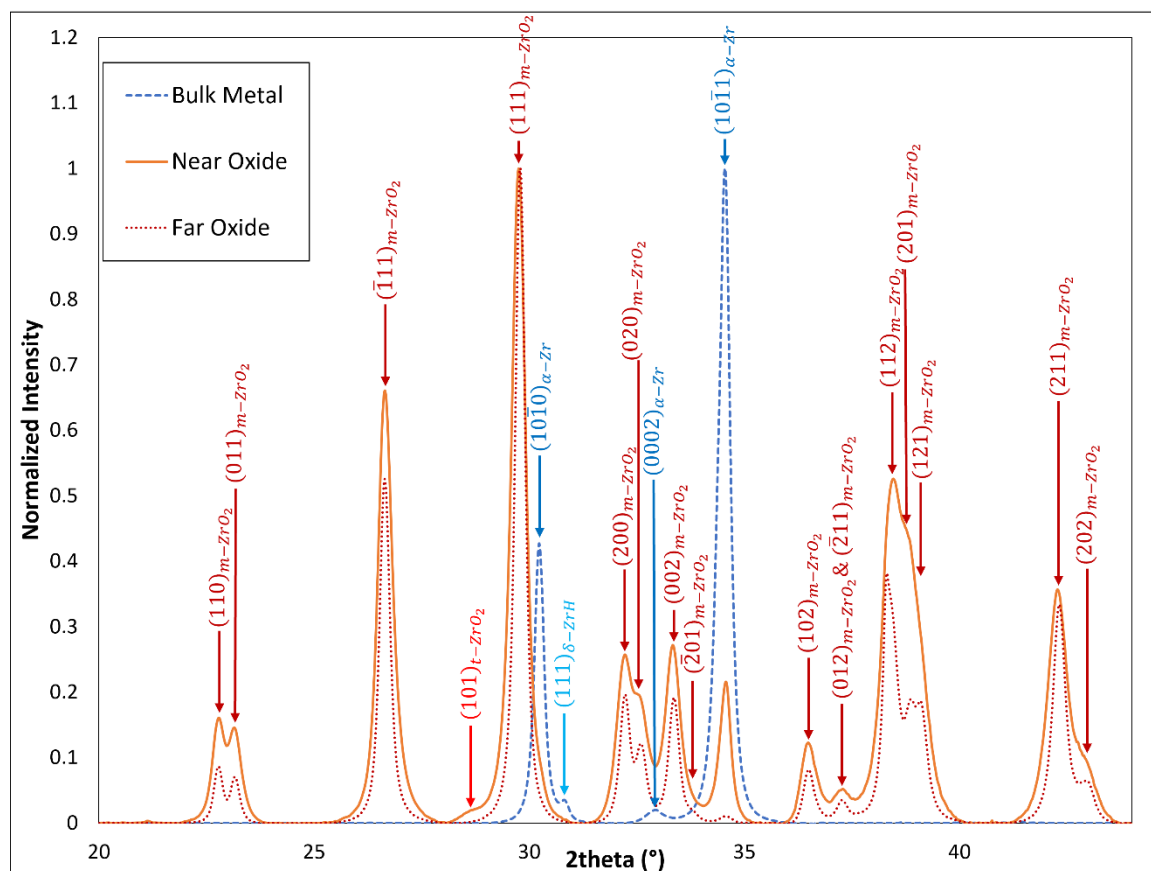


Figure 4-4: Integrated X-ray diffraction patterns in the three regions of material 11 presented above: metal region (blue dashed line); near oxide region (orange line); far oxide region (red dotted line). XRD patterns have been processed with DIOPTAS as presented in SECTION 2.4.4.

In the metal XRD pattern (dashed blue line) in Figure 4-4, it can be seen that the intensity of the (0002) α -Zr crystal plane is much lower than that of (10 $\bar{1}$ 0), while their PDF intensities are similar: 33% and 32% of (10 $\bar{1}$ 1) intensity. This discrepancy in intensity reflects the preferred orientations of the metal grains [23, 116] and is further discussed in section 4.3. The main peak for tetragonal zirconia (101) and for the delta hydride (111) can be on each side of the (10 $\bar{1}$ 0)

reflection in the bulk metal pattern. The rest of the reflections are attributed to the monoclinic ZrO_2 grains as labelled. Similar to the metal reflections, the differences in intensity between the XRD peaks in the near oxide (orange line) and in the far oxide (red dotted line) indicate preferred orientation of the nanometric oxide grains. Moreover, it can be seen that the monoclinic reflections in the near oxide are broader than in the far oxide. Broadening of the XRD peaks originates from the grain growth as the oxide thickness increases so that the grains in the far oxide are bigger than the grains near the metal/oxide interface, as further investigated in section 4.2.3. It should be noted that non-uniform stresses in the oxide may increase broadening of the peak as well [89] but it is generally accepted that stresses are in-plane near the oxide/metal interface in the oxide layers of *Zr* alloys [87]. Additionally, the increase of monoclinic grain sizes in the oxide layers was observed by TEM [89] suggesting that peak narrowing in the far oxide is mainly due to grain growth. Therefore, peak broadening was assumed to result from grain growth and from instrumental broadening only in this study, considering the stresses to be uniform in the regions investigated.

The integrated 1D 2θ plots were then fitted with the identified peaks and the resulting centroid (averaged over the whole oxide thickness) are compared to the PDF diffraction angles in Table 4-1, while the d -spacing differences ($\Delta d/d$) are gathered in Table 4-2. The crystal planes for which no centroid was used during the fit are identified with *NA* in the tables. As such, the first two low intensity monoclinic peaks – (110) and (011) – were not seen in the diffraction patterns of materials 9 and 12. As mentioned before and further detailed in the next section, the sample holder edge was closer for these two materials so that the 2θ range was shortened, and no signal was collected at these diffraction angles (22.75° and 23.12° respectively). All of the measured centroids are close to the PDF values ($\Delta 2\theta < 0.2^\circ$) except for the tetragonal peak (101) located about 0.5° above its literature value in all of the materials. This shift to higher diffraction angles has been observed in previous work [52, 89, 91, 120, 236, 325] and has been hypothesized

to result from the high compressive stresses [86, 325, 333]. In an extensive study of the existence of $t\text{-ZrO}_2$ by Liao *et al.* [87], the authors argue that in order to stabilize $t\text{-ZrO}_2$ at reactor and room temperatures, a deviation of $t\text{-ZrO}_2$ from its normal state must exist. The deviation can consist of the presence of compressive stress, but also of alloying elements or oxygen vacancies doping, or of very fine crystallite sizes, which will commonly lead to variations in lattice parameters. Therefore, the shift to higher diffraction angles for the tetragonal reflection is inherent to the metastability of $t\text{-ZrO}_2$ in the monoclinic oxide layer of Zr alloys.

Investigating the (111) $\delta\text{-ZrH}$ centroids, a shift to higher diffraction angle is seen in all materials (0.3° to 0.17°) suggesting a systematic decrease of the hydrides crystal plane d -spacing (negative values in Table 4-2). This smaller d -spacing may reflect the presence of compressive stresses in the metal near interface as reported in previous studies [89, 91, 325]. Additionally, the tendencies of the (200) family ($m\text{-ZrO}_2$) are seen consistent in all materials with lower d -spacings for the (200) and (002) planes and a larger d -spacing for (020) planes. Therefore, (200) and (002) planes are under tensile stresses in the oxide layer while the (020) planes are in compression. In section 3.4, it is observed that the (200) direction is somewhat aligned with the oxide growth direction. Because $\beta = 99.53^\circ$ in monoclinic zirconia, compressive stresses parallel to the metal/oxide interface applied on the aligned oxide grains squeeze the (020) crystal planes while the (200) - and (002) to a lesser extent - d -spacing increases. As the values are average of the whole oxide layer, these crystal plane d -spacing differences suggest that residual stresses are present throughout the whole oxide layer in these materials.

Lastly, no clear differences could be drawn from the analysis of the averaged XRD peak centroids in terms of hydrogen pickup, fluence, elevation or time in the reactor. Therefore, macroscopic stresses are likely not responsible for the enhancement of hydrogen pickup during the additional cycle in the reactors.

Table 4-1: Peak centroids of the Zry-2 metal and oxide phases from the data collected in the low (Mat. 9 - low elevation; Mat. 11 - high elevation) and high (Mat. 12 - low elevation; Mat. 14 - high elevation) hydrogen pickup materials and from the Powder Diffraction Files. XRD beam energy was set at 8.5 keV at beamline 32-ID-E of the APS (ANL). Peak centroids in the materials were averaged over the metal and oxide regions scanned.

Phase	(hkl)	d-spacing PDF [Å]	Intensities PDF	2θ [°]				
				PDF	Mat. 9	Mat. 11	Mat. 12	Mat. 14
<i>m</i> -ZrO ₂	(110)	3.698	14%	22.75	NA	22.77	NA	22.77
<i>m</i> -ZrO ₂	(011)	3.639	10%	23.12	NA	23.17	NA	23.15
<i>m</i> -ZrO ₂	($\bar{1}$ 11)	3.165	100%	26.65	26.64	26.65	26.63	26.64
<i>t</i> -ZrO ₂	(101)	2.995	100%	28.19	28.69	28.64	28.64	28.63
<i>m</i> -ZrO ₂	(111)	2.841	68%	29.75	29.77	29.78	29.73	29.75
α -Zr	(10 $\bar{1}$ 0)	2.798	33%	30.22	30.26	30.26	30.21	30.25
δ -ZrH	(111)	2.761	100%	30.64	30.81	30.76	30.67	30.73
<i>m</i> -ZrO ₂	(200)	2.623	21%	32.29	32.21	32.22	32.18	32.20
<i>m</i> -ZrO ₂	(020)	2.606	11%	32.50	32.59	32.61	32.56	32.59
α -Zr	(0002)	2.573	32%	32.93	32.91	32.88	32.88	32.91
<i>m</i> -ZrO ₂	(002)	2.540	13%	33.37	33.34	33.35	33.31	33.33
α -Zr	(10 $\bar{1}$ 1)	2.459	100%	34.51	34.53	34.56	34.48	34.54
δ -ZrH	(200)	2.761	47%	35.52	NA	NA	NA	NA
<i>m</i> -ZrO ₂	(102)	2.334	4%	36.42	36.47	36.49	36.44	36.48
<i>m</i> -ZrO ₂	(012)	2.285	0.1%	37.23	37.25	37.27	37.21	37.22
<i>m</i> -ZrO ₂	($\bar{2}$ 11)	2.253	0.1%	37.78	NA	NA	NA	NA
<i>m</i> -ZrO ₂	(112)	2.253	12%	38.47	38.46	38.42	38.43	38.44
<i>m</i> -ZrO ₂	(201)	2.192	5%	38.87	38.83	38.83	38.79	38.81
<i>m</i> -ZrO ₂	(121)	2.181	5%	39.08	39.11	39.11	39.07	39.09
<i>m</i> -ZrO ₂	(211)	2.020	7%	42.32	42.29	42.30	42.25	42.27
<i>m</i> -ZrO ₂	(202)	1.991	6%	42.98	42.92	42.93	42.86	42.91

Table 4-2: Relative differences in d-spacing of the Zry-2 metal and oxide phases between the data collected in the low (Mat. 9 - low elevation; Mat. 11 - high elevation) and high (Mat. 12 - low elevation; Mat. 14 - high elevation) hydrogen pickup materials and the values from the Powder Diffraction Files. XRD beam energy was set at 8.5 keV at beamline 32-ID-E of the APS (ANL). d-spacings differences in the materials were averaged over the metal and oxide regions scanned.

Phase	(hkl)	d-spacing PDF [Å]	Powder Diffraction File #	$\Delta d/d$			
				Mat. 9	Mat. 11	Mat. 12	Mat. 14
$m\text{-ZrO}_2$	(110)	3.698	37-1484	NA	-0.001	NA	-0.001
$m\text{-ZrO}_2$	(011)	3.639	37-1484	NA	-0.002	NA	-0.001
$m\text{-ZrO}_2$	($\bar{1}11$)	3.165	37-1484	± 0.000	± 0.000	+0.001	± 0.000
$t\text{-ZrO}_2$	(101)	2.995	42-1164	-0.017	-0.015	-0.015	-0.015
$m\text{-ZrO}_2$	(111)	2.841	37-1484	-0.001	-0.001	+0.001	± 0.000
$\alpha\text{-Zr}$	(10 $\bar{1}0$)	2.798	05-1665	-0.001	-0.001	± 0.000	-0.001
$\delta\text{-ZrH}$	(111)	2.761	34-0649	-0.006	-0.004	-0.001	-0.003
$m\text{-ZrO}_2$	(200)	2.623	37-1484	+0.002	+0.002	+0.003	+0.003
$m\text{-ZrO}_2$	(020)	2.606	37-1484	-0.003	-0.003	-0.002	-0.003
$\alpha\text{-Zr}$	(0002)	2.573	05-1665	+0.001	+0.002	+0.002	+0.001
$m\text{-ZrO}_2$	(002)	2.540	37-1484	+0.001	+0.001	+0.002	+0.001
$\alpha\text{-Zr}$	(10 $\bar{1}1$)	2.459	05-1665	-0.001	-0.002	+0.001	-0.001
$\delta\text{-ZrH}$	(200)	2.761	34-0649	NA	NA	NA	NA
$m\text{-ZrO}_2$	(102)	2.334	37-1484	-0.001	-0.002	-0.001	-0.002
$m\text{-ZrO}_2$	(012)	2.285	37-1484	-0.001	-0.001	± 0.000	± 0.000
$m\text{-ZrO}_2$	($\bar{2}11$)	2.253	37-1484	NA	NA	NA	NA
$m\text{-ZrO}_2$	(112)	2.253	37-1484	± 0.000	+0.001	+0.001	+0.001
$m\text{-ZrO}_2$	(201)	2.192	37-1484	+0.001	+0.001	+0.002	+0.001
$m\text{-ZrO}_2$	(121)	2.181	37-1484	-0.001	-0.001	± 0.000	± 0.000
$m\text{-ZrO}_2$	(211)	2.020	37-1484	+0.001	+0.001	+0.002	+0.001
$m\text{-ZrO}_2$	(202)	1.991	37-1484	+0.001	+0.001	+0.003	+0.001

4.1.2 Background signal from metal and oxide regions

In this section, the author investigates the background signal from different locations in the metal and oxide regions of the Zry-2 materials. Additionally, the reduced XRD patterns during the examination of materials 9 and 12 are discussed. In Figure 4-5, the integrated 1D patterns prior to data reduction and background removal are plotted for the three locations on material 11 described in the previous section: bulk metal (blue dashed line), near oxide (orange line), far oxide (red dotted line). The plots were normalized by the maximum count to allow for better comparison between the three locations.

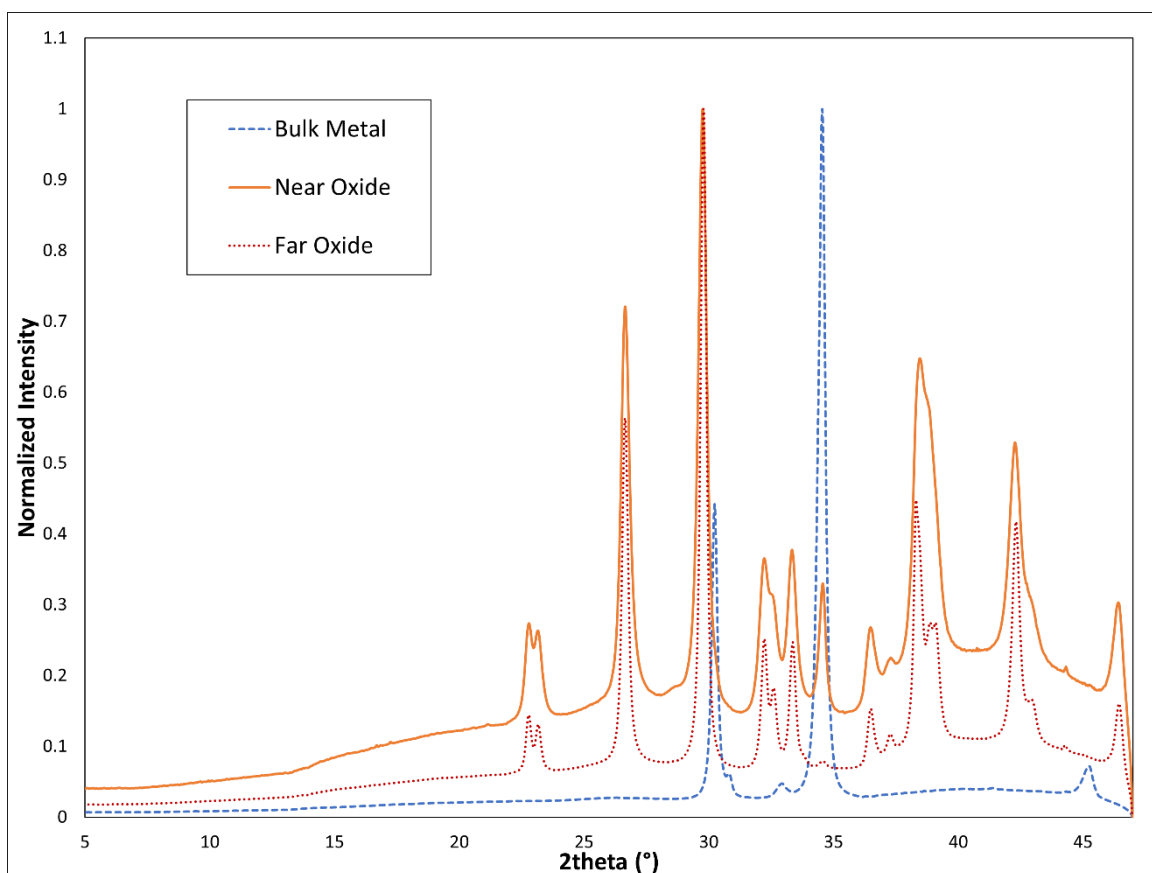


Figure 4-5: Integrated XRD patterns prior to background removal from the three regions of material 11 as presented in the previous SECTION: bulk metal (blue dashed line); near oxide (orange line); far oxide (red dotted line).

It can be seen that the signal-to-noise ratio is the highest in the bulk metal, then lower in the far oxide region, and the lowest in the near oxide region. This observation - generic to all four materials (9, 11, 12, 14) - suggests a lower degree of crystallinity in the oxide layer compared to the bulk material and is coherent with the high disorder due to nucleation of the oxide grains near the metal/oxide interface. Cracks and nano-pores are present in the oxide layer of in pile Zry-2 materials (section 3.2) and may contribute to the background noise as well in the oxide layer.

In Figure 4-6, the integrated 1D pattern prior to background removal from the near oxide region of each of the four materials (9, 11, 12, 14) are displayed. The range of the diffraction angle has been reduced to $[20^\circ; 44^\circ]$ (ROI) and the first intensity points at $2\theta = 20^\circ$ have been aligned for clarity. Firstly, the background signal from all materials is similar to material 14 showing a slightly higher level of noise, suggesting more disorder in material 14 which is coherent with its high fluence and hydrogen content. It can be noticed that the near oxide XRD patterns in material 9 (blue dotted line) and material 12 (orange dashed line) are almost identical while the XRD pattern in material 11 (blue line) is closer to that of material 14 (red line). An interesting feature is the absence of the (110) and (011) reflections of $m\text{-ZrO}_2$ at low 2θ and a reduced (111) $m\text{-ZrO}_2$ (at $2\theta = 26.65^\circ$) in the patterns of material 9 and 12. Lastly, at $2\theta = 32.29^\circ$, the (200) $m\text{-ZrO}_2$ peak is significantly lower for materials 9 and 12 compared to that of materials 11 and 14. While examining the preferred orientation later in this chapter, it can be seen that the (200) reflections are located mostly at the low and high (horizontal) azimuthal angles in the 2D XRD patterns, locations that were partially blocked by the sample holder during examinations of material 9 and 12. Therefore, this difference in (200) intensities is not believed to represent variations in grain orientations between the samples but is rather the result of the blocking of the diffracted beam by the sample holder as described in the previous section and further detailed below. It is worth mentioning that the materials can still be investigated in terms of hydrogen pickup without any correction by comparing material 9 and 12, and materials 11 and

14 by pairs of similar experiment setup (and elevation). In order to compare the tetragonal fraction between all materials, a correction was applied to the intensity of $(\bar{1}11)$ $m\text{-ZrO}_2$ as described in section 4.2.1.

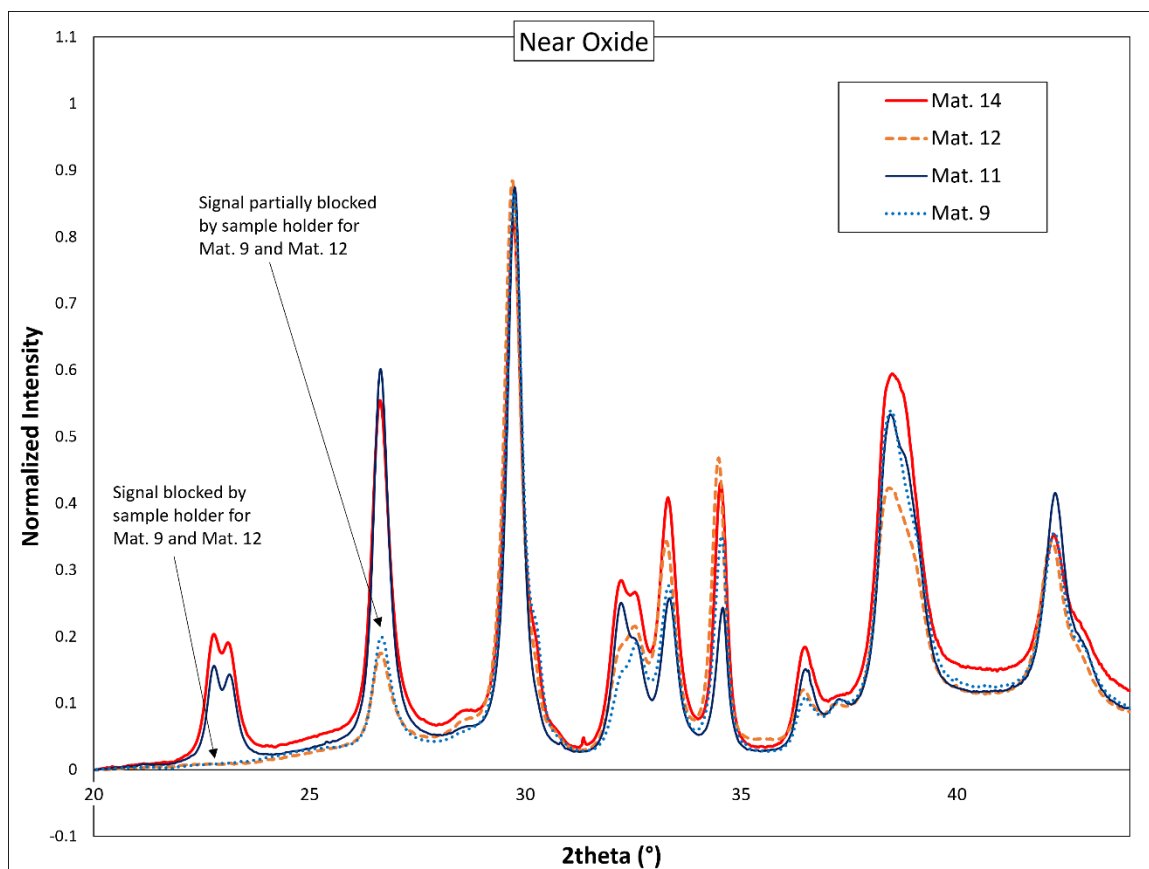


Figure 4-6: Integrated XRD patterns prior to background fit and removal (first intensity points at $2\theta = 20^\circ$ have been aligned for clarity) from the near oxide region ($1.5\ \mu\text{m}$ from the metal/oxide interface) in all four materials.

As mentioned in the previous section and in the precedent paragraph, the XRD patterns collected in materials 9 and 12 suffered from the proximity to the sample holder edge which reduced the 2θ range of the data. This issue is illustrated in Figure 4-7 which gathers the pictures of the sample holders as aligned during examinations (top left image), the schema of the blocking of the beam by the edge of the sample holder (top right image) and the resulting diffraction

patterns for material 11-14 (green arrows and beam, bottom left pattern) and materials 9-12 (red arrows and beam, bottom right pattern). The sample holder was designed for XANES measurements of radioactive samples for which the X-ray detector is placed directly above the sample. The sample edges allowed for easier encapsulation of the radioactive materials but require that the experimenter rotate the samples in order to acquire XRD spectra with the same 2θ range for all materials, utilizing previous beamtime at the APS. Another option is to consider placing only one cross-section sample per holder, but similarly to the first option, it would use additional time in order to exchange the samples at the beamline. Lastly, a flat aluminum plate may be considered for synchrotron measurements, provided that it passes the radioactivity safety review by the APS.

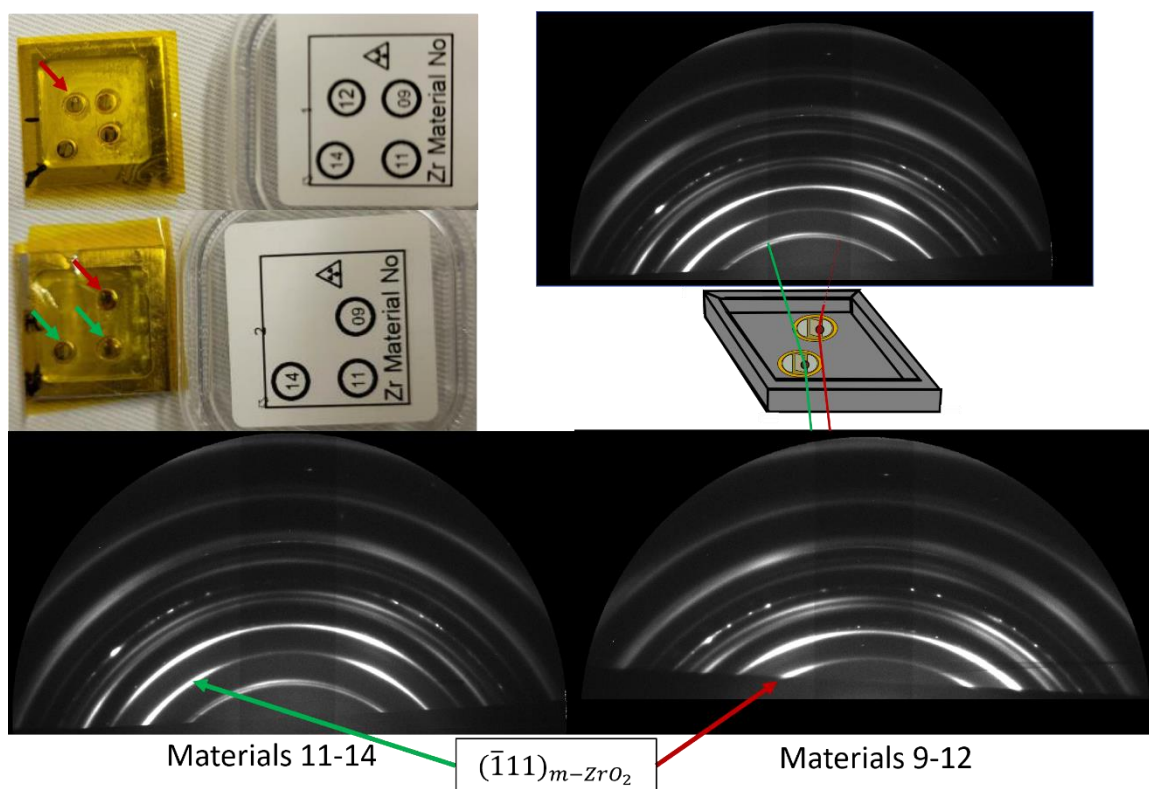


Figure 4-7: Illustration of the blocked beam due to the sample holder for materials 9 and 12 (red arrows and beams) because they were closer to the top of the holder compared to materials 11 and 14 (green arrows and beams)

4.1.3 General observations

In this section, the 1D integrated XRD patterns in the Zry-2 materials as a function of distance from the metal/oxide interface are presented. The integrated XRD patterns evolution across the oxide layers of the low hydrogen pickup samples (materials 9 and 11) are displayed in Figure 4-8, while Figure 4-9 gathers the integrated XRD patterns across the oxide layers of the high hydrogen pickup samples (materials 12 and 14). The flat view of these 2D plots is shown in Figure 4-10 and Figure 4-11 respectively. For each of the materials, the XRD patterns were integrated from 5 μm in the metal up until the water/oxide interface. The general observations of the XRD patterns in the low and high hydrogen pickup materials are now discussed.

First of all, as mentioned in the previous sections, the XRD patterns for material 9 ((b) in Figure 4-8 and Figure 4-10) and material 12 ((b) in Figure 4-9 and Figure 4-11) were shortened due to the proximity of the cross-sections to the sample holder during XRD examination. This issue led to the extinction of the (110) and (011) peaks, and lower ($\bar{1}11$) and (200) reflections in these materials.

Investigating the metallic signal in these patterns, we can see that the high intensity ($10\bar{1}1$) α -Zr reflection has significantly higher counts in materials 12 and 14 (Figure 4-9, Figure 4-11) compared to materials 9 and 11 (Figure 4-8, Figure 4-10). This observation suggests that the orientation of the metal grains at the examined locations in materials 12 and 14 allow for higher reflections when the beam hits the sample with a 14° incident angle and parallel to the metal/oxide interface. The orientations of the highly textured grains in the bulk of Zry-2 varies significantly within micrometers in the samples. Indeed, it can be seen in Figure 4-9 (and Figure 4-11) that the ($10\bar{1}1$) α -Zr intensity reaches a maximum of about 1100 counts at about 2 μm into the metal of material 14, before lowering down to the level in material 9. Similarly, the ($10\bar{1}1$) α -Zr intensity in material 11 ((a) of Figure 4-8 and Figure 4-10), is seen much lower than

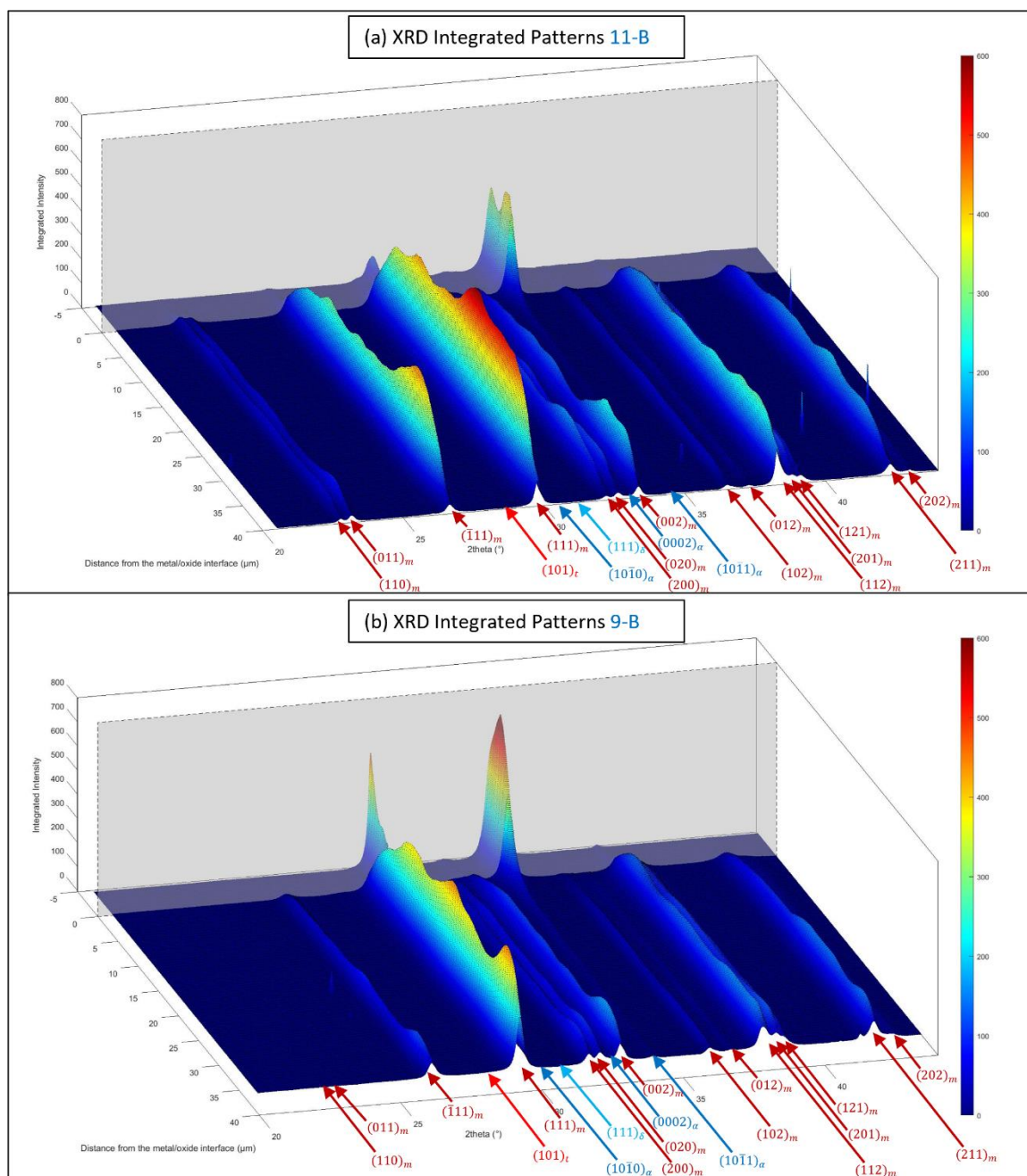
in any other material, but a prolonged scan into the metal (not shown here) revealed much higher counts around 6-7 μm from the metal/oxide interface. These observations suggest several grain orientations ahead of the metal/oxide interface. It is worth mentioning that although the grains are micrometric in the metal region, $\alpha\text{-Zr}$ grain size ranges from 0.5 μm to 30 μm in recrystallized Zr alloys [330]. Therefore, considering the sampling volume of about 4 μm^3 (section 2.3.3) during the XRD measurements, multiple grains with various orientations can be scanned over a range of 10 μm , resulting in discrepancies in metal peak intensities. These observations are further discussed in section 4.3.1 when investigating the orientation of the oxide grains near interface.

When considering the monoclinic crystal planes ($\bar{1}11$) and (111) at $2\theta = 26.65^\circ$ and $2\theta = 29.75^\circ$ respectively, it was already mentioned that ($\bar{1}11$) is significantly lowered in materials 9 and 12 due to the experimental setup. However, the ($\bar{1}11$) reflection was used to determine the metal/oxide interface position by considering the interface as the location where ($\bar{1}11$) intensity is half of that of the first plateau (within the next 10 μm of oxide) as further detailed in the next section. Additionally, it can be seen that the (111) intensity is typically higher than that of the ($\bar{1}11$) reflection, even for materials 11 and 14, and is a marker of preferred orientation in the material, which is further examined in the next section as well by computing the (111)/($\bar{1}11$) ratio across the oxide layer.

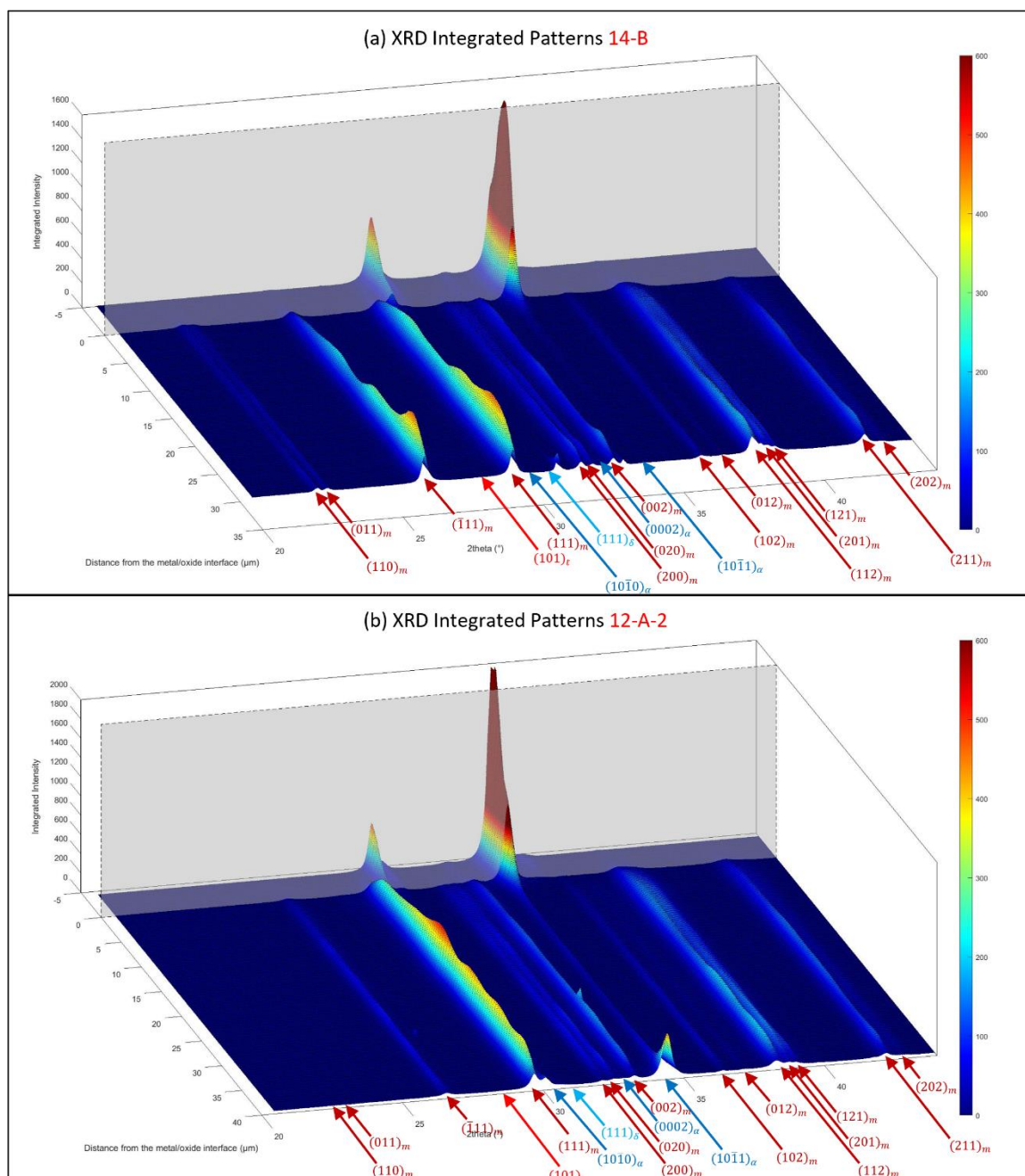
One other interesting observation is the apparent higher monoclinic oxide intensities in the far oxide region ([20 μm ; 35 μm] in both material 11 ((a) in Figure 4-8 and Figure 4-10) and material 14 ((a) in Figure 4-9 and Figure 4-11), whereas for material 9 ((b) in Figure 4-8 and Figure 4-10) and material 12 ((b) in Figure 4-9 and Figure 4-11), the monoclinic peaks are rather constant throughout the whole oxide layer. This may reflect differences in elevation between the two sets of materials leading to different oxidizing conditions. Indeed, materials 11 and 14 were

cut from the high elevation parts of the Zry-2 water rods, where the coolant has reached saturated temperature, and some steam is present. On the other hand, materials 9 and 12 were obtained from low elevation in the water rods where the coolant temperature is lower than the saturated temperature. Considering the variations in power output during operation and the higher neutron flux at high elevation, the oxide layer microstructure in materials 11 and 14 may be more impacted by these parameters than in materials 9 and 12. The first few μm of oxide built on the high elevation materials would have better crystallinity and ordering than the layers built later during operation.

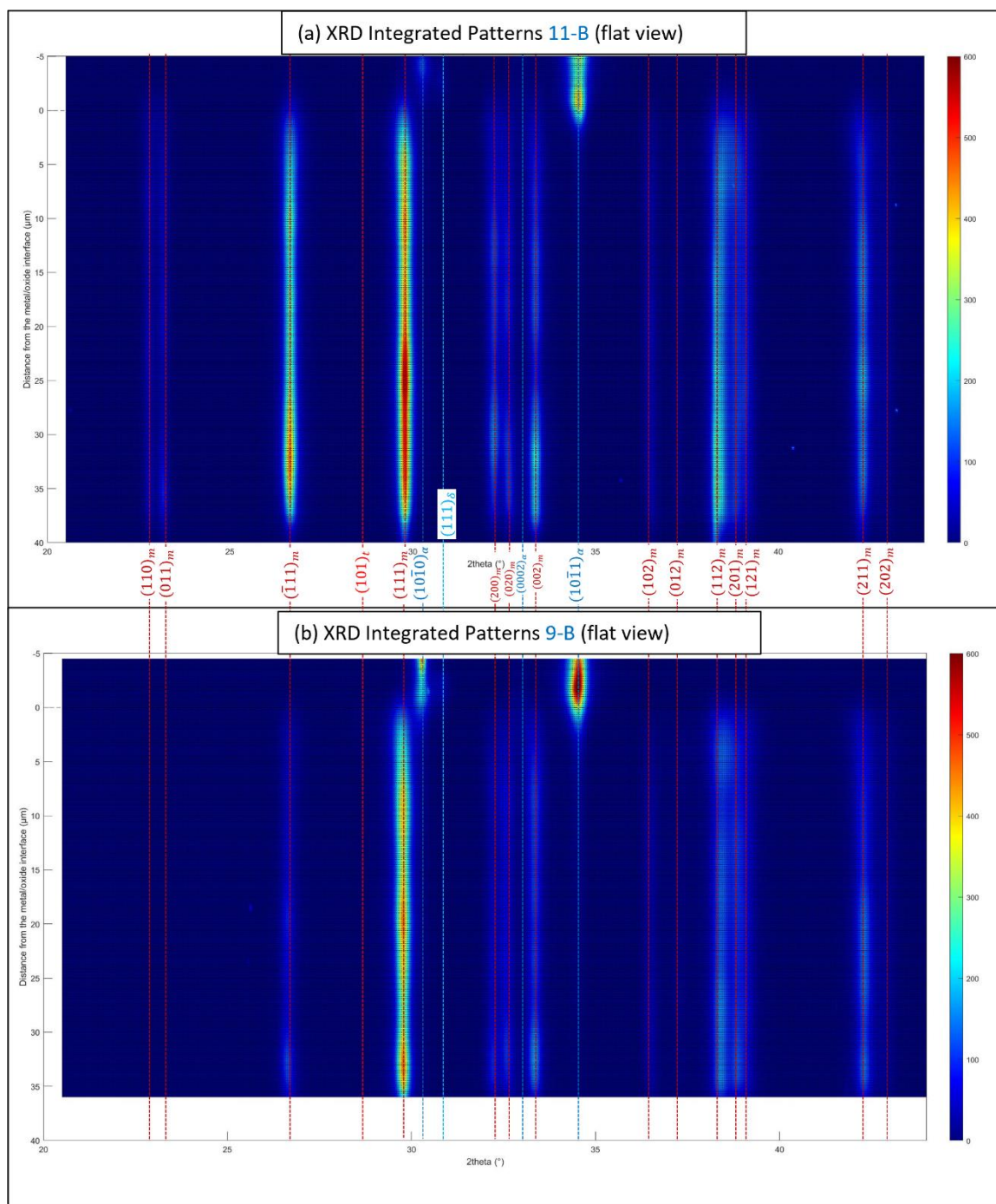
Lastly, the (101) tetragonal zirconia reflection is too low to clearly appear in any of the 2D XRD integrated plots, even close to the metal/oxide interface. The main tetragonal reflection was seen in the XRD pattern (as shown in Figures 4-2, 4-4, 4-5 and 4-6) near the metal/oxide interface, but the counts are too low to be seen in the 2D plots. This resulted in a lower tetragonal volume fraction across the whole oxide layer than previously observed in literature and is further discussed in section 4.2.2.



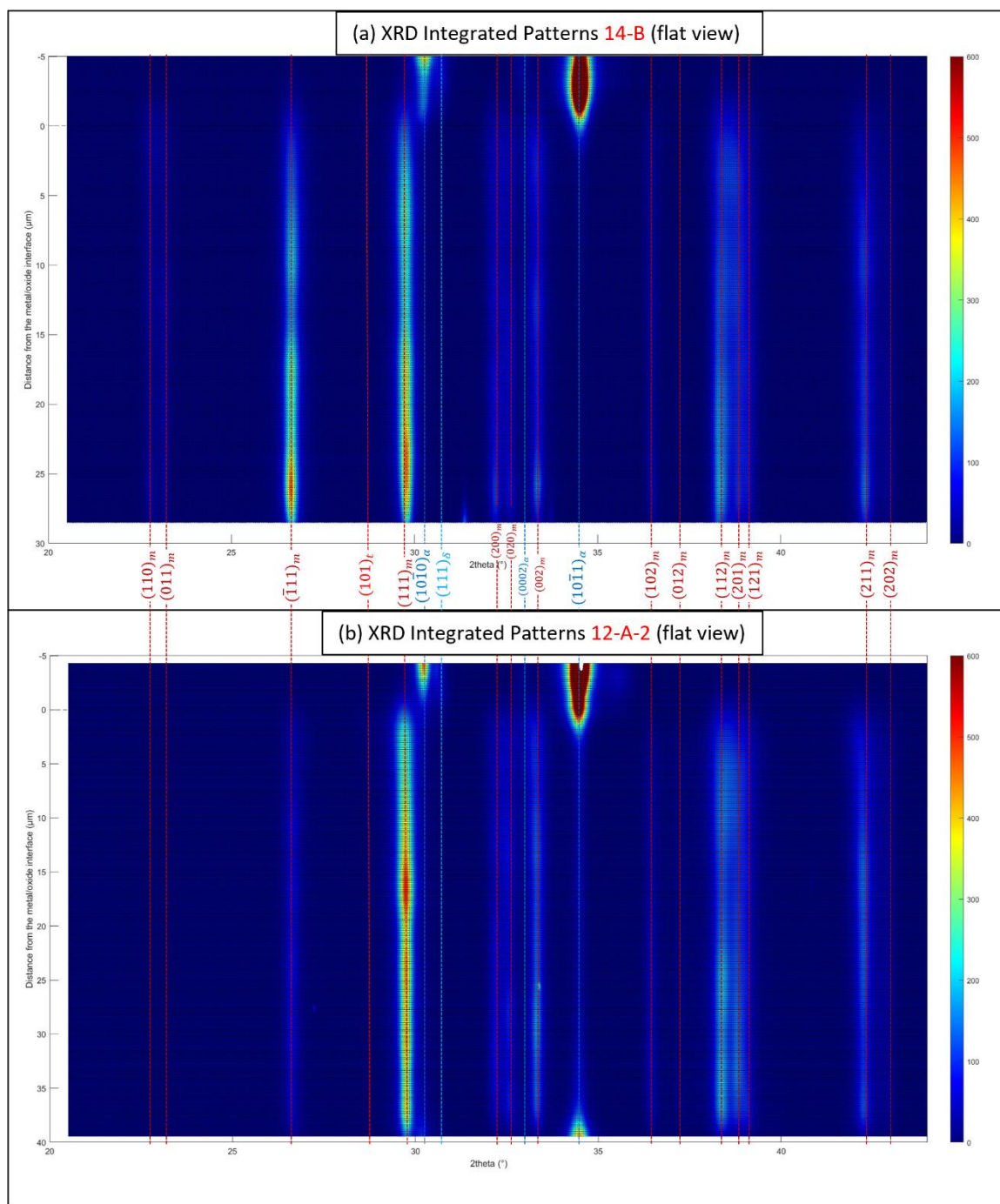
*Figure 4-8: Integrated XRD patterns as a function of distance from the metal/oxide interface at the XANES location of the second scan in the **low** hydrogen pickup materials: (a) Sample 11-B (high elevation, 3 cycles); (b) Sample 9-B (low elevation, 3 cycles).*



*Figure 4-9: Integrated XRD patterns as a function of distance from the metal/oxide interface at the XANES location of the second scan in the **high** hydrogen pickup materials: (a) sample 14-B (high elevation, 4 cycles); (b) sample 12-A-2 (low elevation, 4 cycles).*



*Figure 4-10: Flat view of the integrated XRD patterns as a function of distance from the metal/oxide interface at the XANES location of the second scan in the **low** hydrogen pickup materials: (a) sample 11-B (high elevation, 3 cycles); (b) sample 9-B (low elevation, 3 cycles).*



*Figure 4-11: Flat view of the integrated XRD patterns as a function of distance from the metal/oxide interface at the XANES location of the second scan in the **high** hydrogen pickup materials: (a) sample 14-B (high elevation, 4 cycles); (b) sample 12-A-2 (low elevation, 4 cycles).*

4.2.1 Phase content in the metal near interface and across the oxide layer

Figure 4-12: Normalized integrated area of the maximum intensity XRD peaks for the four phases identified in material 9 (low elevation, low HPUF, 3 cycles): (-111) m-ZrO₂ (red diamond); (101) t-ZrO₂ (orange triangle); (10-10) α-Zr (black square); (101) δ-ZrH (grey circles).

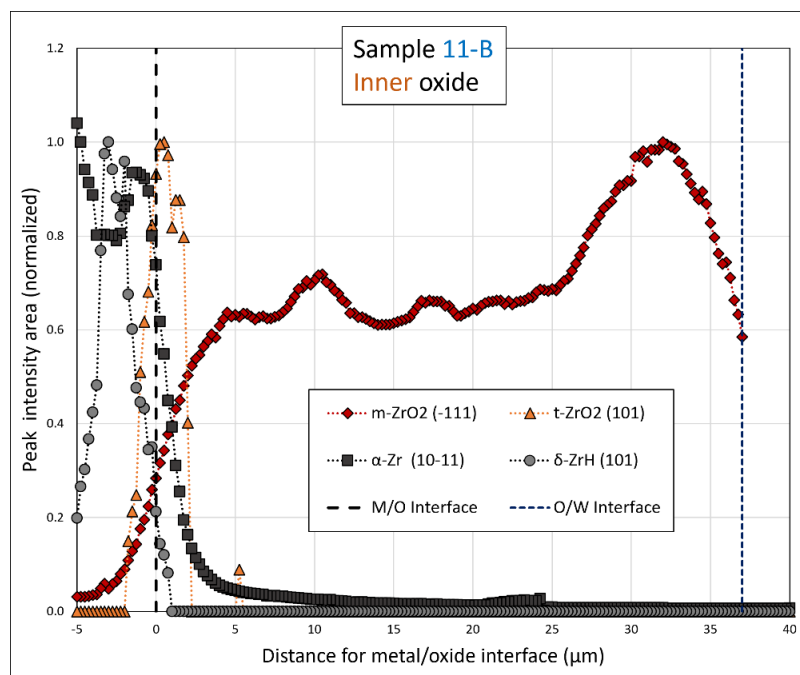


Figure 4-13: Normalized integrated area of the maximum intensity XRD peaks for the four phases identified in material 11 (high elevation, low HPUF, 3 cycles): (-111) $m\text{-ZrO}_2$ (red diamond); (101) $t\text{-ZrO}_2$ (orange triangle); (10-10) $\alpha\text{-Zr}$ (black square); (101) $\delta\text{-ZrH}$ (grey circles).

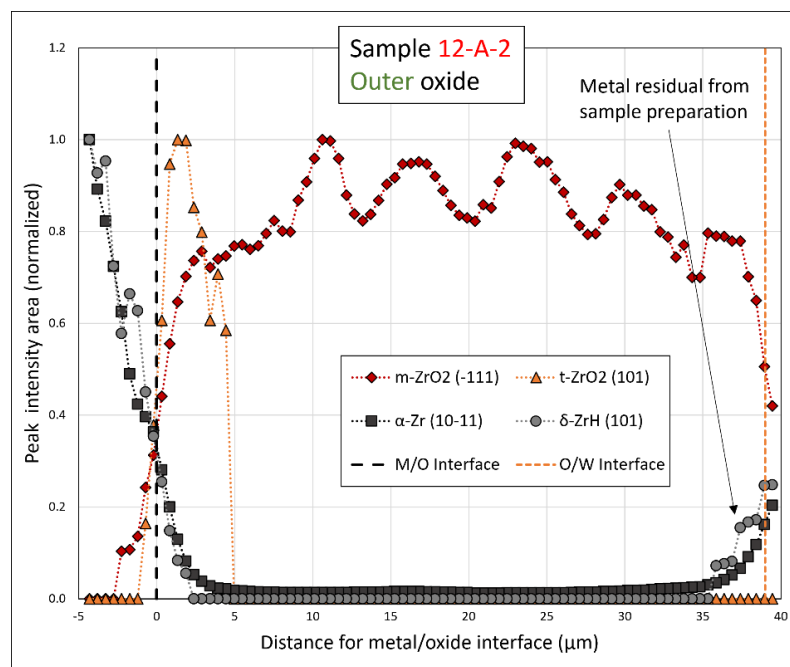


Figure 4-14: Normalized integrated area of the maximum intensity XRD peaks for the four phases identified in material 12 (low elevation, high HPUF, 4 cycles): (-111) $m\text{-ZrO}_2$ (red diamond); (101) $t\text{-ZrO}_2$ (orange triangle); (10-10) $\alpha\text{-Zr}$ (black square); (101) $\delta\text{-ZrH}$ (grey circles).

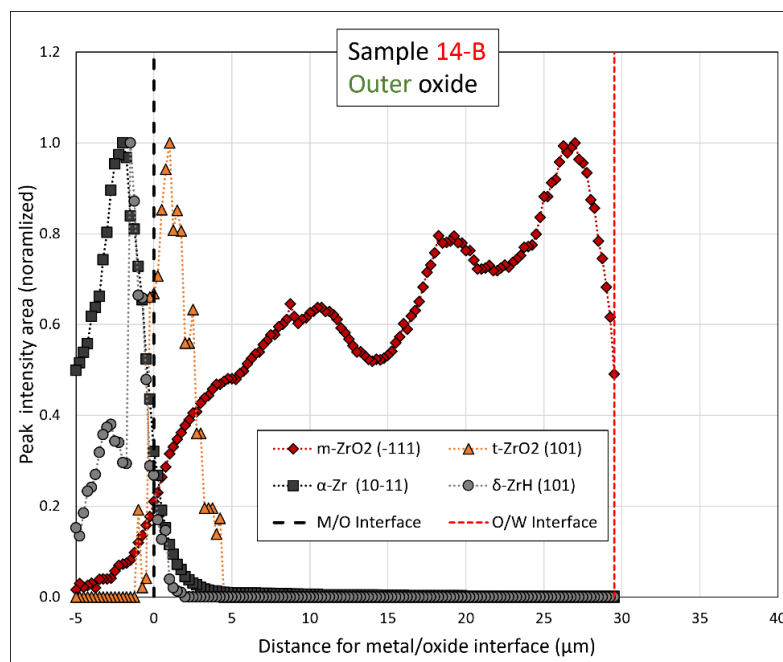


Figure 4-15: Normalized integrated area of the maximum intensity XRD peaks for the four phases identified in material 14 (high elevation, high HPUF, 4 cycles): (-111) $m\text{-ZrO}_2$ (red diamond); (101) $t\text{-ZrO}_2$ (orange triangle); (10-11) $\alpha\text{-Zr}$ (black square); (101) $\delta\text{-ZrH}$ (grey circles).

Starting with the reflections in the metal near the oxide interface, it can be seen in all materials that the (10 $\bar{1}$ 1) $\alpha\text{-Zr}$ peak undergoes clear variations within 5 μm of metal grains. These micrometric fluctuations (pseudo-periodic) in reflection intensity of the main metal peak are coherent with the microstructure of Zry-2 recrystallized materials which is mainly composed of equiaxed grains with a size range of about 1-10 μm [23, 330]. The grains properly oriented with the incident beam provide a strong diffraction signal on the 2D XRD detector while the grains with a less favorable orientation generate a weaker diffraction signal, leading to fluctuations of the high intensity metal peak.

Similarly, (111) ZrH peak was observed in all materials across the metal region and followed micrometric variations within the 5 μm of metal scanned. However, the frequency of variations for (111) ZrH seems higher than for (10 $\bar{1}$ 1) $\alpha\text{-Zr}$, suggesting a lower grain size range for the δ -hydrides, of about 1-5 μm . Hydrides of sizes from 1 to several μm were observed in

high burn up Zry-2 cladding as well by Chollet *et al.* [325]. The presence of hydrides in all materials is coherent with the concentrations of hydrogen being well above the terminal hydrogen solubility for precipitation at room temperature in all materials, as mentioned previously. It is worth mentioning that the terminal hydrogen solubility at 300°C is only 60 wt.ppm [163] of hydrogen, therefore the zirconium hydrides were mainly formed during operation in all materials, while about 60 wt.ppm precipitated during the cooling period.

Surprisingly, both $(10\bar{1}1)$ α -Zr and (111) δ -ZrH peaks can be seen near the oxide/water interface in material 12 (Figure 4-14). After examinations of the scan location in sample 12-A (Figure 3-14), a piece of the alloy cut during sample preparation can be seen above the oxide layer (top left corner) and was identified as the origin of the zirconium and hydride peaks near the water interface.

Focusing now on the main peaks of the oxides phases, $(\bar{1}11)$ m -ZrO₂ reflection was used to locate the metal/oxide interface in these samples. The interface position was set where $(\bar{1}11)$ m -ZrO₂ peak area reached half of the value of the first plateau in the oxide layer. This position corresponded to the position at which 70% of the nickel atoms were still metallic in the oxide layer of all the samples scanned during the second round of measurements (Figure 3-21). Because this correlation was seen in all materials independent of elevation, irradiation time or hydrogen content, the interface location for the samples analyzed during the first round of measurements (Figure 3-20) was set at $f_m = 0.7$ (70% metallic nickel) as described previously.

Once the $(\bar{1}11)$ m -ZrO₂ intensity has reached the first plateau, pseudo-periodic variations follow across the oxide layers of all four materials investigated, of width ranging from 3 to 10 μm . In an extensive study of the oxide layer of Zr alloys corroded in autoclave by Yilmazbayhan [89], the variations in monoclinic intensities were seen shorter (about 2 μm wide) and were associated with the transitions in oxidation kinetics. However, the variations are seen wider in the reactor corroded Zry-2 materials investigated in this study and therefore are not

believed to represent oxide transitions, as was previously observed by Shivprasad at other locations in these water rods [91]. Another source of fluctuations originates from the orientation of the examined grains, but it was mentioned in section 4-1 that the oxide grains are nanometric (20 to 50 nm in size) and therefore the micrometric fluctuations of the monoclinic main peak do not reflect orientation differences from grain to grain. Instead, the author believes that the intensity changes reflect the orientation of the metal grains that were used to build the oxide. Indeed, as mentioned by Chollet *et al.* [325] and presented in section 4.3, the orientation of oxide grains was seen correlated to that of the metal grains near interface, suggesting that the oxide particle orientation is somewhat influenced by the orientation of the metal grains. This would lead to microscopic variations of the oxide grain orientation as observed in all the samples investigated in this study. Therefore, the variations of the monoclinic reflection are considered to result from the preferred orientation of the oxide grains at a microscopic level following the orientation of the metal grains used to build the oxide layer.

Additionally, maximum intensity for the $(\bar{1}11) m - ZrO_2$ reflection is seen in the outer oxide region of materials 9, 11 and 14, as was previously seen by Shivprasad at two other locations from the Zry-2 water rods [91]. In material 12, the presence of metal on the beam path in the outer oxide region (as mentioned above) lowered the intensity of the monoclinic zirconia peak. Still, a bump can be identified in the region $[35 \mu m - 40 \mu m]$ in this material (Figure 4-14). These high intensities near the water interface may reflect that the outer oxide is relatively more ordered than the rest of the oxide layer as this region corresponds to the first few μm of oxide built on the materials, where the oxidation rate is parabolic or cubic (section 1.3.3). In the oxide built closer to the metal interface, the corrosion rate may have followed faster linear kinetics, reducing long range order in the oxide.

Lastly, $(101) t-ZrO_2$ reflection was identified in all materials in the oxide layer close the metal interface only. This observation is coherent with past examinations of Zr alloys oxide and

is further discussed in the next section where the tetragonal fraction is plotted as a function of distance from the metal/oxide interface using the Garvie-Nicholson formula (Eq. 2-7) [275].

In order to continue the analysis of the oxide layer of the Zry-2 water rods as a function of elevation, irradiation time and hydrogen pickup, it was necessary to apply a correction to the $(\bar{1}11)$ $m\text{-ZrO}_2$ peak intensity measured in materials 9 and 12, as a significant portion of the reflection intensity was blocked by the sample holder as mentioned previously. A correction factor, K , was introduced so that the corrected intensity of the $(\bar{1}11)$ $m\text{-ZrO}_2$ peak is given by:

$$I_{corrected} = K * I_{measured} \quad (\text{Eq. 4-1})$$

The correction factor was estimated using a mask on the XRD pattern collected in the near oxide of material 14, as shown in Figure 4-16. In Figure 4-16-(a), the XRD pattern collected in material 14 is displayed, and the corresponding integrated 2θ plot is shown in Figure 4-16-(b). On the same pattern, a mask (red area) representing the shadow of the sample holder was inserted as seen in Figure 4-16-(c), and the resulting integrated 2θ plot is shown in Figure 4-16-(d). In Figure 4-17-(e) is plotted the XRD pattern at the same distance from the metal/oxide layer in material 9 (with the resulting integrated 2θ plot shown in Figure 4-17-(f)) and one can see that the mask in Figure 4-16-(c) corresponds to the sample holder shadow. The peak intensity area for the $(\bar{1}11)$ $m\text{-ZrO}_2$ reflection in both patterns of material 14 (with and without mask) was fitted with PEAKFIT and yielded the correction factor: $K \sim 2.5$. Similar values were observed at other locations in the oxide and therefore $K = 2.5$ was used to compute the $(111)/(\bar{1}11)$ ratio and tetragonal fraction across the oxide layer of materials 9 and 12.

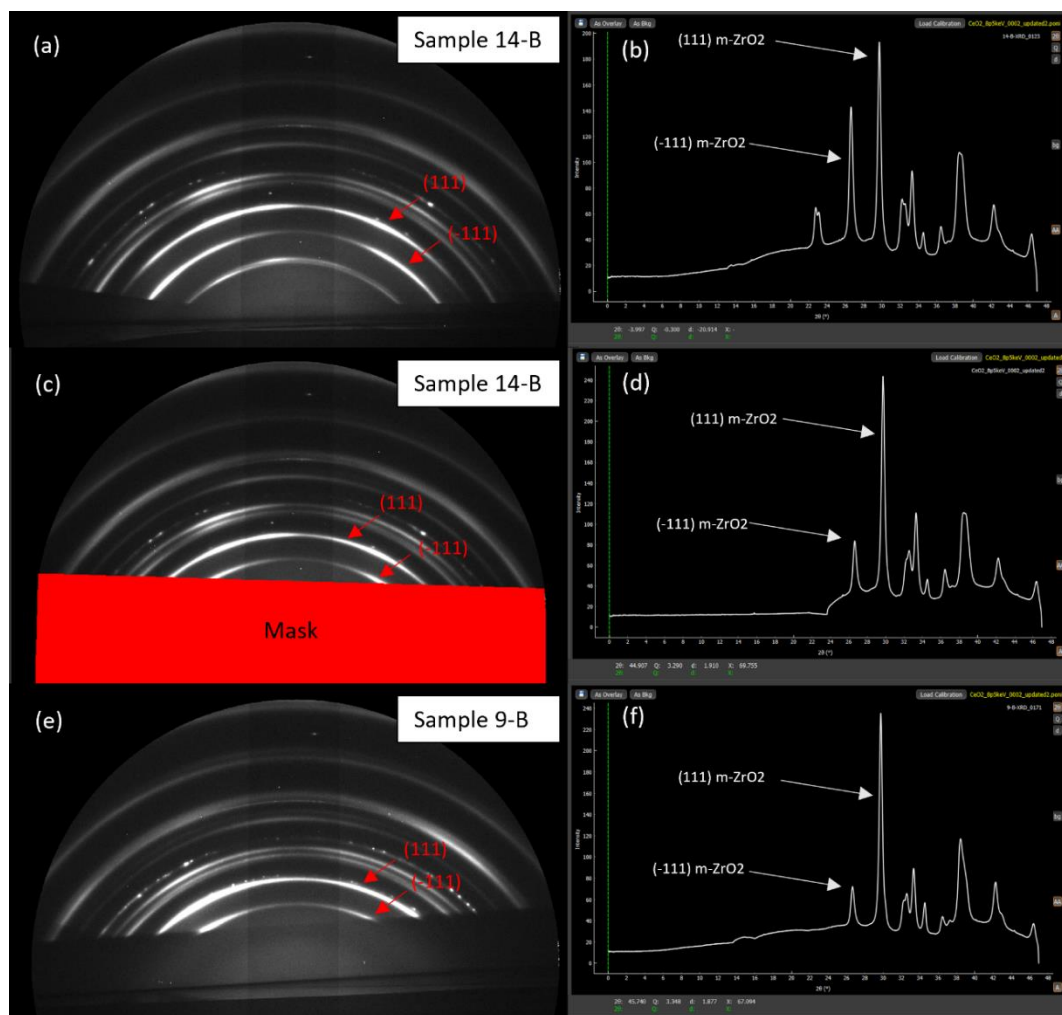


Figure 4-16: XRD images and integrated patterns in the near oxide ($4\ \mu\text{m}$) of: (a)-(b) sample 14-B; (c)-(d) sample 14-B with mask (red rectangle); (e)-(f) sample 9-B. The mask was added in the XRD pattern of material 14 to estimate the correction factor for comparison of the (111) and (-111) peak ratios and tetragonal fraction between all four materials.

In Figure 4-17 and Figure 4-18, the variations of the $(\bar{1}11)\ m\text{-ZrO}_2$ and $(111)\ m\text{-ZrO}_2$ peaks (respectively) across the oxide layer of each of the four Zry-2 materials are compared. As mentioned above and seen in previous work [89, 91, 120, 236], pseudo-periodic fluctuations are seen for both crystal plane XRD intensities in the four Zry-2 materials considered. The widths of these variations have been hypothesized earlier to represent the metal grains from which the oxide layer was built, as the nanometric oxide grains seem to follow the orientation of the metal grains

[325] (section 4.3.1), rather than the periodic oxide transition (usually smaller than $3\ \mu\text{m}$). When comparing materials in terms of hydrogen content, elevation, or irradiation time, no clear differences can be found from the analysis of the two main peaks of monoclinic zirconia.

The large area detector available at beamline 34-ID-E of the APS allowed data collection over a large azimuthal range (100° - 120°). Still, the ratio of the two main peaks of the monoclinic oxide phase $(111)/(\bar{1}\bar{1}1)$ $m\text{-ZrO}_2$ was seen higher than for uniformly oriented oxide grains ($(111)/(\bar{1}\bar{1}1) = 0.68$ from PDFs, Table 4-1) in all the materials considered in this study as seen in Figure 4-19 where the $(111)/(\bar{1}\bar{1}1)$ $m\text{-ZrO}_2$ across the different oxide layers are plotted. Because of the sample holder shadow on the XRD patterns of materials 9 and 12, the correction presented above was applied to the intensity of the $(\bar{1}\bar{1}1)$ $m\text{-ZrO}_2$ peaks so that:

$$(111)/(\bar{1}\bar{1}1)_{\text{corrected}} = (111)/(2.5 * (\bar{1}\bar{1}1)_{\text{measured}})$$

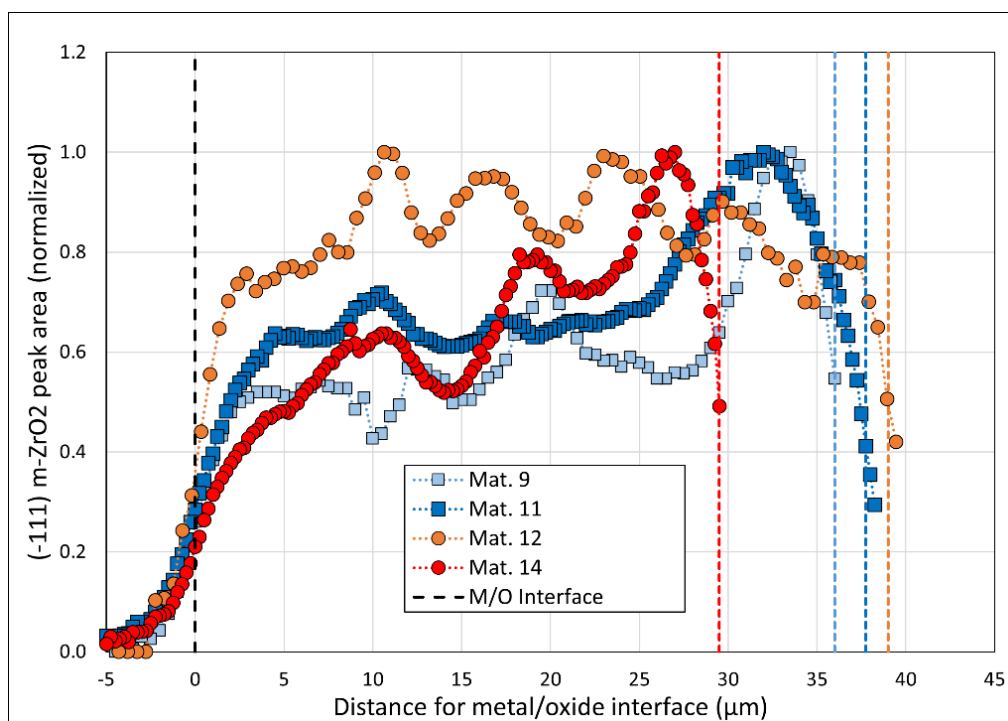


Figure 4-17: (-111) $m\text{-ZrO}_2$ peak area (normalized) in the oxide layers of the Zry-2 materials.

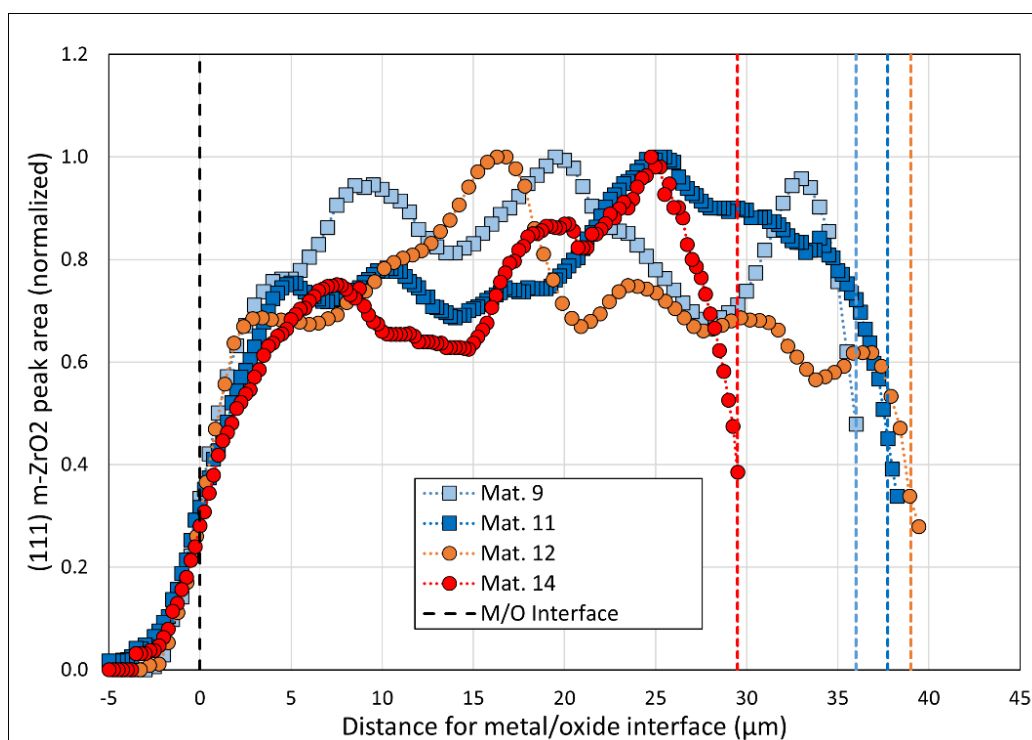


Figure 4-18: (111) $m\text{-ZrO}_2$ peak area (normalized) in the oxide layers of the Zry-2 materials.

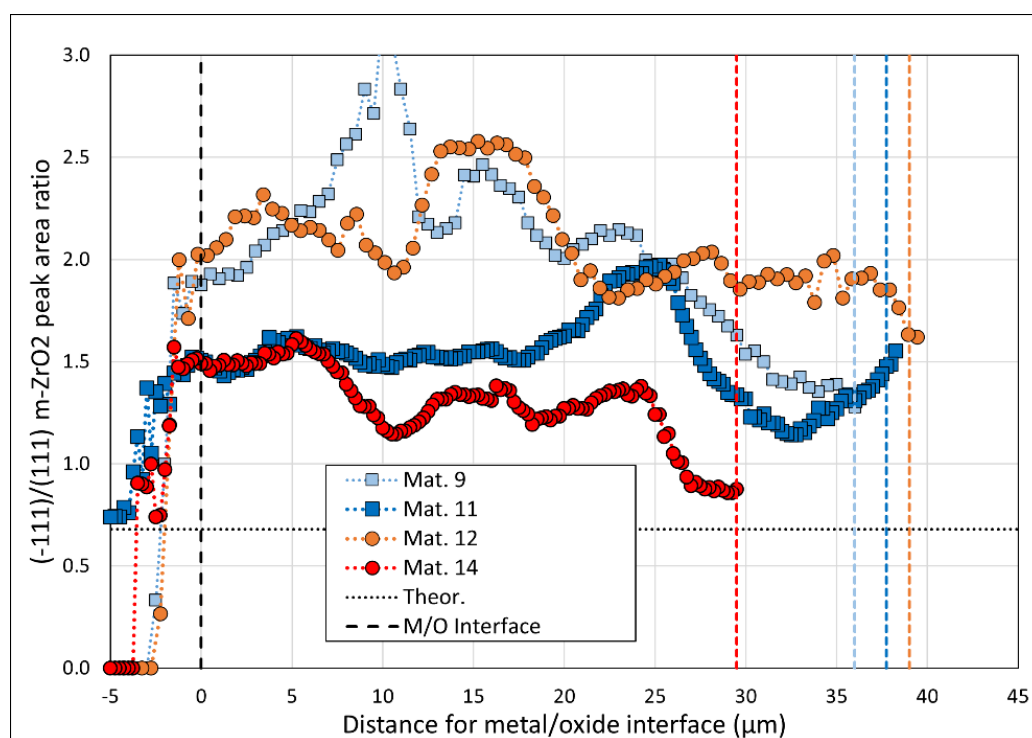


Figure 4-19: (111)/(-111) $m\text{-ZrO}_2$ peak area ratio in the oxide layers of the Zry-2 materials.

From Figure 4-19, the ratio of the peak intensities in material 14 is seen the closest to that of randomly oriented oxide grains with values around 1.5 in the near oxide layer and lowering down to 0.85 in the outer layer. Similarly, the $(111)/(\bar{1}\bar{1}1)$ ratio in material 11 was around 1.5 in the near oxide but only lowering to about 1.3 after a momentary increase in the outer layer. Examining material 12 results, the ratio value near interface is seen higher than in the two high elevation materials (11 and 14) at about 2.0. Ensues a slow decrease throughout the oxide layer to reach about 1.7 in the outer layer, punctuated by a maximum of 2.5 reached $15\ \mu\text{m}$ from the metal interface. Similarly, the intensity ration in material 9 is seen around 2.0 in the near oxide but increases to reach more than 3.0 about $10\ \mu\text{m}$ from the metal interface, and then decreases to attain 1.4 in the outer layer. These higher values for the $(111)/(\bar{1}\bar{1}1)$ ratio observed in the Zry-2 oxide layers suggests preferred orientation of the oxide grains, as reflected in the analysis of the XRD patterns throughout this chapter. The reflection ratio is closer to the theoretical value for uniformly oriented grains in the outer layer of all materials, which suggests a lower degree of preferred orientation in the first oxide layer built on these materials.

No clear differences are seen in terms of hydrogen pickup and irradiation time, but the intensity ratio is seen higher for the low elevation materials compared to the high elevation materials. However, this difference may result from the error associated with the correction factor which was used for both of these materials (9 and 12). In the next sections, the tetragonal volume fraction is quantitatively investigated using the (101) $t\text{-ZrO}_2$, (111) $m\text{-ZrO}_2$, and $(\bar{1}\bar{1}1)$ $m\text{-ZrO}_2$ reflections, and the monoclinic grain sizes are computed using the broadening of the (111) $m\text{-ZrO}_2$ peak.

4.2.2 Tetragonal fraction in Zry-2 oxide layers

The tetragonal fraction across the oxide layers was calculated using Garvie-Nicholson formula (Eq. 2-7), as done in previous work [52, 89, 120, 236, 275]. The results are plotted for all four materials as a function of distance from the metal/oxide interface in Figure 4-20.

For each of the material, the tetragonal phase was observed only close to the metal/oxide interface, leading to a null tetragonal volume fraction past $5\ \mu\text{m}$ of oxide, independently of fluence, elevation or hydrogen content. The reason that the tetragonal phase is absent for the rest of the oxide layer is due to the tetragonal-to-monoclinic phase transformation as the oxide grows, as observed in previous studies [52, 76, 89, 91, 334]. The phase transformation is driven by crystallite growth and by crack formation during oxide transition, which releases stresses in the matrix. As a result, tetragonal grains are no longer metastable within the monoclinic oxide grains and the phase transformation takes place.

When comparing low and high hydrogen Zry-2 materials [91], Shivprasad had observed a higher tetragonal fraction for the materials with low hydrogen pickup. This hypothesis is supported by the higher tetragonal fraction observed in material 9 (low H pickup, low elevation, 3 cycles), and to some extent in material 11 (low H pickup, high elevation, 3 cycles). However the differences are lower ($< 2\%$) than observed by Shivprasad [91] ($\sim 10\%$). Similarly, the maximum tetragonal fraction is seen between 3-6% in our set of materials, much lower than the 15-30% observed at different elevation in these water rods [91]. When investigating the tetragonal phase in different Zr alloys corroded in autoclave, Yilmazbayhan [89] observed tetragonal fraction maxima ranging from 4 to 15% depending on the alloy composition and corrosion medium and temperature. Therefore, this lower tetragonal fraction observed at low and high elevation in the Zry-2 water rods corroded in BWR may reflect differences in oxidation environments. Additionally, differences in experimental setup and azimuthal range may

contribute to the differences between the results presented in this study and Shivprasad's work on similar materials [91].

Observing the results of material 14 which had the highest hydrogen content of all materials (1721 wt.ppm), the tetragonal volume fraction is almost identical to that of material 11 which was located at a similar elevation in the reactor but contained much less hydrogen (329 wt.ppm) and was taken out of a reactor a cycle earlier. This suggests that the tetragonal fraction is affected by the oxidation conditions as well, as observed in literature [89, 335]. Examinations of the tetragonal volume fraction in the oxide layers of the Zry-2 water rods did not reveal major differences between the low and high hydrogen pickup materials, and it is not believed to contribute to the severe increase in hydrogen pickup seen in materials 12 and 14.

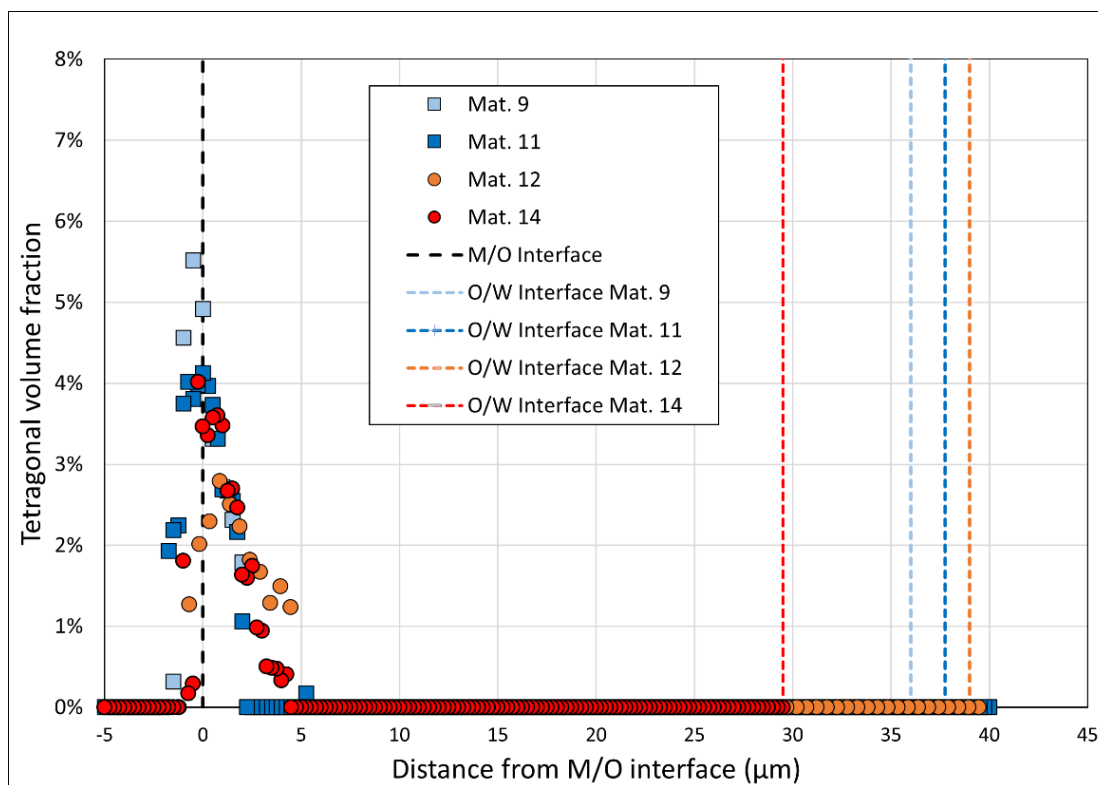


Figure 4-20: Tetragonal volume fraction across the oxide layers of the Zry-2 materials.

4.2.3 Grain evolution in Zry-2 oxide layers

The grain sizes of the oxide layers were investigated in the Zry-2 water rod materials using the Scherrer equation (Eq. 2-8) with the (111) monoclinic peak and the results are presented in Figure 4-21 as a function of distance from the metal/oxide interface for all four in-pile materials. The grain size induced broadening of the (111) $m\text{-ZrO}_2$ peak was calculated with (Eq. 2-9) using the measured total peak broadening and the instrumental peak broadening. From discussions with beamline scientist Wenjun Liu, the major contribution to instrumental broadening at beamline 34-ID-E would be the X-ray beam divergence since the beam is focused with KB-mirrors. The beam divergence is approximately 0.1° both horizontally and vertically and the instrumental peak broadening, B_i , was then estimated to 0.15° .

The results indicate that, at both locations examined in the two water rods, the monoclinic oxide grains start between 17-20 nm in diameter at the metal/oxide interface and grow as the oxide layer thickens to reach 33-38 nm in the outer layer. Interestingly, the maximum grain size in the outer layer is lower for the low elevation materials (9 and 12) than for the high elevation materials (11 and 14). Because the high elevation materials endured a high neutron flux throughout the different cycles in the reactor, larger grains in the outer layer of materials 11 and 14 than in materials 9 and 12 suggest that neutron irradiation accelerates oxide grain growth, as previously observed for irradiated Zry-4 by Ensor [52]. It was shown as well in Ensor's study that no direct relationship could be established between oxidation temperature and oxide grain sizes, so that the bigger grains observed in this work likely result from the high neutron flux rather than from the higher temperature at high elevation.

Additionally, the oxide grains in material 11 (high elevation, low H pickup, 3 cycles) grow significantly within the first 10 μm of oxide and then at a slower rate for the rest of the oxide layer. On the contrary, the grain growth in material 14 (high elevation, high H pickup, 3

cycles) is slower in the near oxide (up to 15-20 μm) and then increases in the outer layer. As discussed in the next chapter, the author believes that the oxidation kinetics significantly increased at high elevation in the high hydrogen pickup water rod (4 cycles) and the oxide built at the location examined in material 14 during the last cycle was estimated to be about 20 μm . The near region in material 14 would then correspond to a more recent oxide which stayed for a shorter period of time in the reactor due to the faster oxidation kinetics during the last cycle, compared to the oxide grown on material 11 which had slower oxidation kinetics. This observation is coherent with previous examinations by Shivprasad where the oxide grains in the near region of the high hydrogen pickup material at mid elevation (Mat. 13, 4 cycles) were smaller than in the near region of the low hydrogen pickup material at similar elevation (Mat. 10, 3 cycles) (Figure 5.24 in [91]).

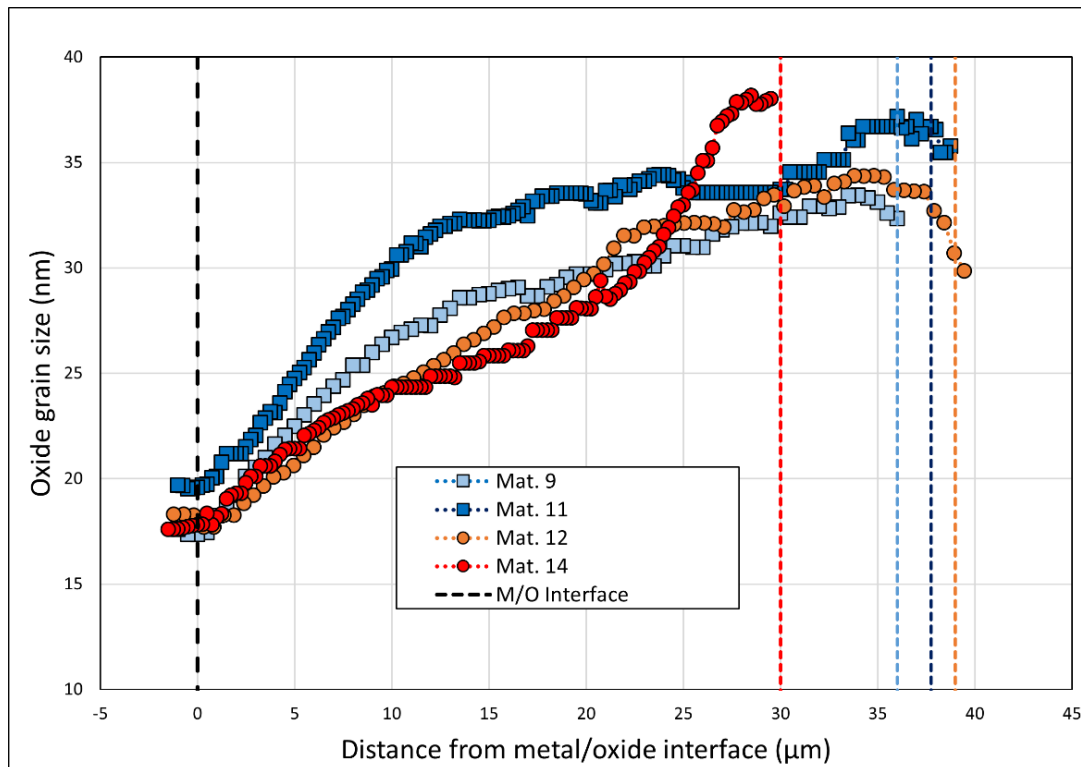


Figure 4-21: Oxide grain size evolution across the oxide layers of the Zry-2 materials.

Lastly, the high hydrogen content may have contributed to the lower grain size observed in the near oxide of material 14. In material 12 (low elevation, high H pickup, 4 cycles), the oxide grain size is seen lower in the near oxide as well compared to the low hydrogen pickup materials (9 and 11). In previous work [52], a higher proportion of equiaxed oxide grains to columnar grains was observed in Zr alloys with high hydrogen contents than in alloys with low hydrogen contents. This higher proportion of equiaxed grains may lower the grain size observed with XRD as seen in the near oxide of material 14 and material 12. However, because the hydrogen content is higher in material 11 (329 *wt. ppm*) than in material 9 (250 *wt. ppm*), oxide grain sizes seem to be influenced primarily by the irradiation flux and/or corrosion kinetics, rather than the content of hydrogen in the material.

4.3 Examination of preferred orientation

As mentioned in section 4.1.1, the azimuthal distribution of the XRD patterns is not uniform in the metal and oxide regions of the Zry-2 water rods investigated in this study, indicating preferred orientation for the metal and oxide grains in these materials. In this section, the author examines in detail the texture of two main regions of the materials: the first region consists of the metal and oxide near interface $[-4\ \mu m; 5\ \mu m]$ and the second of the far oxide $[10\ \mu m; 25\ \mu m]$. The observations discussed below were seen in all four materials (9, 11, 12, 14) without clear differences in azimuthal distribution between the samples. Because the results were so similar in all materials, XRD patterns from material 14 only are discussed in this section but the observations apply to materials 9, 11 and 12 as well, and the XRD patterns across the oxide layers in these materials (9, 11 and 12) are available in Appendix B.

4.3.1 Texture in metal and oxide near interface

In order to investigate the texture of the metal and oxide grains in the Zry-2 water rods, the diffraction patterns and “cake” χ -2 θ -plots at two locations in the metal region near interface ($-4\ \mu\text{m}$; $-1\ \mu\text{m}$) of material 14 are shown in Figure 4-22 and at two locations in the oxide region near interface ($2\ \mu\text{m}$; $5\ \mu\text{m}$) of the same material in Figure 4-23. In particular, the azimuthal distributions of the reflections corresponding to the $(10\bar{1}0)$ and $(10\bar{1}1)$ of α -Zr and to the $(\bar{1}11)$, (111) , (200) , (020) and (002) of m -ZrO₂ are investigated to determine the preferred orientation of the metal and oxide grains. In each of the XRD patterns, the azimuthal regions of high intensity are highlighted with color arrows.

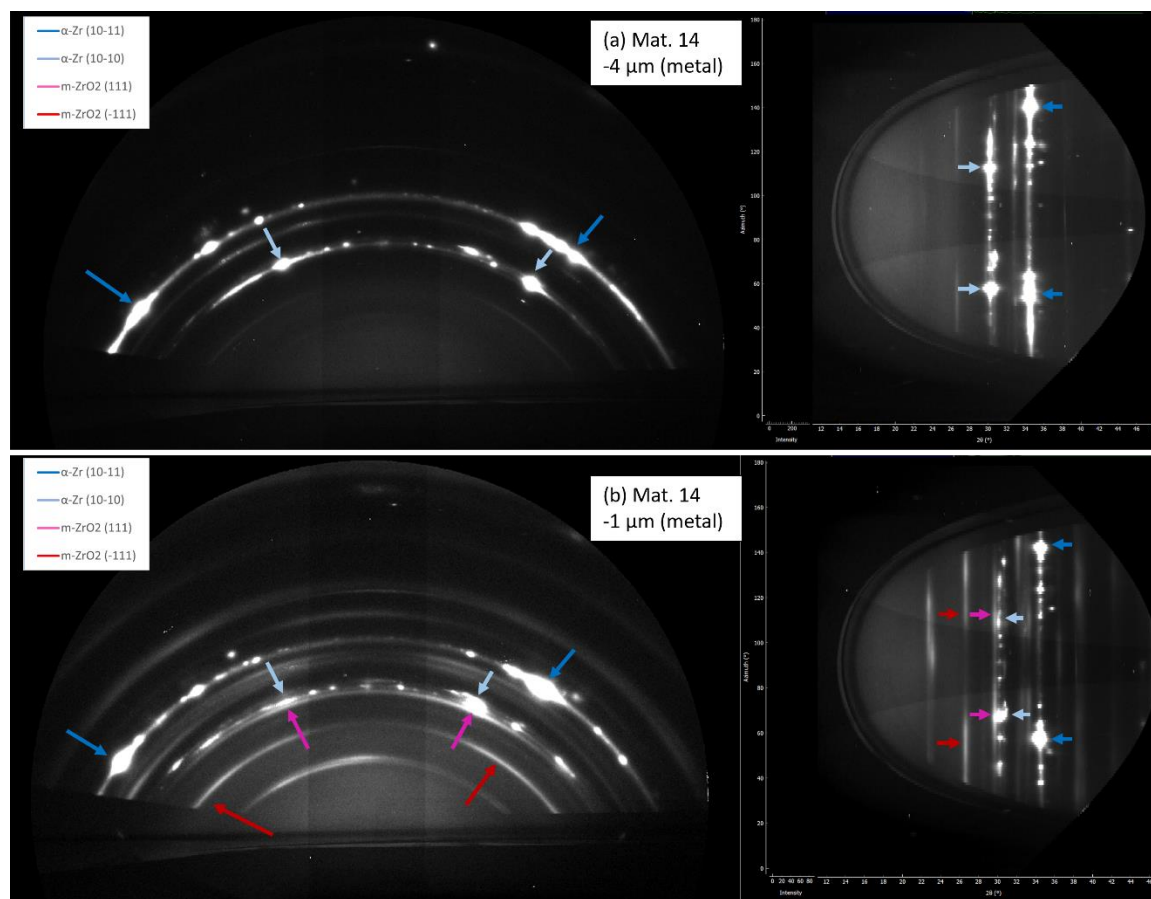


Figure 4-22: XRD pattern (image on the left, and “cake” on the right) at two locations in the near metal region of material 14: (a) $-4\ \mu\text{m}$; (b) $-1\ \mu\text{m}$. The high intensity region for the main peaks of α -Zr and m -ZrO₂ are indicated by the colored arrows.

Considering the XRD pattern collected in the metal ($4\ \mu\text{m}$) in Figure 4-22-(a), the $(10\bar{1}0)$ intensity ($2\theta = 30.22^\circ$, light blue arrows) is maximum at oblique angles on the pattern, corresponding to azimuthal angles near 60° and 115° , and some intensity is seen around the vertical position $\chi = 90^\circ$. Therefore, the azimuthal range for the $(10\bar{1}0)$ reflection is seen to be $[50^\circ\text{-}130^\circ]$ with maximums at 60° and 115° . On the other hand, the $(10\bar{1}1)$ intensity ($2\theta = 34.51^\circ$, blue arrows) is present on the oblique and horizontal sides of the pattern at azimuthal angles above 110° and below 70° . Another interesting observation is the much lower intensity observed for the (0002) $\alpha\text{-Zr}$ reflection ($2\theta = 32.93^\circ$) in between the other two main metal reflections. From the PDF of $\alpha\text{-Zr}$ (Appendix A), the (0002) intensity is 32% of the $(10\bar{1}1)$ intensity, similar to the $(10\bar{1}0)$ intensity at 33% but is almost extinct in the XRD patterns. This suggests that the (0002) planes of the oxide are mainly perpendicular to the beam direction so that none of those grains can diffract the beam onto the XRD detector.

Zr alloys are known to be highly textured in literature and the previous observations are consistent with preferred orientation. After cold processing of the Zry-2 water rods, the $(10\bar{1}0)$ direction is parallel to the rolling direction [23, 116]. The Zry-2 materials were then heat treated for improved behavior in the boiling reactor (section 1.2.2 and 2.1), which has the effect of rotating the grains by 30° along the c -direction, so that the $(11\bar{2}0)$ direction is then aligned with the rolling direction [23]. In our materials, the rolling direction is perpendicular to the sample surface as the materials were cut in cross-section from the water rods. As a result, the $(10\bar{1}0)$ reflections are maximized near the vertical azimuthal angle ($\chi = 90^\circ$) and extinct near the horizontal azimuthal angles ($\chi = 0^\circ$, $\chi = 180^\circ$). On the other hand, the $(10\bar{1}1)$ would be minimum at the horizontal and vertical azimuthal angles ($\chi = 0^\circ$, $\chi = 90^\circ$, $\chi = 180^\circ$) and maximum at oblique angles ($\chi = 45^\circ$, $\chi = 135^\circ$); and the (0002) crystal planes would be only present at horizontal azimuthal angles $\chi = 0^\circ$, $\chi = 180^\circ$. As described above, the XRD patterns

in the materials are consistent with this preferred orientation, confirming that the $(11\bar{2}0)$ direction is aligned with the rolling direction after the additional heat treatment on the Zry-2 RX (recrystallized, or alpha annealed) materials.

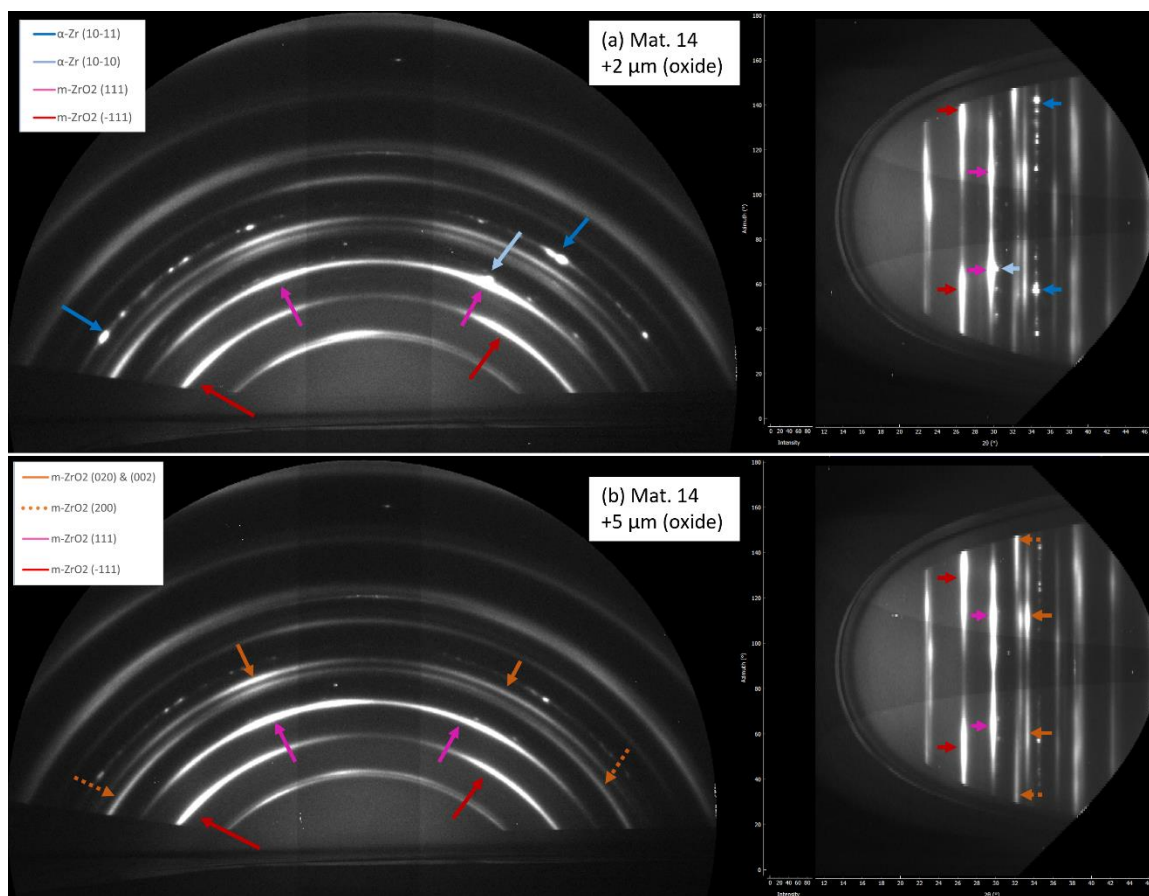


Figure 4-23: XRD pattern (image on the left, and “cake” on the right) at two locations in the near oxide region of material 14: (a) +2 μm; (b) +5 μm. The high intensity region for the main peaks of α -Zr and m -ZrO₂ are indicated by the colored arrows.

In the metal region near interface as shown in Figure 4-22-(b), the (111) and $(\bar{1}11)$ m -ZrO₂ reflections become apparent at preferred azimuthal angles. The (111) intensity ($2\theta = 29.75^\circ$, pink arrows) is maximum at the same azimuthal angles than for the $(10\bar{1}0)$ α -Zr reflection $[50^\circ\text{--}130^\circ]$, suggesting a crystallographic relationship between the two phases, as

observed in previous work [325]. As a result, the $(\bar{1}11)$ ($2\theta = 26.65^\circ$, red arrows) reflections are minimum at vertical angles and maximum at oblique and horizontal azimuths. These preferred azimuthal angles for (111) and $(\bar{1}11)$ are seen clearly on the XRD patterns from the oxide near interface shown in Figure 4-23-(a) and Figure 4-23-(b) at $2\ \mu m$ and $5\ \mu m$ from the metal/oxide interface respectively. Additionally, the (200) , (020) , and (002) preferred azimuthal rings are highlighted in Figure 4-23-(b). It can be seen that the (200) intensity ($2\theta = 32.29^\circ$, orange dotted arrows) is maximum at horizontal angles ($\chi < 55^\circ$, $\chi > 120^\circ$) and extinct at vertical angles. On the other hand, the (020) and (002) intensities ($2\theta = 32.50^\circ$ and $2\theta = 33.37^\circ$ respectively, orange arrows) are located mostly at oblique azimuthal angles ($\chi = 60^\circ$, $\chi = 115^\circ$), and minimum at vertical and horizontal angles. Observed in all the materials, this preferred orientation is coherent with that of the (111) reflections and suggest that the (200) direction is close to the oxide growth direction for all the Zry-2 in-pile materials selected as further discussed in the next section.

4.3.2 Texture in the oxide layers

In the previous section, the texture in the metal and oxide regions near the metal/oxide interface of the Zry-2 materials was investigated. In this section, the texture in the far oxide regions [$10\text{-}25\ \mu m$] of the materials is presented. The diffraction patterns and “cake” χ - 2θ -plots at four locations in the deep oxide region ($10\ \mu m$; $15\ \mu m$; $20\ \mu m$; $25\ \mu m$) of material 14 are shown in Figure 4-24-(a), Figure 4-24-(b), Figure 4-25-(a), and Figure 4-25-(b) respectively. The azimuthal distributions of the reflections corresponding to the $(\bar{1}11)$, (111) , (200) , (020) and (002) of $m\text{-}ZrO_2$ are investigated to determine the preferred orientation of the oxide grains.

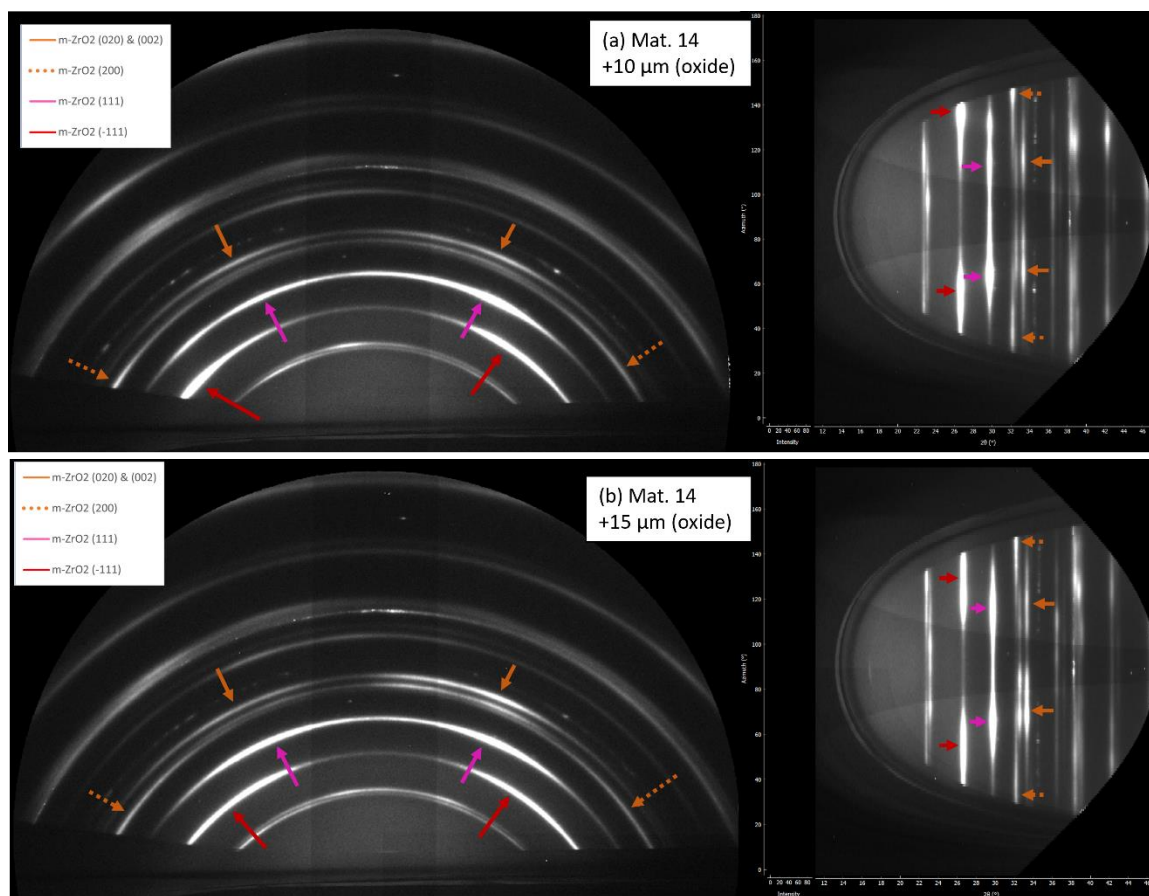


Figure 4-24: XRD pattern (image on the left, and “cake” on the right) at two locations in the mid oxide region of material 14: (a) +10 μm ; (b) +15 μm . The high intensity region for the main peaks of $\alpha\text{-Zr}$ and $m\text{-ZrO}_2$ are indicated by the colored arrows.

When considering the XRD patterns at the four locations in the deep oxide, it is clear that the preferred orientation described in the previous section in the oxide near interface is maintained throughout the whole oxide layer. Therefore, the same crystallographic orientation in the oxide layer was seen for all Zry-2 materials, independent of elevation, hydrogen content and time spent in the reactor. While previous studies had shown that the oxide grain orientations affect both oxygen [144] and hydrogen [324] transport in the oxide layer, the increase of H absorption in materials 12 and 14 cannot be linked to differences in oxide texture. This observation suggests that the enhancement of hydrogen pickup in these materials may not originate from an increase in H diffusion in the oxide layer, which is further discussed in the next chapter.

Some variations along the azimuthal range [50-130 μm] for the (111) $m\text{-ZrO}_2$ are seen when comparing the four locations. The authors believe that it reflects the variations along the azimuthal range for the (10 $\bar{1}$ 0) $\alpha\text{-Zr}$ reflections, because of the crystallographic relationship between the two set of planes observed near the metal/oxide interface of the materials investigated in this study and in literature [325].

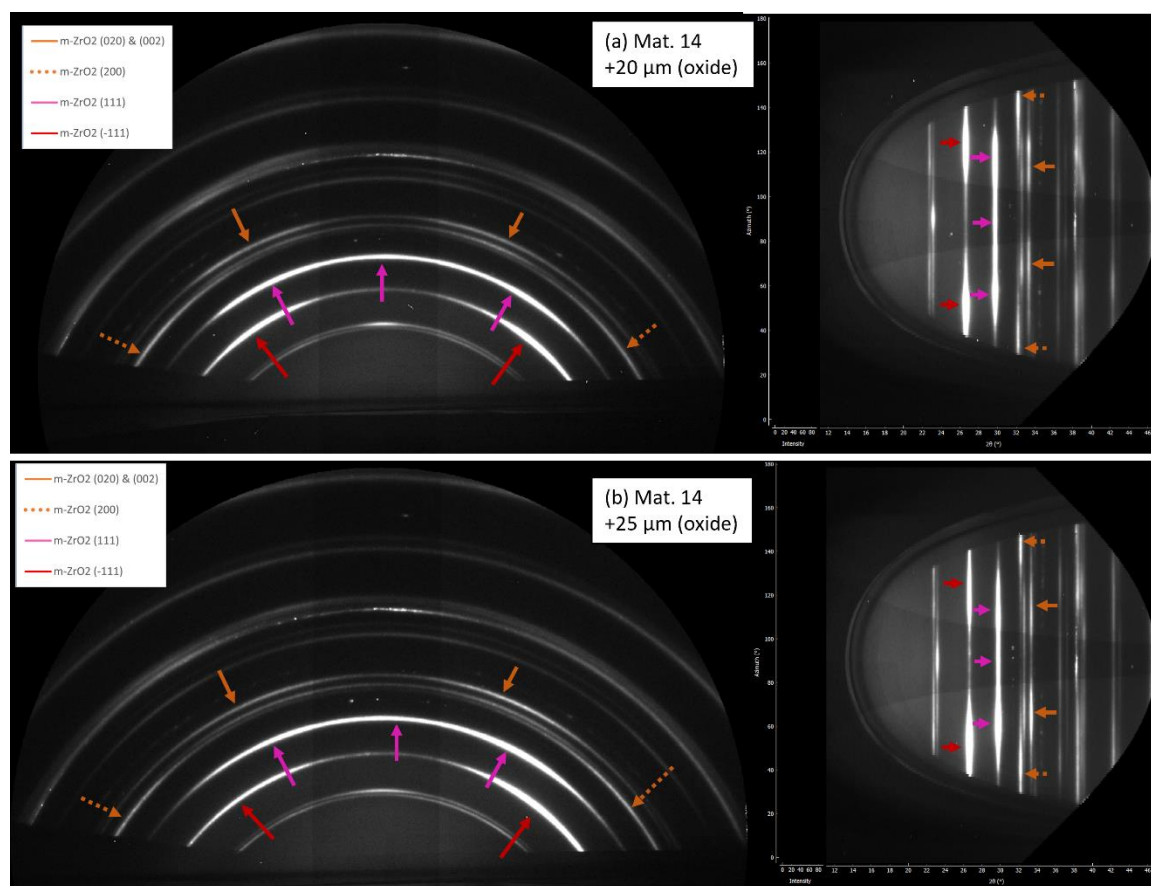


Figure 4-25: XRD pattern (image on the left, and “cake” on the right) at two locations in the far oxide region of material 14: (a) +20 μm ; (b) +25 μm . The high intensity region for the main peaks of $\alpha\text{-Zr}$ and $m\text{-ZrO}_2$ are indicated by the colored arrows.

The preferred azimuthal ranges for the (200), (020) and (002) $m\text{-ZrO}_2$ reflections allow to further investigate the orientation of the oxide grains in relation to the metal/oxide interface. In all of the diffraction patterns collected in the oxide layer of the Zry-2 materials, the (200) reflection was minimum at vertical and oblique azimuthal range, and maximum at diffraction angles close to the horizontal azimuth. The (020) and (002) reflections are maximum

near the vertical azimuthal angles, and minimum near the horizontal azimuthal angles. Considering the beam direction is parallel to the oxide/metal interface during examination, these observations suggest that the (200) direction of the monoclinic grains is close to the metal/oxide interface normal direction (oxide growth direction), as illustrated in Figure 4-26. While the (200) direction is close to the oxide growth direction, the oxide grains may be oriented differently by rotating the a -axis in Figure 4-26-(b). Although not represented in the schema in Figure 4-26-(b) for simplicity, the monoclinic lattice is not cubic, and the angle between the a and c axis is slightly higher at 99.53° . This allows for the (020) and (002) reflections to be maximized at azimuthal angles close to the vertical region as shown with the X-ray diffracted path represented by the colored straight and dotted lines. However, a minimum in reflection intensity is observed at the vertical azimuth ($\chi = 90^\circ$) for these two sets of planes suggesting that the (200) direction is about 20° away from the oxide growth direction. This preferred orientation of the monoclinic grains was observed in previous studies as well [89, 91] and seen in all materials investigated in this study. It is worth mentioning that about 1/3 of the full azimuthal range of the XRD pattern was collected during the investigation of the cross-section samples (120° azimuthal range) and hence, not all grain orientations could be investigated. However, preferred orientation of the monoclinic oxide grains has been observed for the oxide layers grown on the Zry-2 water rod materials, and the (200) direction was reported to be close to the oxide growth direction.

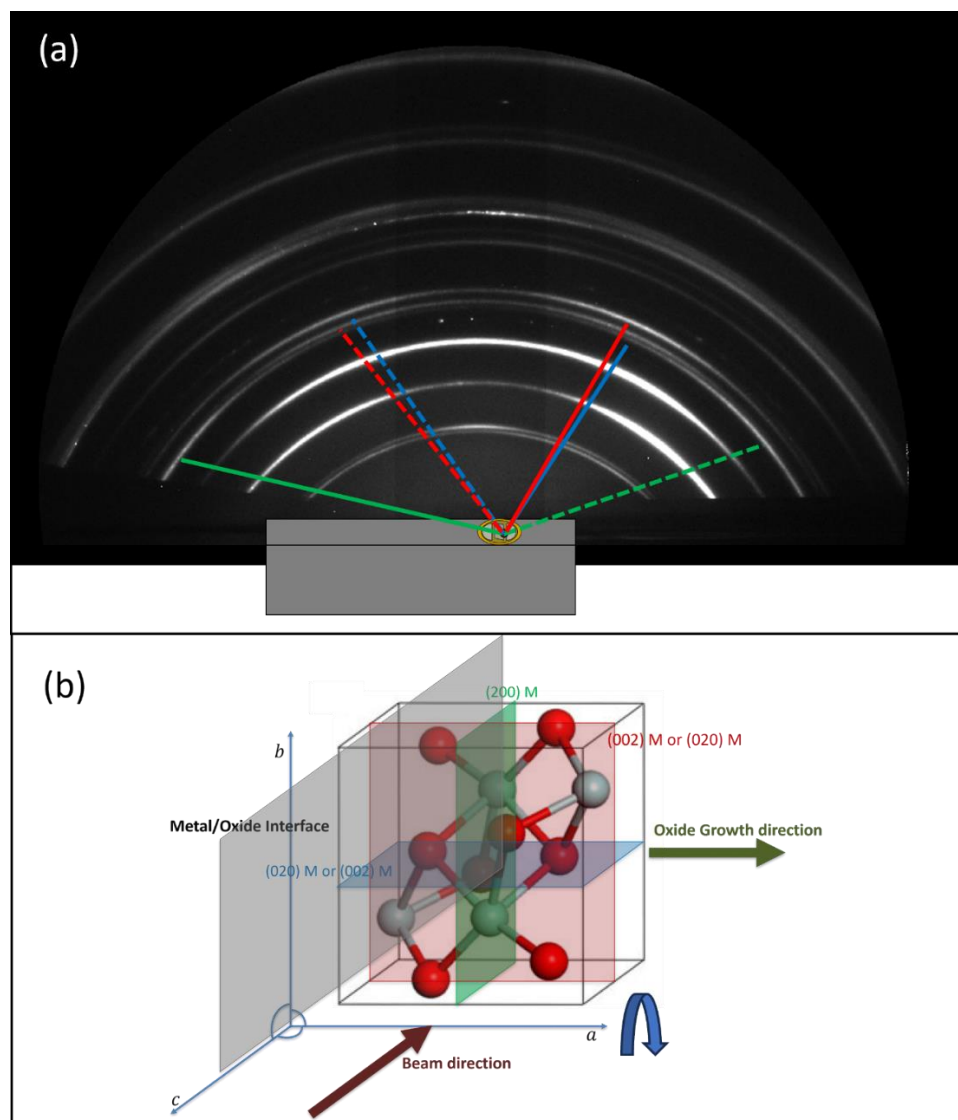


Figure 4-26: (a) XRD pattern in material 14 (25 μm , far oxide) with the illustration of the X-ray diffracted beam paths for the (200) $m\text{-ZrO}_2$ family of planes. (b) Schema of the preferred orientation of monoclinic oxide grain with the (200) $m\text{-ZrO}_2$ family of planes, the M/O interface, and the oxide growth direction. It should be noted that the (200) plane is maintained parallel to the M/O interface while the (020) and (002) have many different orientations (represented by the blue arrow near axis a). Additionally, a cubic lattice is used for illustration of the (200) preferred orientation while the monoclinic lattice is close to cubic but with $\beta = 99.53^\circ$ and slightly different lattice parameters (section 1.3.1).

4.4 Conclusions on XRD examinations of in-reactor corroded Zry-2

In this chapter, we presented the results of the in-depth microstructure analysis across the oxide layers of BWR-corroded Zry-2 water rod materials with low and high hydrogen pickup using X-ray diffraction with synchrotron radiation. In previous work [91], the tetragonal fraction was correlated to high H content materials and the selection of materials in this study allowed to further study this relationship. Additionally, the microbeam XRD analysis of the phase content, the grain size, and of the texture in the oxide layer of reactor corroded Zry-2 materials provides insights into the microstructure of oxide layers built in reactor condition. While the role that microstructure may play in enhancing hydrogen pickup is further discussed in the next chapter, the main observations of the XRD analysis are summarized below:

- (1) In all four materials, α -Zr and δ -ZrH_{1.66} phases were identified in the XRD patterns from the metal region near interface, while m -ZrO₂ reflections were seen in the oxide layer, and low intensity t -ZrO₂ reflections were apparent in the oxide near interface only. No suboxide phases reflections could be detected with synchrotron microbeam XRD in the 3 and 4 cycles-irradiated Zry-2 water rod materials.
- (2) The α -Zr and δ -ZrH_{1.66} XRD pattern contained incomplete low intensity arcs and high intensity spots, coherent with the micrometric grain size of these two phases, while the oxide reflections consisted only of high intensity arc, indicating nanometric oxide grains, as previously reported in literature.
- (3) The main intensity reflection for α -Zr and m -ZrO₂ followed pseudo-periodic variations throughout the oxide layers, ranging from few μm to 10 μm and these variations were identified with the different orientations of the metal grains in the Zry-2 materials. The main peak variations of the hydride phase were seen slightly shorter suggesting smaller crystallite size 1-5 μm .

- (4) The tetragonal volume fraction observed in the near oxide layer of the Zry-2 water rods was lower than previously measured at different elevations, with maxima between 3-6%. The tetragonal fraction was lower in the high hydrogen content materials, but the difference was reduced at high elevation in the reactor. No tetragonal reflections could be seen past $5\mu m$ of oxide in all four materials, indicating a tetragonal-to-monoclinic phase transformation as the oxide grows, similar to observations in literature.
- (5) Monoclinic oxide grain size was measured to be 17-20 nm near the metal/oxide interface, and then increased further in the oxide to reach 33-38 nm in the outer layer. The largest grains were observed in the oxide layer close to the water interface of the high elevation materials, suggesting irradiation-induced grain growth in the oxide layer. Additionally, small grains compose the oxide region near the metal/oxide interface of material 14 (high elevation, high HPUF, 4 cycles) when compared to material 11 (high elevation, low HPUF, 3 cycles) which may indicate faster oxidation kinetics during the additional cycle at high elevation in the reactor.
- (6) Strong texture was reported for the metal and oxide grains of the Zry-2 water rods. In the metal region, the azimuthal variations of α -Zr were consistent with the (11 $\bar{2}$ 0) being aligned with the rolling direction, as previously reported for alpha annealed Zr alloys. Near the interface, a crystallographic relationship between the (111) m -ZrO₂ and the (10 $\bar{1}$ 0) α -Zr was seen for all four materials. A preferred orientation is consistently present in the oxide layers of the different samples examined and the results indicate that for a significant fraction of the oxide grains, the (200) m -ZrO₂ direction is close to the oxide growth direction. This is coherent with previous XRD examinations of autoclave and in-reactor corroded Zr alloys.

Chapter 5

Discussions on the acceleration of H pickup at high burnup in Zry-2

In the previous chapters, the results of the XANES, XRD and SEM examinations of the Zry-2 water rods corroded in 3 and 4 cycles in BWR were presented. In this chapter, the author discusses these results in terms of hydrogen uptake and elevation in the reactor and proposes a mechanism for the enhancement of hydrogen pickup in Zry-2 materials at high burnup. Additional oxide thickness and hydrogen content data at different elevations in the two water rods were provided by Global Nuclear Fuel (GNF) and are compared to the metallic nickel measurements in the first section while the second section is dedicated to the discussions on the conditions and mechanism leading to accelerated hydrogen uptake in the Zry-2 water rod during the 4th cycle in the BWR, based on the results presented in this study and on an extensive review of available literature.

5.1 *Ni* valence in relation to corrosion and *H* pickup of high burnup BWR Zry-2 water rods

The nickel metallic fraction measurements with XANES across the oxide layers of the two Zry-2 water rods with low and hydrogen pickup fraction corroded for 3 and 4 cycles (respectively) in Limerick-1 boiling water reactor are compiled in terms of elevation in the reactor in Figure 5-1. Additionally, the fluence, hydrogen content and oxide thickness are added to the plots. While the oxide layers of Mat. 9, Mat. 11, Mat. 12 and Mat. 14 (low and high elevation) were analyzed in the present work, Mat. 10 and Mat. 14 (mid elevation) were investigated by A. Shivprasad in a previous study [99]. The hypothesis that metallic nickel remaining in the oxide layer of the Zircaloy-2 water rod is responsible for the enhancement of hydrogen ingress at high burnup is now being discussed.

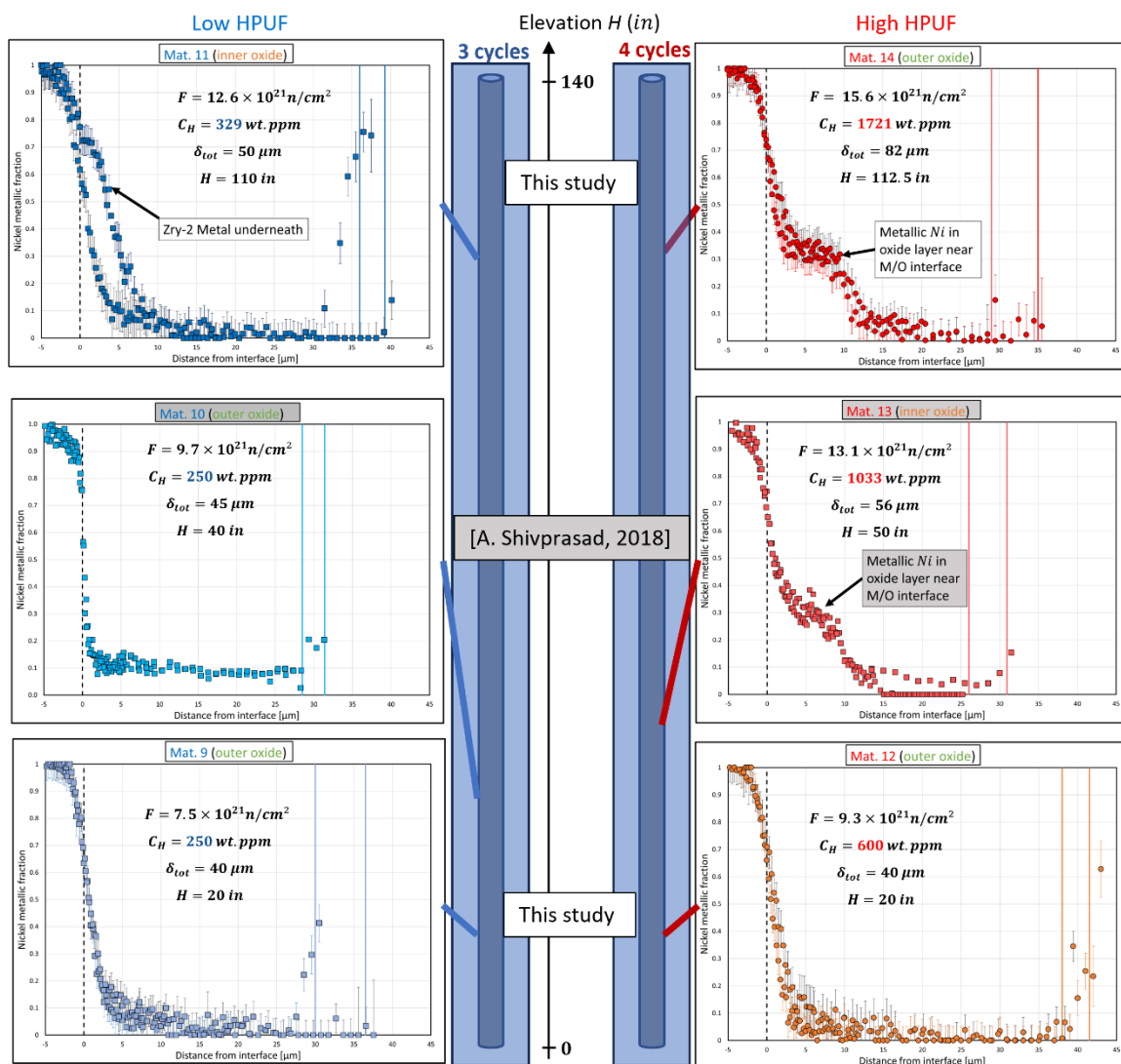


Figure 5-1: Review of the metallic fraction measurements across the oxide layers of the 3 and 4 cycles water rod samples in terms of elevation in the reactor. Results for Mat. 9, Mat. 11, Mat. 13 and Mat. 14 (low/high elevation) were presented in this work while results for Mat. 10 and Mat. 13 (mid elevation, grey title boxes) were reported by A. Shivprasad [99]. Additionally, the fluence, hydrogen content, total oxide thickness are shown on each plot (data presented in Table 2-1). The oxide/water interfaces are represented by the colored lines in each plot (two scans were performed in all materials).

For all 3 materials (Mat. 9, Mat. 10, Mat. 11) selected from the low hydrogen pickup water rod (3 cycles, left plots in Figure 5-1), the nickel atoms are fully oxidized within 3-4 μm into the oxide layer. For one of the scans in material 11 (high elevation, 3 cycles), a plateau at 70% metallic nickel was observed for about 3 μm near the metal interface, but the XANES signal from these metallic nickel atoms suggested a bond with Zr atoms and therefore we

identified the metallic plateau to the presence of a metal region underneath the oxide layer (see section 3.4.2). At mid elevation (Mat. 13) and at high elevation (Mat. 14) in the high hydrogen uptake water rod (4 cycles, right plots in Figure 5-1), about 30% of metallic nickel remained in the oxide layer up to 10-12 μm past the metal/oxide interface. Although not shown here, Shivprasad [99] examined two other Zry-2 materials from water rods corroded for 3 and 4 cycles in Dresden-2 BWR, and the high hydrogen content material (Mat. 21, 4 cycles) contained 30-40% metallic nickel in the near oxide layer as well while in the low HPUF material (Mat. 17, 3 cycles), all nickel atoms were oxidized past 3 μm of oxide. The XANES measurements presented in this study for Mat. 9, Mat. 11 and Mat. 14 support the hypothesis that metallic nickel is responsible for the acceleration of H pickup of Zry-2 materials at high burnup in the BWR environment. However, examinations of Mat. 12 (high HPUF, low elevation, 4 cycles) revealed no metallic nickel past 3-4 μm into the oxide layer, as was measured in the low hydrogen pickup materials. The increased hydrogen pickup fraction during the additional cycle in the reactor does not result from the presence of metallic nickel in the oxide layer. Instead the author believes that the hydrogen excess was absorbed at higher elevation in the material, and then diffused down the water rod during the last cycle. This hypothesis is further supported by the additional measurements of oxide thickness and hydrogen content at multiple locations in the two GNF water rods (additional data were provided by EPRI) as detailed below.

Furthermore, nickel metallic fractions ranging from 20% to 60% were measured near the outer surface of the oxide layers. These metallic fractions in the outer layer were identified as crud deposits from the corrosion of other reactor components, as detailed in chapter 3. However, this observation was generic to most samples with the highest metallic fraction measured in the outer layer of material 11 (low hydrogen pickup, high elevation, 3 cycles). For this reason, metallic nickel atoms at the oxide/water interface are not likely to have played a role in enhancing the hydrogen uptake in the materials examined.

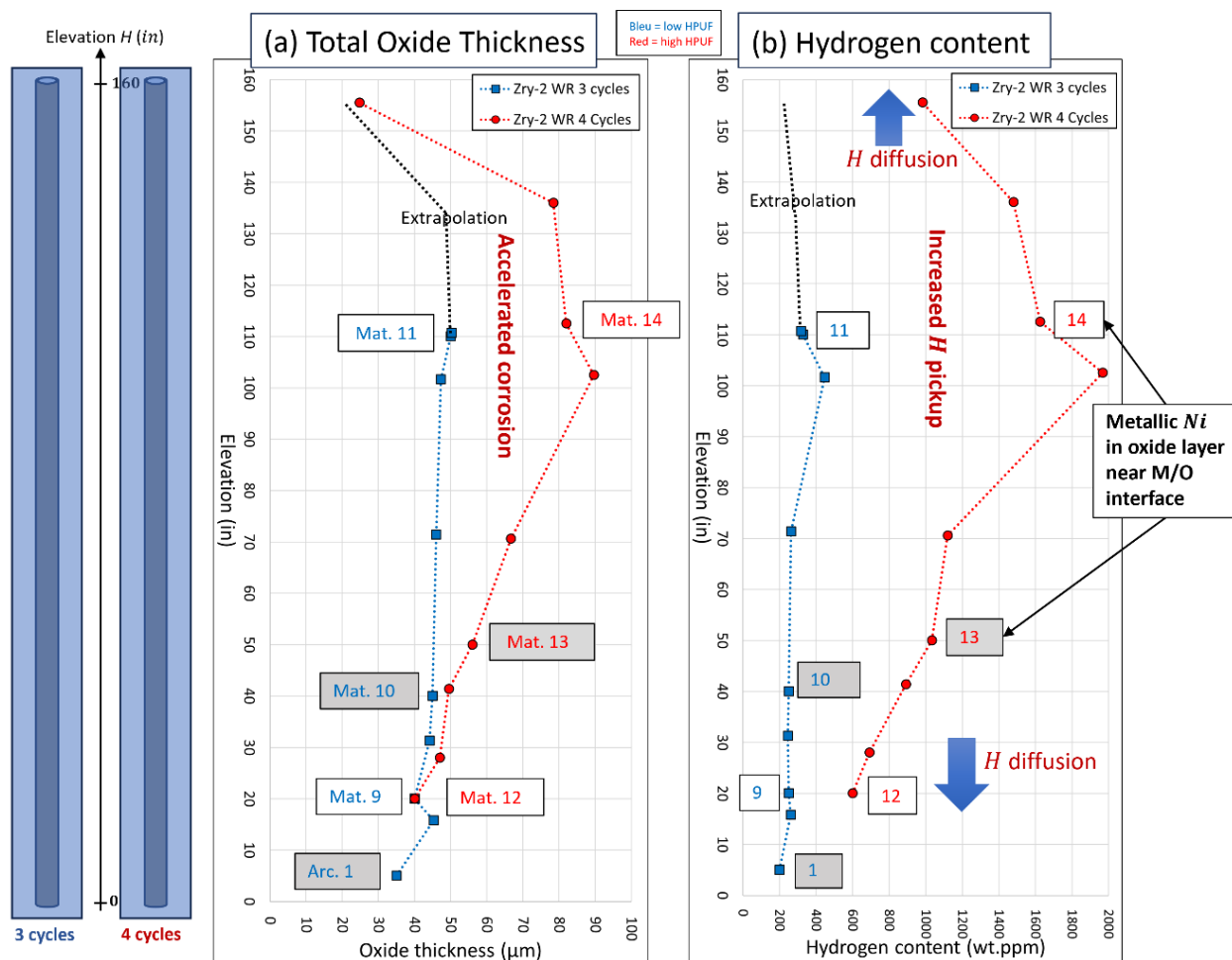


Figure 5-2: (a) Total oxide thickness and (b) hydrogen content as a function of elevation in the 3-cycles (blue squares) and 4 cycles (red circles) water rods. Additional data on the GNF water rods were provided by EPRI. The elevations of the materials examined in this study are shown with the white boxes on the two plots, while the grey boxes refer to data from previous work [99].

The total oxide thickness and the hydrogen content in the two Zry-2 water rods corroded in Limerick-1 reactor for 3 and 4 cycles are plotted as a function of elevation in Figure 5-2. The materials investigated are labeled on the two plots, with the gray boxes indicating that metallic nickel was seen in the near oxide of the material. From the total oxide thickness data (Figure 5-2(a)), it can be seen that the corrosion kinetics increased during the last cycle at elevations above 60 in from the bottom of the water rod with total oxide thicknesses up to 90 μm (102.5 in) after 4 cycles while the maximum total oxide thickness seen at a similar elevation in the 3 cycles water

rod is $50\ \mu\text{m}$, suggesting that an additional $40\ \mu\text{m}$ was built during the last cycle only at this elevation. At low elevation in the water rod ($< 40\ \text{in}$, or $1.0\ \text{m}$), slow corrosion took place during the additional cycle as similar or slightly thicker ($2\text{-}3\ \mu\text{m}$) oxide layers were measured in the water rod corroded for 4 cycles in comparison with the low elevation examinations of the 3-cycle water rod. Additionally, the thinnest oxide was measured at the very high elevation ($155\ \text{in}$, $25\ \mu\text{m}$). The total oxide thickness and hydrogen at very high elevation in the 3-cycle water were extrapolated by the author based on the axial variations observed in previous studies [212, 336]. Additionally, when comparing the oxide thicknesses of material 21 (4 cycle, high elevation, high HPUF, $25\ \mu\text{m}$ total oxide thickness) to that of material 17 (3 cycle, high elevation, low HPUF, $7\ \mu\text{m}$ total oxide thickness) from water rods corroded in Dresden-2 reactor (investigated by A. Shivprasad [99]), it is clear that acceleration of corrosion kinetics occurred during the 4th cycle at high elevation in material 21 as well, which also contained partially metallic nickel atoms in the near oxide layer.

The hydrogen content data as a function of elevation in the two water rods (Figure 5-2-(b)) clearly indicate an acceleration of hydrogen uptake in the 4-cycle irradiated water rod. While the hydrogen content in the 3-cycle is found between 200 and 400 *wt.ppm* at various elevations in the reactor, the hydrogen content after 4 cycles is at least 600 *wt.ppm* (low elevation, Mat. 12) and reaches 900 to 2000 *wt.ppm* at mid and high elevations. When comparing with the total oxide thickness measurements (Figure 5-2-(a)), the hydrogen content axial variations of the 4-cycle water rod follow the corrosion kinetics variations, suggesting that a significant portion of the hydrogen atoms absorbed during the additional cycle were produced during the oxidation of the bulk. The author estimated the HPUF at mid and high elevations during the 4th cycle using (Eq. 1-9) with the assumption that the oxide thickness and hydrogen content measurements of the water rod taken out after 3 cycles in the reactor correspond to the oxide thickness and hydrogen

content values at the end of the 3rd cycle in the water rod that was left for an additional 24-month period in the reactor. The results yielded pickup fraction above 100% at most elevations which indicate that some of the hydrogen atoms absorbed were picked up from the coolant directly, without oxidation of the bulk. This observation suggests that a strong catalytic effect for the hydrogen ingress reaction took place at the material surfaces during the last cycle. Such catalytic effects on the hydrogen absorption surface reaction have been observed in the presence of metallic *Ni* in previous studies [216, 337], as further argued in section 5.2.

Additionally, the accelerated corrosion kinetics seem to be correlated to enhanced hydrogen pickup as mentioned previously. The absence of accelerated oxidation kinetics at low elevation during the 4th cycle suggests that the hydrogen ingress is not accelerated at these elevations either. This is coherent with the full oxidation of the nickel atoms in the near oxide of material 12 (low elevation, hydrogen pickup) reported in this work. The excess of hydrogen is thought to have been absorbed at higher elevation where metallic nickel acted as a catalyst for *H* ingress into the alloys and diffused to lower elevation due to the concentration gradient (Fick's law) and temperature gradient (Soret effect). While the concentration gradient results from the hydrogen build up at higher elevation as more hydrogen is picked up during the 4th cycle, the temperature at low elevation is lower than at the higher elevation as the inlet temperature is about 10-15° below the saturation temperature of the BWR. As hydrogen is attracted to colder regions, the Soret effect combines with Fick diffusion to push hydrogen atoms down the water rod. The hydrogen diffusion downward is illustrated in Figure 5-2-(b) with the large arrows. Because the hydrogen pickup fraction at the highest elevation (155 *in*) is the largest of all materials at 108% on average over the range of the 4 cycles, or about twice the hydrogen pickup fraction measured in the rest of the water rods, it is likely that some of the excess hydrogen at 155 *in* originated from the high hydrogen content region right below, similar to the diffusion at low elevation. The oxidation state of nickel was not measured yet at this elevation; therefore it is not straightforward to rule out

acceleration of hydrogen ingress at this location. It is worth mentioning that this elevation corresponds to the end of the water rod near the steam separator and the radius of the water rod diameter at this location may be lower than for the rest of the water rod, resulting in increased *wt. ppm* values for the same amount of hydrogen absorbed [212].

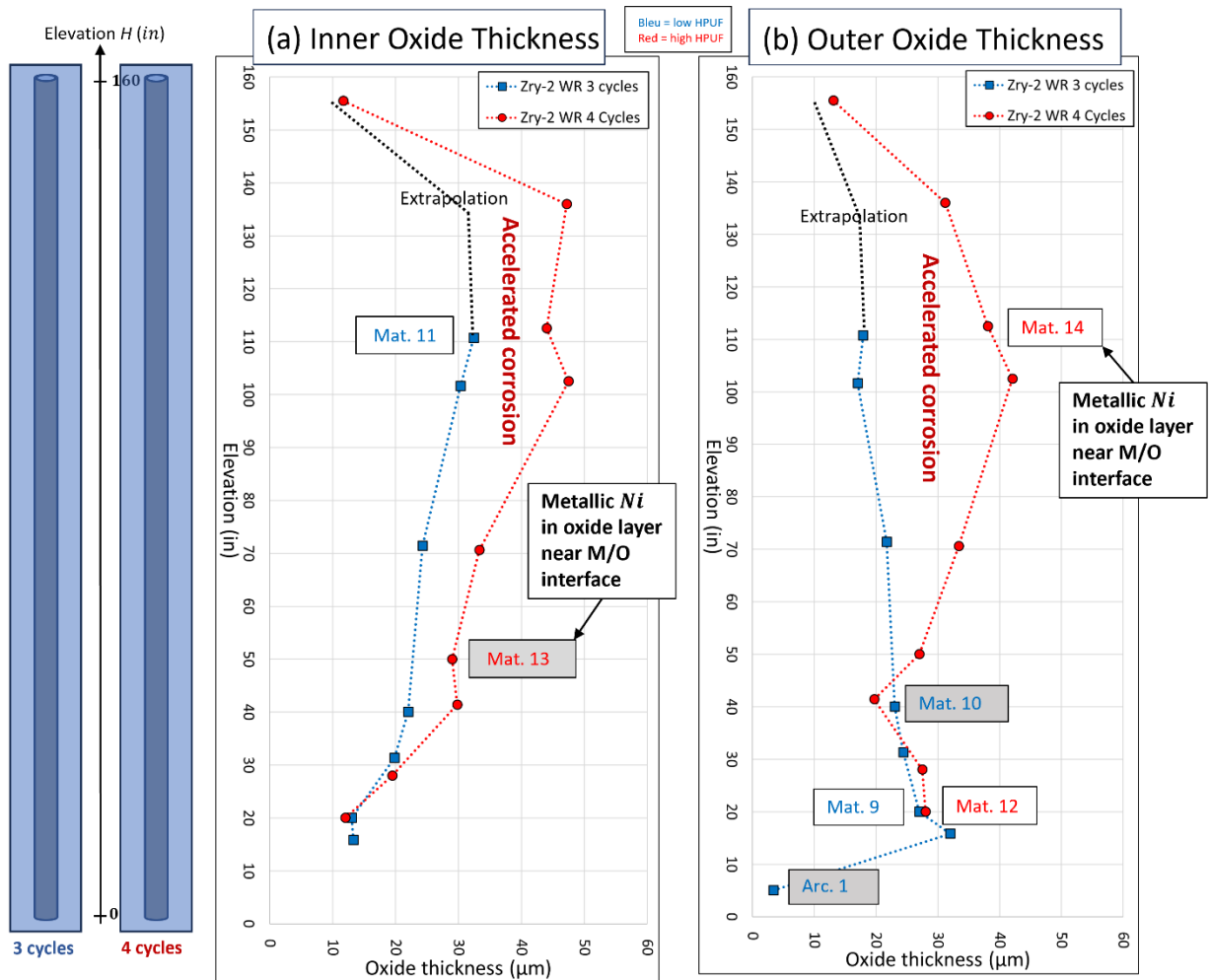


Figure 5-3: (a) Inner and (b) outer oxide thickness as a function of elevation in the 3-cycles (blue squares) and 4 cycles (red circles) water rods. Additional data on the GNF water rods were provided by EPRI. The elevations of the materials examined in this study are shown with the white boxes on the two plots, while the grey boxes refer to data from previous work [99].

Last but not least, the inner and outer oxide thicknesses are plotted as a function of elevation for the two Zry-2 water rods corroded in Limerick-1 BWR in Figure 5-3. It can be seen that accelerated corrosion occurred in both the inner and outer part of the water rod at mid and

high elevation but is more pronounced on the outer side, and that metallic nickel was observed in both the inner (Mat. 13 examinations) and outer layer (Mat. 14 examinations) of the 4-cycles water rod. In turn, these observations indicate that the acceleration of hydrogen pickup occurred in both the inner and outer sides of the Zry-2 water rod.

5.2 The role of metallic *Ni* in enhancing corrosion and *H* pickup of *Zr* alloys in LWRs

In light of the results presented in this work and of an extensive review of the literature, the author presents in this section discussions on the mechanism by which metallic nickel measured in the near oxide of Zry-2 enhances hydrogen uptake of the material, and on the conditions (e.g. burnup, fluence) leading to the presence of partially metallic nickel past 2-3 μm in the oxide layer.

As mentioned before, *Ni* has been associated with increased hydrogen uptake since the early development of Zircalloys in the 1960's [22, 161] but Zircaloy-2 is still used in BWR environment because of its great resistance to nodular corrosion. While investigating in-pile corroded Zry-2 and Zry-4 materials taken out of the reactors, many examinations reported a high hydrogen pickup fraction at high burnup, especially for water rods and structural materials (such as channel box) as reviewed extensively by Garzarolli *et. al* [59] (section 1.4.5). In this review [59], the authors suspected that, due to the high nobility of nickel compared to the other alloying elements and bulk *Zr*, low oxygen pressure in the porous oxide layer close to the metal oxide interface would stabilize metallic nickel past the typical 2-3 μm of oxide. When examining the oxidation state of nickel as a function of depth in the oxide layer with microbeam synchrotron XANES, Shivprasad [99] observed the presence of metallic nickel near the metal/oxide interface (up to 10-12 μm) of two high burnup / high hydrogen pickup water rods (used in Limerick-1 and Dresden-2 BWRs for 4 cycles) while in the low hydrogen pickup materials (lower burnup, 3

cycles), nickel atoms were fully oxidized past 2-3 μm from the metal interface. In chapter 3, the nickel metallic fraction derived from the XANES analysis across the oxide layer of 4 additional Zry-2 materials at different elevation in Limerick-1 BWR confirmed the presence of metallic *Ni* in the near oxide of the high hydrogen pickup water rod but at high elevation only. The author proposed earlier in this chapter that material 12 (low elevation, high HPUF) did not suffer from enhanced *H* ingress during the additional cycle, but rather the hydrogen was picked up at higher elevation and diffused down the water rod. As a result, the author establishes that the presence of metallic nickel is dependent on the location in the reactor, and the acceleration of hydrogen pickup occurred at mid/high elevation only in the water rod.

Additionally, Kuri *et al.* recently published XANES analysis in the near oxide and in the far oxide of a high burnup/high hydrogen content Zry-2 fuel cladding rod used in BWR [220], but concluded that no metallic nickel was observed in the oxide layer. However, a pre-edge feature can be seen in the *Ni* XANES spectra collected in the near oxide, similar to the features seen in the high hydrogen uptake materials in the present work and in [91] and which was identified as the signal originating from partially metallic nickel atoms. Because metallic nickel is a strong catalyst for *H* ingress while oxidized nickel is not [59, 216, 337], the author argues that this pre-edge feature does represent metallic nickel atoms in the oxide layer. As result, metallic nickel can be seen in the near oxide of a high HPUF / high burnup BWR Zry-2 fuel rod as well.

It is worth mentioning that in [337], Wells *et. al* observed the reduction of oxidized nickel particles deposited on the surface of Zircaloy-4 coupons corroded in high hydrogenated water; and in recent DFT calculation by Than *et. al* [153] of the alloying elements defect formation energy in *t-ZrO₂*, the author reported that metallic nickel bonded with an oxygen vacancy was the most stable defect at low oxygen levels, while the stable defects for *Fe* and *Cr* involved oxidized atoms at all oxygen pressures. Therefore, reduction and/or stability of metallic

nickel in the oxide layer may occur at low oxygen pressure and/or high hydrogen content in the coolant next to the interface.

In previous studies by Pettersson *et al.* [216] and Takagi *et al.* [338] investigating the enhancement of hydrogen uptake when metallic nickel is added to *Zr* alloys, it was reported that hydrogen atoms were catalytically picked up from the hydrogenated water or deuterium gas only if nickel was deposited on the surface of the materials and no oxide layer was present on the sample surface. These observations indicate that metallic nickel act as a catalyst for hydrogen absorption in *Zr* alloys when deposited on free surfaces close to the metal bulk, as suggested in previous work investigating the role of nickel in *H* pickup at high burnup [99, 217].

When comparing the oxide thickness and hydrogen pickup in the 4-cycle water rod to that of the 3-cycle water rod (Figure 5-2, section 3.2), both accelerated corrosion and hydrogen pickup are observed as a result of the additional cycle, and regions of high hydrogen content match with the regions of accelerated corrosion. Interestingly, the variations of *H* pickup and oxide thickness coincide with the neutron flux axial profile in BWR [339] where the peak flux is located about 100 *in* above the bottom of the core. This observation is coherent with examinations by Urbanic [336] of Zry-2 pressure tubes corroded in CANDU-PHW reactors for up to 3700 full power days, where the pressure tubes showed a sharp increase in the corrosion and deuterium (as heavy water is used as coolant in CANDU reactors) uptake in the region of highest neutron flux. This correlation suggests that the neutron flux plays a significant role in the acceleration of corrosion and hydrogen uptake in Zircaloy-2 at high burnup.

As reviewed extensively by Kautz in a recent paper [315], irradiation-accelerated corrosion is one of the major in-pile phenomena that autoclave corrosion studies of zirconium alloys could not reproduce [127, 134, 265, 340, 341], and may arise from different mechanisms in the nuclear reactors. As mentioned in chapter 1, amorphization and dissolution of the secondary phase particles (SPPs) due to irradiation in BWRs was reported as accelerating corrosion at high

burnup in Zry-2 materials [228, 342-344], and the authors argue that the barrier layer protectiveness deteriorates when dissolution of the SPPs occurs. This mechanism explaining the accelerated in-reactor oxidation is supported by a more recent study of Zry-4 materials corroded in a reactor test loop [345].

As mentioned in chapter 4, Chollet *et al.* [325] suggested that the diffusion of O in Zr alloys is enhanced by irradiation, which in turn increases the corrosion kinetics as the diffusion of O in the oxide layer is limiting the corrosion rate in Zr alloys (see section 1.3).

Another mechanism for irradiation-accelerated corrosion may be associated with the modification of the oxide structure near the metal interface. Under irradiation, the tetragonal-to-monoclinic transformation is more spontaneous and may lead to porosity or crack formation in the oxide layer. These nanopores and cracks can then short-circuit the oxide (also known as percolation of water in the oxide layer), allowing the water coolant to reach metal matrixes more easily [14, 346]. The percolation of water through the oxide layer all the way to the metal interface was measured recently for many reactor-corroded Zircaloy-2 materials by Prabhakaran *et al.* [347] using electrochemical impedance spectroscopy (EIS). The authors report that for over the various samples, there is a distribution of oxide layers that allow the water to communicate directly with the metal. Additionally, the formation and growth of equiaxed oxide grain under irradiation may increase porosity in the outer layer [315].

The percolation of the oxide layer, whether due to irradiation induced phase transformation, oxide grain growth or other mechanisms in the reactor, has been suggested by Arimescu [217] to explain the acceleration of corrosion and hydrogen uptake at high burnup in the reactor, arguing that the local water chemistry (modified by radiolysis) in the oxide layer may play a key role in the corrosion and H ingress kinetics once a thick oxide layer has been built on the materials. The “thick oxide” effect has been reported in many previous studies with a thickness threshold estimated at 10-15 μm [59, 173, 217], but is not sufficient to explain the

increase in corrosion kinetics and hydrogen uptake [31]. As seen in this study and in Shivprasad's work [91], no acceleration of hydrogen uptake is seen in the water rod taken out after 3 cycles in the reactor, but oxide layers up to $30\ \mu\text{m}$ were measured at several elevations (Figure 5-3). On the other hand, metallic nickel was seen in the thin oxide layer of material 21 ($16\ \mu\text{m}$, high elevation, high HPUF, Dresden-2 BWR) up to $10\ \mu\text{m}$ from the metal/oxide interface [99], suggesting that the oxide thickness was around $5\text{-}6\ \mu\text{m}$ when the hydrogen pickup increased during the 4th cycle. These observations indicate that a combination of specific conditions leads to the acceleration of corrosion and hydrogen uptake at high burnup in BWR.

Lastly, radiolysis has been extensively investigated in BWR and PWR, namely because of the stress corrosion cracking (SCC) effect in the structural components due to the increase in oxidizing species in the coolant under irradiation [212]. Radiolysis of the water under irradiation leads to the formation of many oxidizing and reducing species in the coolant. Due to the short lifetime of many of these species in water, only the O_2 and H_2O_2 (oxidizing) and H_2 molecules are stable in the coolant system. These oxidizing and reducing species may in turn affect the electrochemical potential near the metal surface of the materials, affecting the corrosion and hydrogen uptake. Especially, O_2 and H_2 are more volatile (H_2 even more) than H_2O_2 and are stripped away from the coolant by the steam present in BWRs. As such, a high H_2O_2 concentration is measured in the recirculating liquid water system, and this phenomenon led to the modification of BWR water chemistry to incorporate hydrogen injection in the recirculating water [348].

In an extensive review of Zry-2 hydrogen pickup data as a function of fluence and burnup in BWRs [173], Nissen *et. al.* reports a relationship between low power regimes following a high power period and the high hydrogen uptake of Zry-2 components. The authors argue that the high power period allows for a thick oxide layer to be formed (the “thick oxide” effect), and the following low power cycle strongly reduces the steam quality in the reactor, so that H_2 is not

removed as efficiently by the steam phase in the coolant, increasing the probability of H absorption into the metal.

Additionally, the enhancement of hydrogen pickup occurred at a lower fluence in Dresden-2 reactor (Mat. 21, high HPUF, high elevation, fluence of $9.4 \times 10^{21} \text{ n/cm}^2$ [99]) than in Limerick-1 reactor where materials 10 and 11 (mid and high elevation, 3 cycles, see *Table 2-1*) had a superior fluence and thicker oxides but the hydrogen pickup fraction did not increase in these materials. Because radiolysis effects are more pronounced in Dresden-2 than in Limerick-1 reactor [349], this observation supports the hypothesis that radiolysis plays an important role in enhancing hydrogen uptake at high burnup, but other factors such as the difference in water chemistry between the two reactors may also be at play.

Based on these discussions and on the results presented in this work, the author proposes a mechanism for the accelerated hydrogen uptake of the Zry-2 water rod during the additional cycle in Limerick-1 BWR, illustrated in Figure 5-4 and described below.

At high fluence, cracks and interconnected nanopores close to the metal interface allow the coolant to reach the metal interface directly. At mid/high elevation in the water rod, the radiolysis events due to the intense irradiation flux increase the concentration of oxidizing and reducing species in the porous oxide layer, affecting the local water chemistry near the metal interface. At low power (fuel rod with a low linear power, water rods, structural components), the lower steam quality (and water flow in some cases) reduces the mixing of the water in the thick oxide layer, allowing for local water chemistry that may be vastly different to that of the bulk. Irradiation-induced acceleration of the corrosion kinetics induces oxygen depletion in the cracks and nanopores, leading to increase in hydrogen concentrations near the metal/oxide interface. Under the more reducing conditions, nickel atoms that are not yet oxidized in the near oxide may

remain metallic at the cracks and nanopipes surfaces. Then, the remaining metallic nickel atoms act as catalyst for the hydrogen uptake surface reactions (and H_2 decomposition), leading to a sharp increase in hydrogen pickup.

The mechanism presented above does not occur at low elevation during the additional cycle because the low irradiation flux limits radiolysis effects in the porous oxide layer and oxidation kinetics are rather slow (low fluence). Therefore, the hydrogen concentration near the metal interface is not high enough to allow metallic nickel to remain in the oxide layer. At high elevation during the 3rd cycle, the oxidation kinetics are not fast enough and/or the percolation of the oxide layer is not complete which prevents the increase in hydrogen concentrations close to the metal interface. Now considering Zry-2 fuel cladding, a low linear power may be required (as hypothesized by Nissen *et. al* [173]) so that boiling due to the heat flux is not as frequent near the metal interface (lower steam quality), lowering the mixing with the coolant bulk so that the local chemistry in the porous oxide can then be modified [59]. In PWRs, this mechanism may be delayed (no observation of HPU acceleration for Zry-2 in PWR [59]) due to the additions of boric acid and lithium hydrides and to the high operation temperature reducing amorphization of the SPPs in the metal bulk [59], or because the oxide is more uniform with fewer cracks in the PWR environment.

Lastly, as detailed in section 3.4.2, detailed analysis of the nickel XANES signal suggests that the nickel atoms remaining metallic in the near oxide layer of the high HPUF materials are in solid solution or in small clusters, rather than in second phase precipitates. This observation is in agreement with recent work by Kucuk *et. al* [329], little to no segregation of nickel atoms was measured with 3D atom probe tomography (APT) in the oxide layers of both the low and high HPUF Zry-2 water rods corroded in Limerick-1 BWR, while the concentration in oxide solid solution corresponds to that of the bulk composition. In the same study, dissolution of the $Zr_2(Fe, Ni)$ at mid elevation after 4 cycles was reported from TEM analysis, but the dissolution

had not yet occurred after 3 cycles at a similar elevation. As discussed above, the hydrogen pickup enhancement is most severe in the highest fluence region of the reactor as mentioned above, and therefore where the amorphization and dissolution of the SPPs is most advanced. For these reasons, metallic nickel atoms contributing to the enhancement of hydrogen uptake at high burnup are likely located in solid solution or in small clusters, rather than in precipitates in the near oxide layer.

Eventually, the role of nickel and of the corrosion environment in enhancing the hydrogen uptake of Zry-2 materials at high burnup was reviewed and a mechanism requiring the presence of high fluence and radiolysis, percolation of the oxide layer and accelerated corrosion during the additional was proposed to explain the hydrogen pickup ingress. The conditions for the onset of enhanced hydrogen pickup have been reviewed, and the presence of metallic nickel near the oxide layer of Zry-2 materials that suffered accelerated hydrogen ingress is confirmed with the present work. Therefore, the author predicts that this hydrogen pickup acceleration observed at high burnup in Zry-2 corroded in BWRs is not likely to occur in modern *Ni*-free alloys. In the next section, the main conclusions of this study and the proposed mechanism for enhanced hydrogen pickup are summarized, followed by the future work suggested by the author.

Chapter 6

Conclusions and Future Work

6.1 Conclusions

In this work, the oxide layers formed on in-reactor Zry-2 water rods were investigated with microbeam X-ray absorption near-edge spectroscopy (XANES), X-ray diffraction (XRD) and scanning electron microscopy (SEM) in an effort to understand the role of nickel in enhancing hydrogen pickup into the metal in the BWR environment at high burnup. Using microbeam synchrotron radiation, both the nickel oxidation state and the oxide layer microstructure were investigated (with XANES and XRD respectively) as a function of distance from the metal/oxide interface in the thick oxide layers of the Zry-2 materials. These quantities measured at different locations in the water rods were compared in terms of the hydrogen pickup observed at those locations. The main conclusions of this investigation are:

- (1) **The presence of metallic nickel in the oxide layer is correlated with enhanced hydrogen pickup.** The correlation was directly verified for the material selected from the high elevation part of the water rod which showed metallic nickel and high hydrogen pickup. For the low elevation material, although the correlation was not directly verified (the hydrogen content at that location was high while the *Ni* atoms in the oxide layers were fully oxidized), it is believed that the high hydrogen content observed at that location results from the diffusion down the water rod of hydrogen atoms absorbed at higher elevation, driven by concentration and temperature axial gradients.

- (2) **The metallic nickel atoms remaining in the oxide layers of the high hydrogen pickup materials are not in second phase precipitates (SPPs).** Detailed analysis of the *Ni* XANES signal from the near oxide regions indicates that the metallic nickel atoms are no longer bonded to zirconium atoms, which shows that the metallic nickel which can affect hydrogen pickup consists of atoms in solid solution or in small clusters in the oxide layer, rather than in second phase precipitates. This is in agreement with recent atom probe tomography (APT) examinations of the selected Zry-2 water rods (high burnup, high hydrogen pickup) in which the nickel atoms were seen uniformly distributed in the oxide layer and only small clusters were observed.
- (3) **Irradiation seems to play an important role in accelerating corrosion and in stabilizing metallic nickel in the oxide layer during the additional cycle.** Increased oxidation kinetics and the presence of metallic nickel in the oxide layer were seen only at mid/high elevation in the water rods, where the irradiation flux is the most intense. This observation indicates that irradiation plays a key role in enhancing corrosion and nickel oxidation state. We argue that the oxide layer barrier deteriorates under irradiation in the reactor and loses its protectiveness at high fluence, allowing the water to reach the metal/oxide interface directly, which increases the corrosion kinetics of the Zry-2 water rods and in turn depletes the near oxide region of oxygen atoms. Additionally, radiolysis effect may change locally the concentration of oxidizing and reducing species in the coolant trapped within the thick and porous oxide layer during the additional cycle, as previously suggested, affecting corrosion kinetics and nickel oxidation state in the oxide layer (and in turn hydrogen pickup).

- (4) **Many cracks were seen in the oxide layers of the Zry-2 water rods selected, with slightly more cracking observed in the high HPUF/high elevation samples.** The oxide layers were rather uniform but extensive oxide thickness variations could be observed between different regions for all the materials, especially regions in the inner oxide layers of the samples prepared for this study. Examinations of the GNF water rods by EPRI confirmed circumferential variations of the oxide thickness in both the inner and outer parts of the two water rods. These variations may result from the differences in coolant flow, steam quality, irradiation flux and SPP distributions in the water rods, as well as the proximity to other structural materials in the reactor. These observations are coherent with previous examinations of Zry-2 oxide layers formed in BWRs.
- (5) **No clear differences in oxide microstructure studied with microbeam XRD could be observed between the low and high hydrogen pickup materials.** In general, the observations agree with what was previously seen in literature. In all the materials selected, the oxide consists mainly of monoclinic ZrO_2 grains and the highest content of the tetragonal oxide phase was measured in the near oxide layer ($< 5 \mu m$), confirming the tetragonal-to-monoclinic transformation as the oxide grows. This maximum tetragonal volume fraction was in the low range of values reported in literature (3-6 %). The monoclinic oxide grain growth was measured in all materials (from 17-20 nm near the metal interface, to 33-38 nm in the outer region). The largest grains were observed in the oxide layer close to the water interface of the high elevation materials, suggesting irradiation-induced grain growth in the oxide layers. Additionally, small grains compose the oxide region near the metal/oxide interface of material 14 (high HPUF, high elevation, 4 cycles) when compared to material 11 (low HPUF, high elevation, 3 cycles) which is coherent with the acceleration of corrosion during the last cycle in the reactor

observed with oxide thickness measurements. Lastly, an orientation relationship between the (111) $m\text{-ZrO}_2$ and the (10 $\bar{1}$ 0) $\alpha\text{-Zr}$ crystal planes is observed in all materials and a strong texture was consistently present in the oxide layers studied. For a significant fraction of oxide grains throughout the whole oxide layer, the (200) $m\text{-ZrO}_2$ direction is close to the oxide growth direction. This is coherent with previous XRD examinations of autoclave and in-reactor corroded Zr -alloys.

- (6) **Metallic nickel atoms from deposits at the oxide/water interface do not enhance hydrogen uptake.** Nickel atoms in the oxide layer near the oxide/water interface - identified as deposits from the corrosion of other reactor components - are in a high percentage metallic for some of the samples examined, with the highest metallic fraction (0.75 or 75%) observed in the low HPUF/high elevation sample (Mat. 11), while little to no metallic nickel was present near the oxide/water interface of the high HPUF/high elevation material (Mat. 14). This observation indicates that the metallic nickel in the crud deposits do not seem to have played a determinant role in the enhancement of hydrogen uptake in the Zry-2 water rods examined. We argue that the distance to the metal interface is too large and the diffusion of hydrogen in the oxide too low for the metallic nickel atoms near the oxide/water interface to enhance hydrogen uptake into the bulk material.

From the presented results and based on previous work – a review of available literature – hypotheses, a mechanism is proposed to explain the acceleration of hydrogen uptake of the Zry-2 water rod during the additional cycle in the BWR and is believed to occur due to a combination of specific conditions in the reactor at high burnup. The proposed mechanism and the required conditions are summarized in Figure 6-1. The acceleration of hydrogen pickup during the

additional cycle in BWR is inherent to the presence of metallic nickel atoms in the bulk material, while *Ni* deposits near the oxide/water interface of the thick oxide layers are not believed to affect the hydrogen ingress. In turn, the author predicts that this phenomenon is not likely to occur at high burnup in modern *Ni*-free alloys.

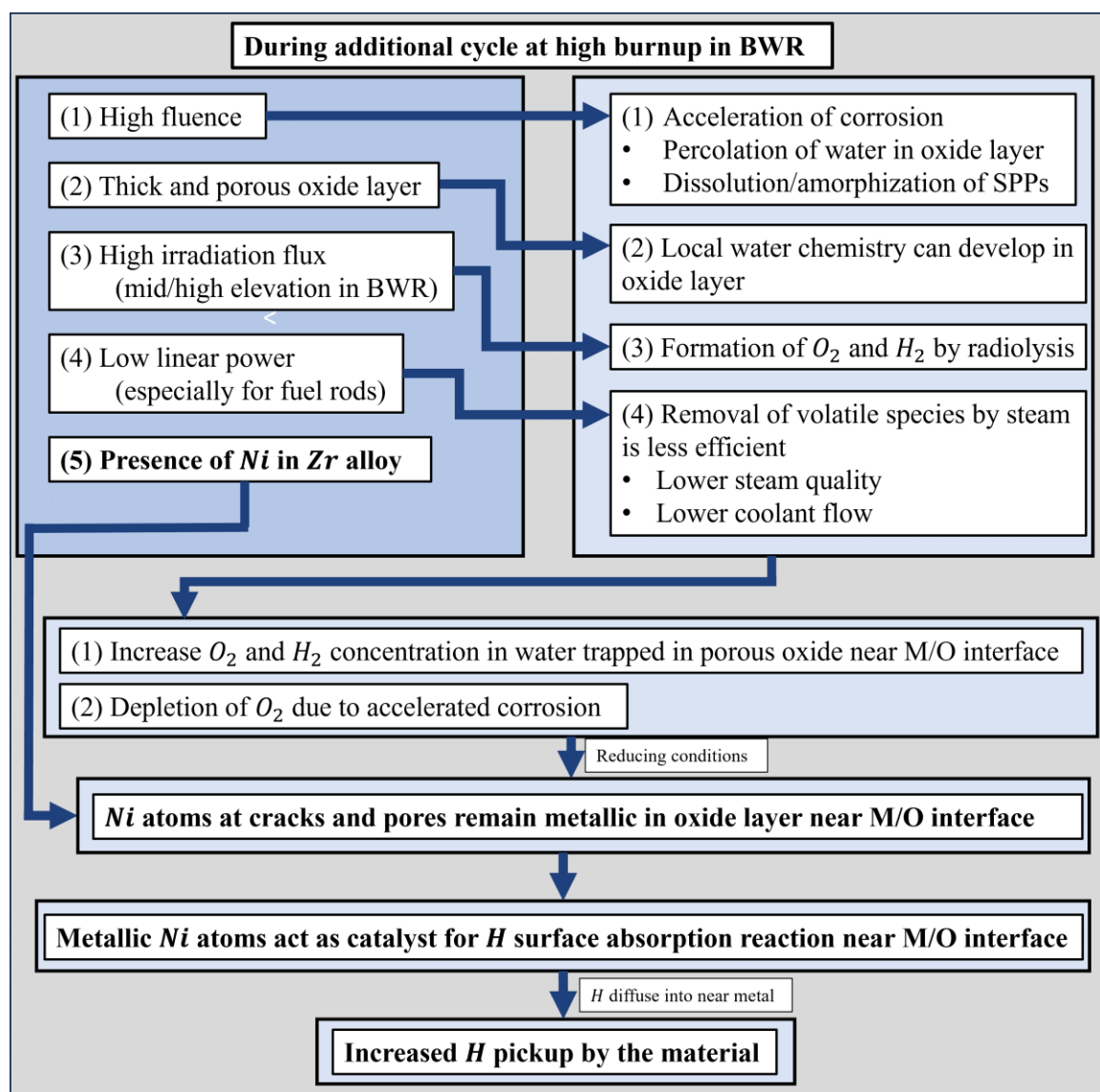


Figure 6-1: Review of the conditions and mechanism leading to increased H pickup of Zry-2 materials during the additional cycle at high burnup in BWR.

6.2 Future work

In order to better understand the conditions leading to the enhancement of hydrogen pickup of Zircaloy-2 materials in BWR at high burnup, and verify the mechanism proposed, the following experiments and simulations are suggested:

- (1) Simulations of the diffusion of hydrogen in the water rods due to the concentration and temperature axial gradients may confirm the hypothesis that hydrogen picked up at mid/high elevation during the additional cycle diffused down the water rod. It is planned to perform Finite Element simulations of the hydrogen evolution in the water rod using MATLAB (and potentially BISON for 3-D simulations) to further investigate this hypothesis.
- (2) Simulations of the XANES signal of metallic *Ni* as a dopant in monoclinic and tetragonal zirconia (using FEFF software) in order to better understand the XANES signal arising from metallic nickel atoms remaining in the near oxide layer of the high hydrogen pickup materials.
- (3) Similarly, EXAFS measurements at the nickel edge in the oxide layers of the water rod investigated in this study would provide insight into the local environment of the partially metallic nickel atoms in the near oxide layer.
- (4) Additional measurements of oxide thickness and hydrogen pickup as a function of elevation in high HPUF Zry-2 BWR materials may confirm the relationship observed in this study between the irradiation profile and the oxidation kinetics and hydrogen pickup enhancements at high burnup which suggests that irradiation plays a key role in enhancing hydrogen uptake.
- (5) Additional electron microscopy analyses of the oxide layers of the different materials may yield interesting results in terms of grain size and shape of the monoclinic oxide

phase. A higher density of equiaxed grains compared to elongated oxide grains has been hypothesized to result from irradiation effect and increase porosity.

- (6) In order to verify that metallic nickel may remain in the oxide layer of the porous oxide due to the high local variations in local chemistry leading to high reducing conditions in some locations, autoclave-corrosion of Zircaloy-2 in high hydrogenated water may be performed followed by the measurement of the oxidation state of nickel in the newly built oxide. Samples must be corroded for long enough to ensure that a significant oxide was formed.
- (7) Calculations of the local water chemistry in the porous oxide layer may be performed assuming that the oxidizing species are either picked up in the material or trapped in the cracks in the porous oxide to estimate the concentration buildup during accelerated corrosion in the reactor.

Appendix A

Powder Diffraction Files (ICDD)

The following tables are the Powder Diffraction Files from the International Center for Diffraction Data (ICDD) used in this study, along with the corresponding diffraction angles at the beam energy used during the XRD experiments $E = 8.5 \text{ keV}$.

Table A-1: ICDD # 05-1665, hexagonal α -Zr, $a = 3.232 \text{ \AA}$, $c = 5.147 \text{ \AA}$

$d(\text{\AA})$	h	k	i	l	Intensity	2θ $E = 8.5 \text{ keV}$
2.79801	1	0	-1	0	33%	30.218
2.57301	0	0	0	2	32%	32.932
2.45899	1	0	-1	1	100%	34.506
1.89399	1	0	-1	2	17%	45.296
1.61601	1	1	-2	0	17%	53.655
1.46300	1	0	-1	3	18%	59.803
1.39899	2	0	-2	0	3%	62.841
1.36800	1	1	-2	2	18%	64.434
1.35000	2	0	-2	1	12%	65.399
1.28700	0	0	0	4	4%	69.038
1.16890	1	0	-1	4	3%	77.208
1.08420	2	0	-2	3	4%	84.548
1.05880	2	1	-3	0	2%	87.073
1.03600	2	1	-3	1	6%	89.493
1.00630	1	1	-2	4	3%	92.896
0.97830	2	1	-3	2	2%	96.403
0.96600	1	0	-1	5	4%	98.049
0.94740	2	0	-2	4	2%	100.674
0.93270	3	0	-3	0	3%	102.877
0.90030	2	1	-3	3	5%	108.208
0.87710	3	0	-3	2	3%	112.509
0.85770	0	0	0	6	1%	116.493
0.82920	2	0	-2	5	2%	123.175
0.82010	1	0	-1	6	2%	125.572

Table A-2: ICDD # 34-0657, cubic β -Zr, $a = 3.5453 \text{ \AA}$

$d(\text{\AA})$	h	k	l	Intensity	2θ $E = 8.5 \text{ keV}$
2.507	1	1	0	100%	33.825
1.7726	2	0	0	17%	48.591
1.4474	2	1	1	33%	60.514
1.2553	2	2	0	10%	71.041
1.1211	3	1	0	15%	81.164
1.0234	2	2	2	4%	90.901
0.9475	3	2	1	23%	100.659
0.8863	4	0	0	3%	110.748
0.8356	4	1	1	15%	121.573
0.7928	4	2	0	25%	133.831

Table A-3: ICDD # 26-1399, hexagonal ω -Zr, $a = 5.039 \text{ \AA}$, $c = 3.136 \text{ \AA}$

$d(\text{\AA})$	h	k	i	l	Intensity	2θ $E = 8.5 \text{ keV}$
3.13	0	0	0	1	20%	26.949
2.53	1	1	-2	0	100%	33.509
1.961	1	1	-2	1	10%	43.667
1.792	2	0	-2	1	40%	48.031
1.566	0	0	0	2	20%	55.514
1.457	3	0	-3	0	80%	60.074
1.33	1	1	-2	2	30%	66.509
1.259	2	2	-4	0	30%	70.800
1.129	3	1	-4	1	30%	80.479
1.066	3	0	-3	2	20%	86.340
0.982	2	2	-4	2	25%	95.921
0.9533	3	2	-5	1	40%	99.822
0.9428	2	0	-2	3	5%	101.350
0.8829	2	1	-3	3	20%	111.390
0.8404	5	0	-5	1	30%	120.413
0.814	4	1	-5	2	40%	127.266
0.7983	4	2	-6	1	20%	132.012
0.7911	3	1	-4	3	10%	134.412

Table A-4: ICDD # 34-0690, tetragonal γ -ZrH

$d(\text{\AA})$	h	k	l	Intensity	2θ $E = 8.5 \text{ keV}$
2.72	1	1	1	100%	31.106
2.484	0	0	2	30%	34.149

Table A-5: ICDD # 08-2018, cubic δ -ZrH_{1.5}

$d(\text{\AA})$	h	k	l	Intensity	2θ $E = 8.5 \text{ keV}$
2.76	1	1	1	100%	30.644
2.4	2	0	0	30%	35.382

Table A-6: ICDD # 34-0649, cubic δ -ZrH_{1.66}

$d(\text{\AA})$	h	k	l	Intensity	2θ $E = 8.5 \text{ keV}$
2.76	1	1	1	100%	30.644
2.391	2	0	0	47%	35.520
1.69	2	2	0	37%	51.132
1.442	3	1	1	43%	60.765

Table A-7: ICDD # 34-0649, tetragonal ε -ZrH_{1.95}

$d(\text{\AA})$	h	k	l	Intensity	2θ $E = 8.5 \text{ keV}$
2.761	1	1	1	100%	30.633
2.4892	2	0	0	30%	34.074

Table A-8: ICDD # 20-1464, tetragonal ZrH₂

$d(\text{\AA})$	h	k	l	Intensity	2θ $E = 8.5 \text{ keV}$
2.76	1	1	1	100%	30.644
2.45	2	0	0	30%	34.637

Table A-9: ICDD # 37-1484, monoclinic ZrO_2 , $a = 5.3129 \text{ \AA}$, $b = 5.2125 \text{ \AA}$, $c = 5.1471 \text{ \AA}$, $\beta = 99.218^\circ$.

$d(\text{\AA})$	h	k	l	Intensity	2θ $E = 8.5 \text{ keV}$
5.087	0	0	1	3%	16.486
3.698	1	1	0	14%	22.749
3.639	0	1	1	10%	23.123
3.165	-1	1	1	100%	26.645
2.841	1	1	1	68%	29.750
2.623	2	0	0	21%	32.287
2.606	0	2	0	11%	32.504
2.54	0	0	2	13%	33.373
2.499	-2	0	1	2%	33.937
2.334	1	0	2	4%	36.417
2.2845	0	1	2	0.1%	37.235
2.2527	-2	1	1	0.1%	37.780
2.2138	1	1	2	12%	38.470
2.1919	2	0	1	5%	38.870
2.1805	-1	2	1	5%	39.081
2.0203	2	1	1	7%	42.323
1.991	-2	0	2	6%	42.976
1.8593	-2	1	2	2%	46.190
1.8481	2	2	0	18%	46.486
1.8187	0	2	2	22%	47.283
1.8038	-2	2	1	13%	47.697
1.783	-1	2	2	5%	48.289
1.6937	0	2	3	11%	51.012
1.6772	2	0	1	0.1%	51.551
1.6571	3	2	2	0%	52.223
1.6524	-3	1	1	9%	52.383
1.6439	0	1	1	6%	52.674
1.61	-1	3	3	7%	53.872
1.5924	-1	1	1	4%	54.516
1.5822	-2	3	2	3%	54.897
1.5459	1	2	1	8%	56.299
1.5393	-2	3	3	7%	56.562
1.5095	3	1	1	5%	57.783
1.496	-3	2	2	5%	58.354
1.4777	1	3	3	8%	59.148
1.452	3	0	0	1%	60.303
1.4486	2	3	0	2%	60.459

1.4343	0	3	2	0.1%	61.126
1.4262	-2	3	1	2%	61.510
1.4201	0	2	3	6%	61.804
1.4165	-1	3	2	4%	61.978
1.3615	2	3	1	1%	64.779
1.3494	3	2	1	0.1%	65.432
1.3398	-3	2	2	0.1%	65.960
1.3253	-2	2	3	2%	66.776
1.3217	-4	0	1	4%	66.982
1.3113	4	0	0	1%	67.584
1.3089	-2	3	2	1%	67.725
1.3035	0	4	0	0.1%	68.043
1.3005	3	1	2	0.1%	68.222
1.2862	-3	1	3	0.1%	69.087
1.27	0	0	4	2%	70.097
1.2647	1	4	0	4%	70.434
1.2455	-1	1	4	1%	71.685
1.2321	3	3	0	0.1%	72.588
1.223	4	0	1	0.1%	73.216
1.2127	0	3	3	1%	73.940

Table A-10: ICDD # 42-1164, tetragonal ZrO_2 , $a = 3.64 \text{ \AA}$, $b = 5.27 \text{ \AA}$.

$d(\text{\AA})$	h	k	l	Intensity	2θ ($E = 8.5 \text{ keV}$)
2.995	1	0	1	100%	28.188
2.635	0	0	2	39%	32.136
2.574	1	1	0	34%	32.919
2.134	1	0	2	2%	39.968
1.841	1	1	2	34%	46.676
1.82	2	0	0	38%	47.247
1.582	1	0	3	12%	54.905
1.5553	2	1	1	13%	55.929
1.4975	2	0	2	7%	58.290
1.385	2	1	2	0.1%	63.550
1.3175	0	0	4	6%	67.223
1.287	2	2	0	8%	69.038
1.2388	1	0	4	0.1%	72.134
1.194	2	1	3	3%	75.297
1.1824	3	0	1	3%	76.167
1.1728	1	1	4	3%	76.904
1.1564	2	2	2	2%	78.201
1.1511	3	1	0	2%	78.630
1.0672	2	0	4	2%	86.219
1.0548	3	1	2	3%	87.486
1.0124	1	0	5	2%	92.173
0.9983	3	0	3	2%	93.867
0.9915	3	2	1	2%	94.711
0.9206	2	2	4	2%	104.787
0.91	4	0	0	3%	106.537
0.8847	2	1	5	1%	111.049
0.8783	0	0	6	1%	112.274
0.8753	3	2	3	1%	112.862
0.8707	4	1	1	1%	113.780
0.8668	3	1	4	1%	114.575
0.8602	4	0	2	1%	115.956
0.858	3	3	0	1%	116.428
0.8313	1	1	6	1%	122.642
0.8158	3	3	2	3%	126.758
0.8139	4	2	0	3%	127.294
0.7957	3	0	5	2%	132.860
0.791	2	0	6	3%	134.446
0.788	4	1	3	3%	135.214
0.7777	4	2	2	3%	139.367

Table A-11: ICDD # 50-1089, *tetragonal ZrO₂*, $a = 3.8984 \text{ \AA}$, $b = 5.152 \text{ \AA}$.

$d(\text{\AA})$	h	k	l	Intensity	2θ $E = 8.5 \text{ keV}$
2.95	0	1	1	100%	28.627
2.575	0	0	2	8%	32.906
2.544	1	1	0	12%	33.319
2.095	0	1	2	1%	40.745
1.8099	1	1	2	43%	47.527
1.7988	0	2	0	22%	47.838
1.5497	0	1	3	14%	56.149
1.5358	1	2	1	24%	56.703
1.4749	2	0	2	7%	59.272
1.2879	0	0	4	3%	68.983
1.272	2	2	0	5%	69.970
1.1744	1	2	3	11%	76.780
1.1685	0	3	1	6%	77.239
1.149	1	1	4	4%	78.802
1.1411	2	2	2	3%	79.455
1.1377	1	3	1	3%	79.740
1.0472	0	2	4	3%	88.285
1.0408	1	3	2	9%	88.971

Table A-12: ICDD # 17-923, *tetragonal ZrO₂*, $a = 5.12 \text{ \AA}$, $b = 5.25 \text{ \AA}$.

$d(\text{\AA})$	h	k	l	<i>Intensity</i>	2θ $E = 8.5 \text{ keV}$
2.96	1	1	1	100%	28.528
2.6	0	0	2	18%	32.581
2.54	2	0	0	25%	33.373
2.12	1	1	2	6%	40.244
1.83	2	0	2	65%	46.973
1.81	2	2	0	35%	47.524
1.71	2	2	1	2%	50.491
			or (300)		
1.575	1	1	3	25%	55.169
1.547	1	3	1	45%	56.256
1.493	2	2	2	12%	58.483
1.377	1	3	2	2%	63.963
			or (123)		
1.363	2	3	1	2%	64.699
1.312	0	0	4	4%	67.543
1.281	4	0	0	8%	69.408
1.233	1	1	4	2%	72.527
1.204	3	3	0	2%	74.565
1.19	1	3	3	12%	75.595
1.179				8%	76.426
1.169				6%	77.200
1.161				4%	77.832

Table A-13: ICDD # 51-1149, *cubic ZrO*, $a = 4.6258 \text{ \AA}$.

$d(\text{\AA})$	h	k	l	<i>Intensity</i>	2θ $E = 8.5 \text{ keV}$
2.6705	1	1	1	100%	31.698
2.3131	2	0	0	91%	36.758
1.635	2	2	0	48%	52.983
1.3945	3	1	1	35%	63.067
1.3353	2	2	2	13%	66.211
1.1565	4	0	0	9%	78.192
1.0611	3	3	1	12%	86.837
1.0342	4	2	0	18%	89.691
0.9444	4	2	2	14%	101.114

Table A-14: ICDD # 22-1025, *hexagonal* Zr_3O , $a = 5.563 \text{ \AA}$, $b = 31.185 \text{ \AA}$.

$d(\text{\AA})$	h	k	i	l	<i>Intensity</i>	2θ $E = 8.5 \text{ keV}$
4.66	0	1	-1	2	50%	18.008
3.84	0	1	-1	5	50%	21.897
3.29	1	0	-1	7	20%	25.615
2.817	1	1	-2	0	80%	30.009
2.601	0	0	0	12	80%	32.568
2.477	1	1	-2	6	100%	34.247
2.273	2	0	-2	5	5%	37.430
2.14	0	2	-2	7	50%	39.852
2.081	0	0	0	15	5%	41.032
1.911	1	1	-2	12	80%	44.871
1.841	2	1	-3	1	10%	46.676
1.795	2	1	-3	4	10%	47.946
1.769	1	2	-3	5	10%	48.696
1.708	2	1	-3	7	10%	50.555
1.667	1	2	-3	8	5%	51.889
1.627	3	0	-3	0	80%	53.264

Table A-15: ICDD # 21-1498, hexagonal $\text{Zr}_3\text{O}_{1-x}$, $a = 5.56 \text{ \AA}$, $b = 15.59 \text{ \AA}$.

$d(\text{\AA})$	h	k	l	Intensity	2θ $E = 8.5 \text{ keV}$
4.13	1	0	2	70%	20.342
3.04	1	0	4	10%	27.762
2.815	1	1	0	80%	30.031
2.599	0	0	6	80%	32.594
2.475	1	1	3	100%	34.276
2.067	2	0	4	50%	41.322
1.909	1	1	6	80%	44.920
1.83	2	1	1	20%	46.973
1.793	2			10%	48.003
1.666	2	1	4	10%	51.923
1.625	3	0	0	80%	53.335
1.586	2	1	5	10%	54.754
1.522	2	0	8	10%	57.264
1.475	1	1	9	80%	59.267
1.42	2	1	7	5%	61.808
1.407	2	2	0	70%	62.443
1.378	3	0	6	80%	63.911
1.359	2	2	3	80%	64.913
1.347	3	1	1	5%	65.563
1.332	3	1	2	20%	66.396
1.299	0	0	12	70%	68.312

Appendix B

XRD patterns of the oxide layers formed on Mat. 9, Mat. 11 and Mat. 12

XRD patterns of the near metal, near oxide, mid oxide and far oxide regions from materials 9 (low elevation, low HPUF), 11 (high elevation, low HPUF) and 12 (low elevation, high HPUF) for orientation analysis (section 4.3).

Material 9 (low elevation, low HPUF): near metal region

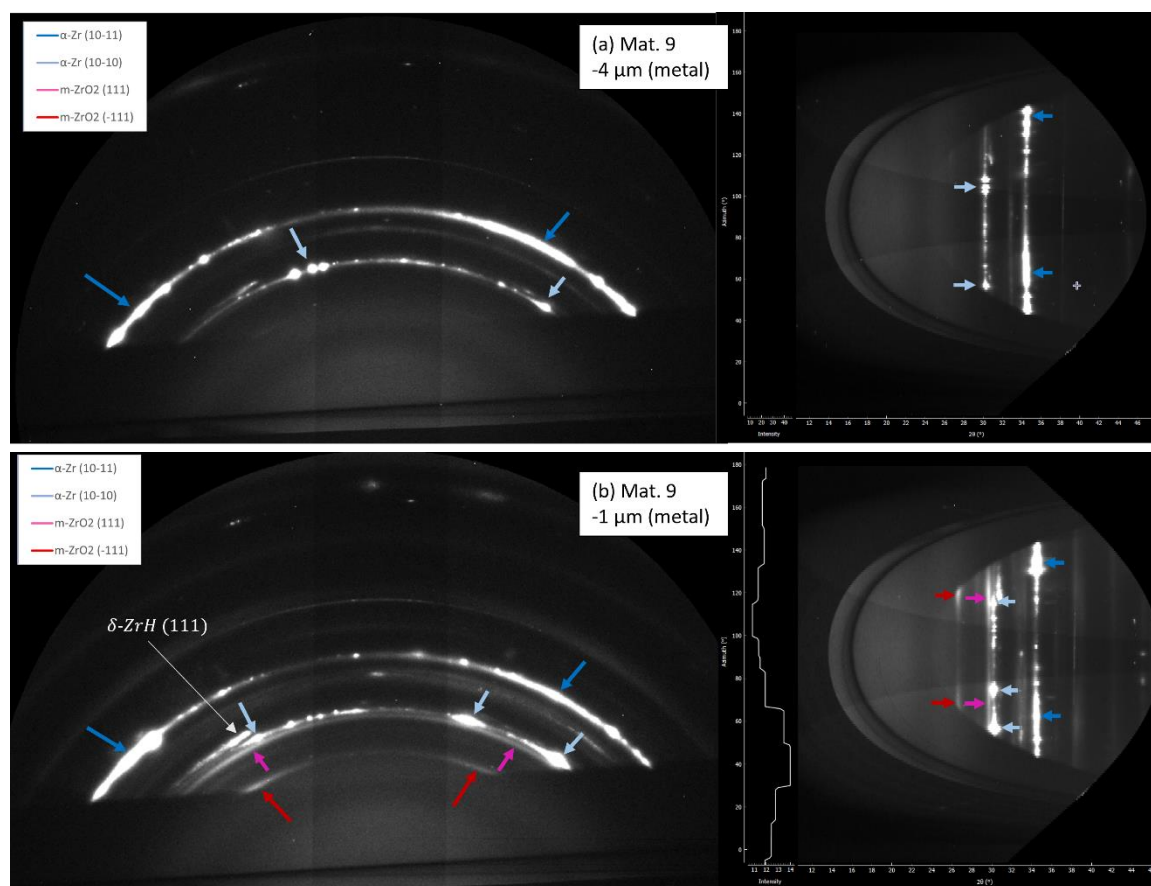


Figure B-1: XRD pattern (image on the left, and "cake" on the right) at two locations in the near metal region of material 9: (a) $-4\ \mu\text{m}$; (b) $-1\ \mu\text{m}$. The high intensity region for the main peaks of α -Zr and m-ZrO₂ are indicated by the colored arrows.

Material 9 (low elevation, low HPUF): near oxide region

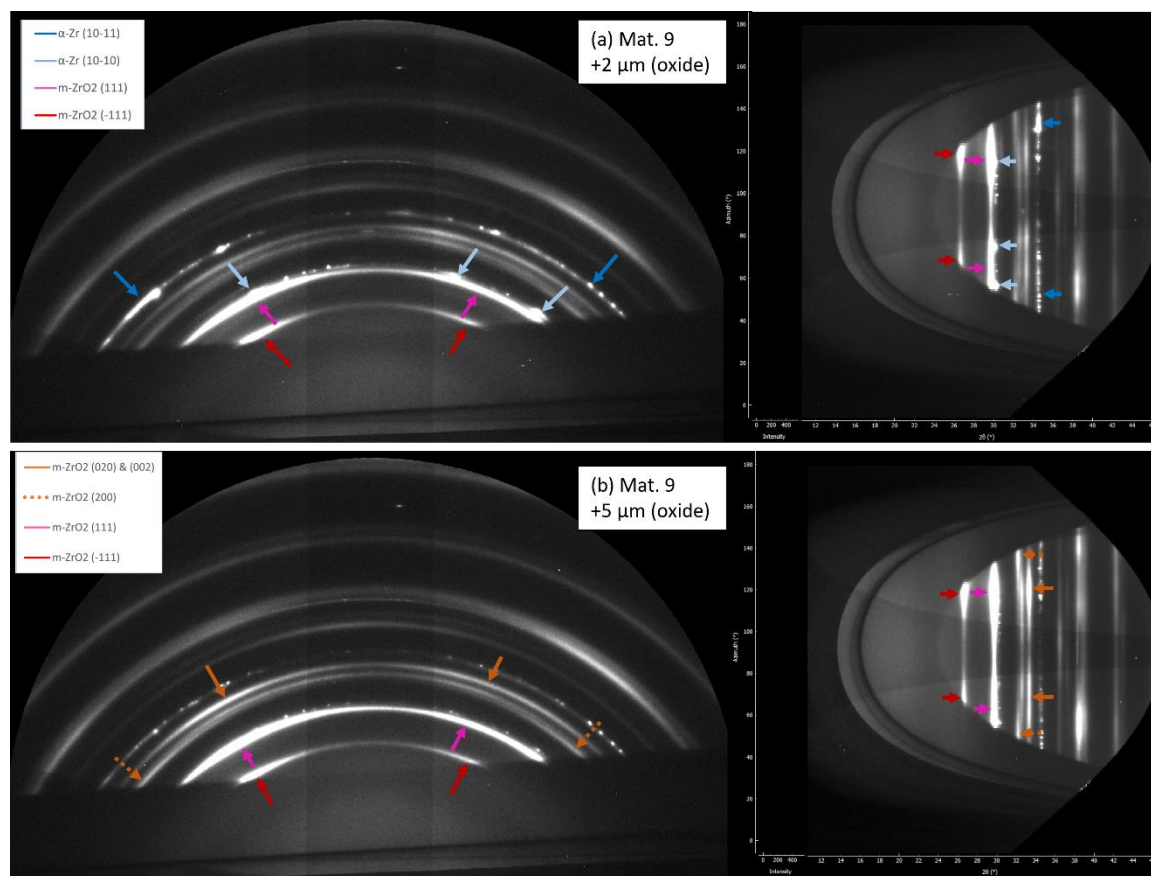


Figure B-2: XRD pattern (image on the left, and "cake" on the right) at two locations in the near oxide region of material 9: (a) +2 μm ; (b) +5 μm . The high intensity region for the main peaks of $\alpha\text{-Zr}$ and $m\text{-ZrO}_2$ are indicated by the colored arrows.

Material 9 (low elevation, low HPUF): mid oxide region

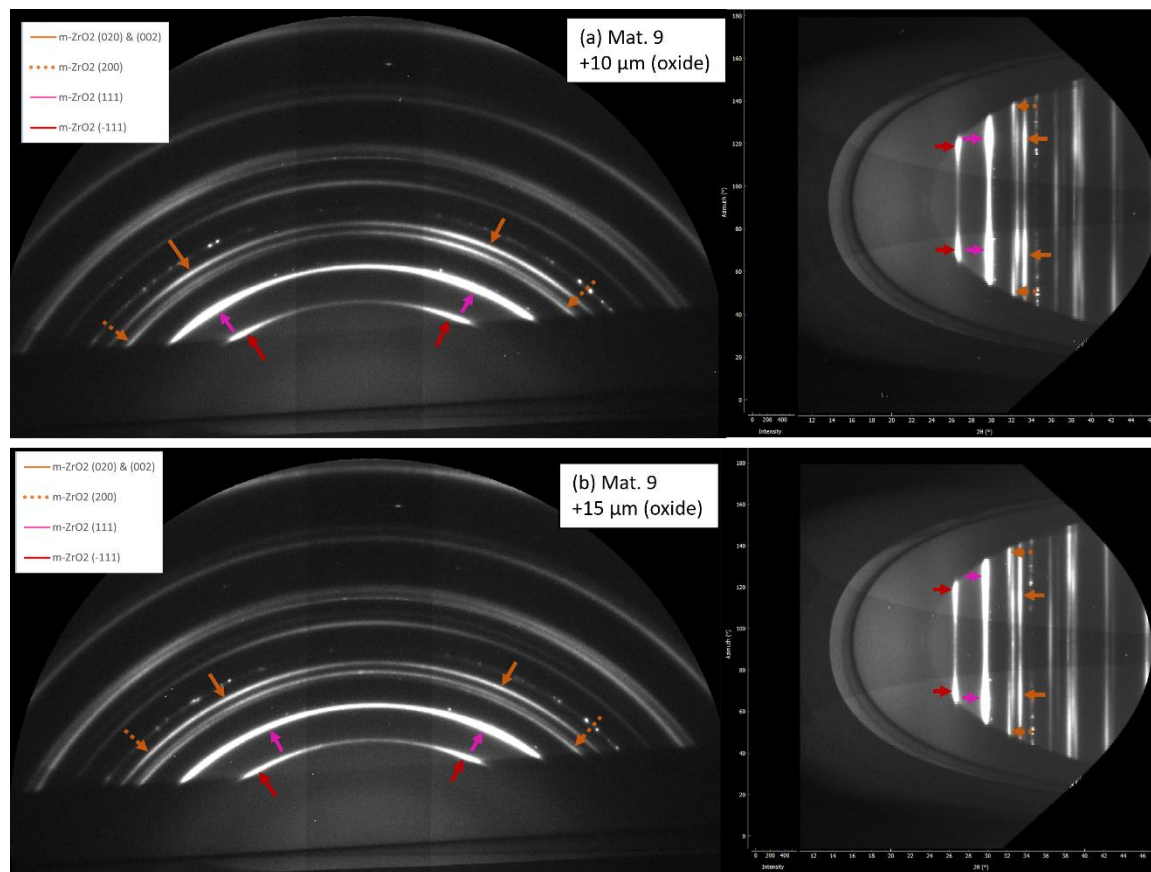


Figure B-3: XRD pattern (image on the left, and "cake" on the right) at two locations in the mid oxide region of material 9: (a) +10 μm; (b) +15 μm. The high intensity region for the main peaks of α-Zr and m-ZrO₂ are indicated by the colored arrows.

Material 9 (low elevation, low HPUF): far oxide region

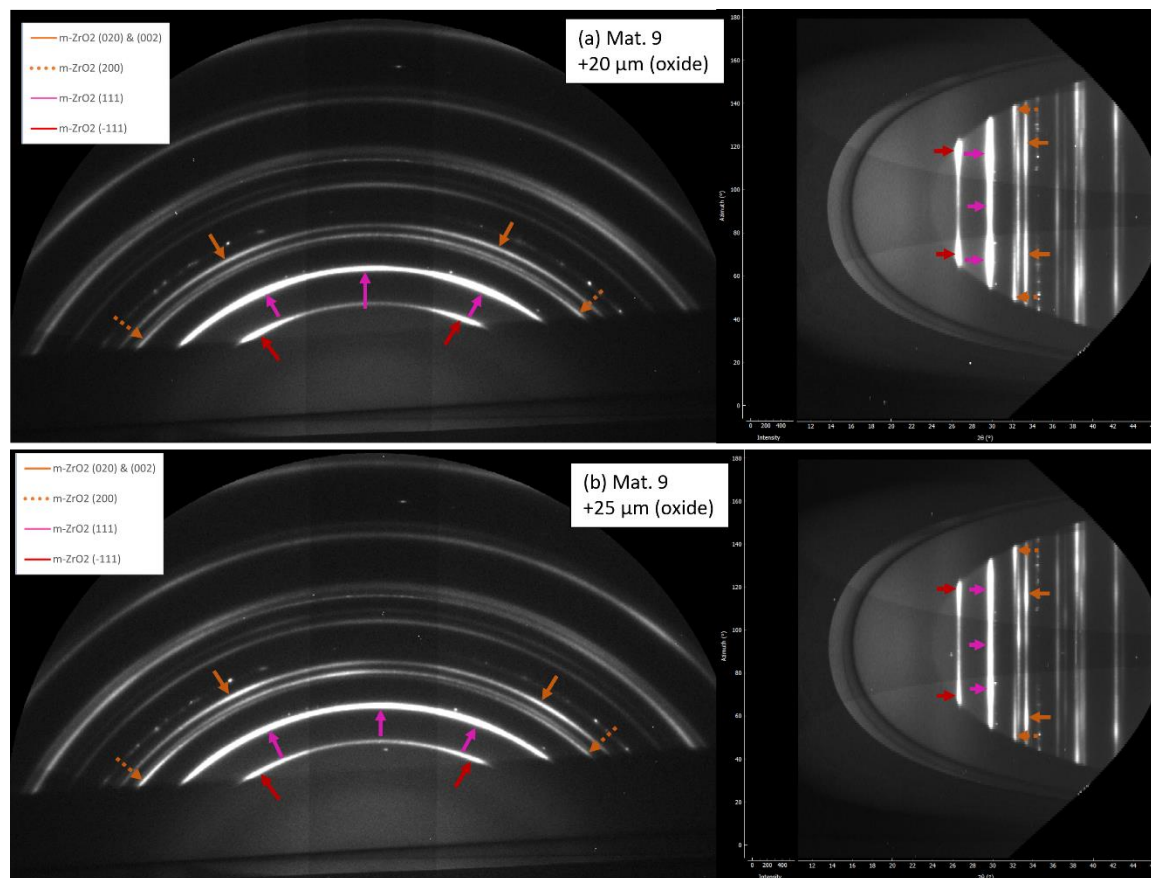


Figure B-4: XRD pattern (image on the left, and “cake” on the right) at two locations in the far oxide region of material 9: (a) +20 μm; (b) +25 μm. The high intensity region for the main peaks of α -Zr and m-ZrO₂ are indicated by the colored arrows.

Material 11 (high elevation, low HPUF): near metal region

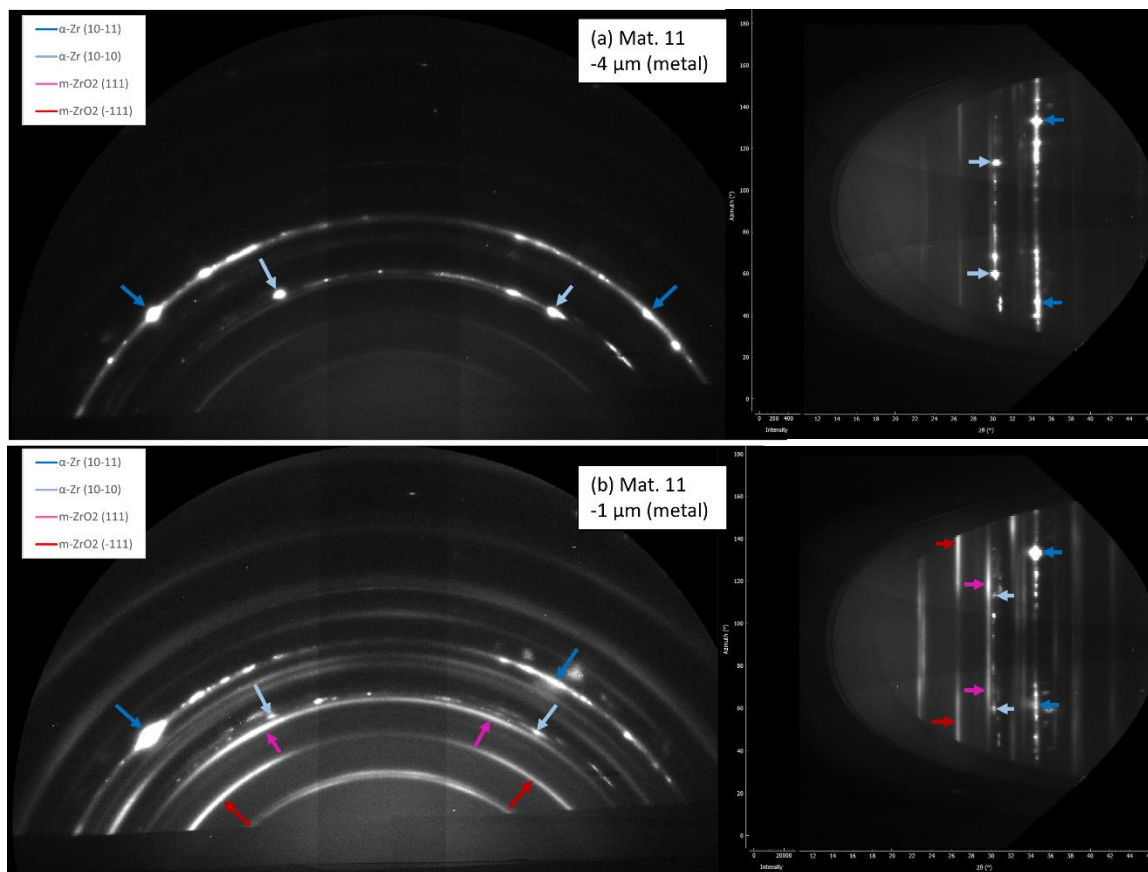


Figure B-5: XRD pattern (image on the left, and “cake” on the right) at two locations in the near metal region of material 11: (a) $-4\ \mu\text{m}$; (b) $-1\ \mu\text{m}$. The high intensity region for the main peaks of α -Zr and m-ZrO₂ are indicated by the colored arrows.

Material 11 (high elevation, low HPUF): near oxide region

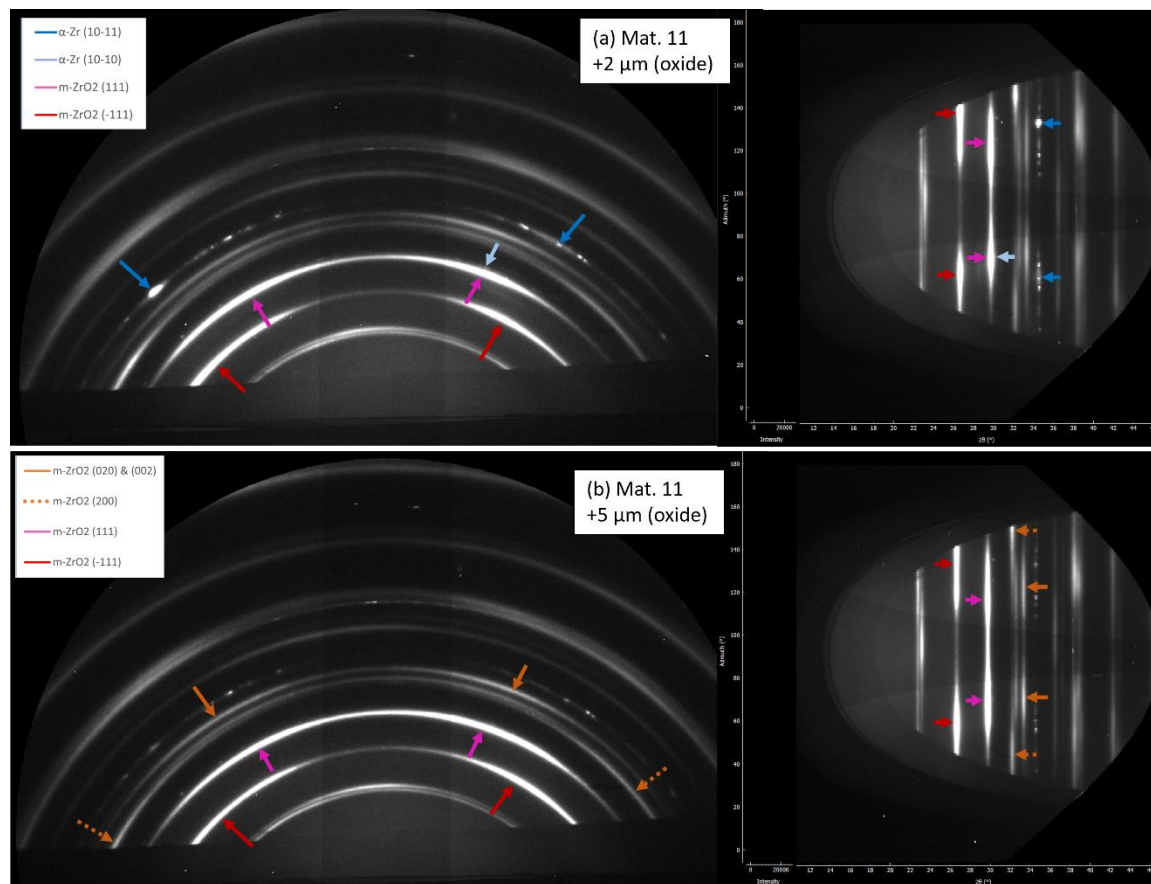


Figure B-6: XRD pattern (image on the left, and “cake” on the right) at two locations in the near oxide region of material 11: (a) +2 μm ; (b) +5 μm . The high intensity region for the main peaks of $\alpha\text{-Zr}$ and $m\text{-ZrO}_2$ are indicated by the colored arrows.

Material 11 (high elevation, low HPUF): mid oxide region

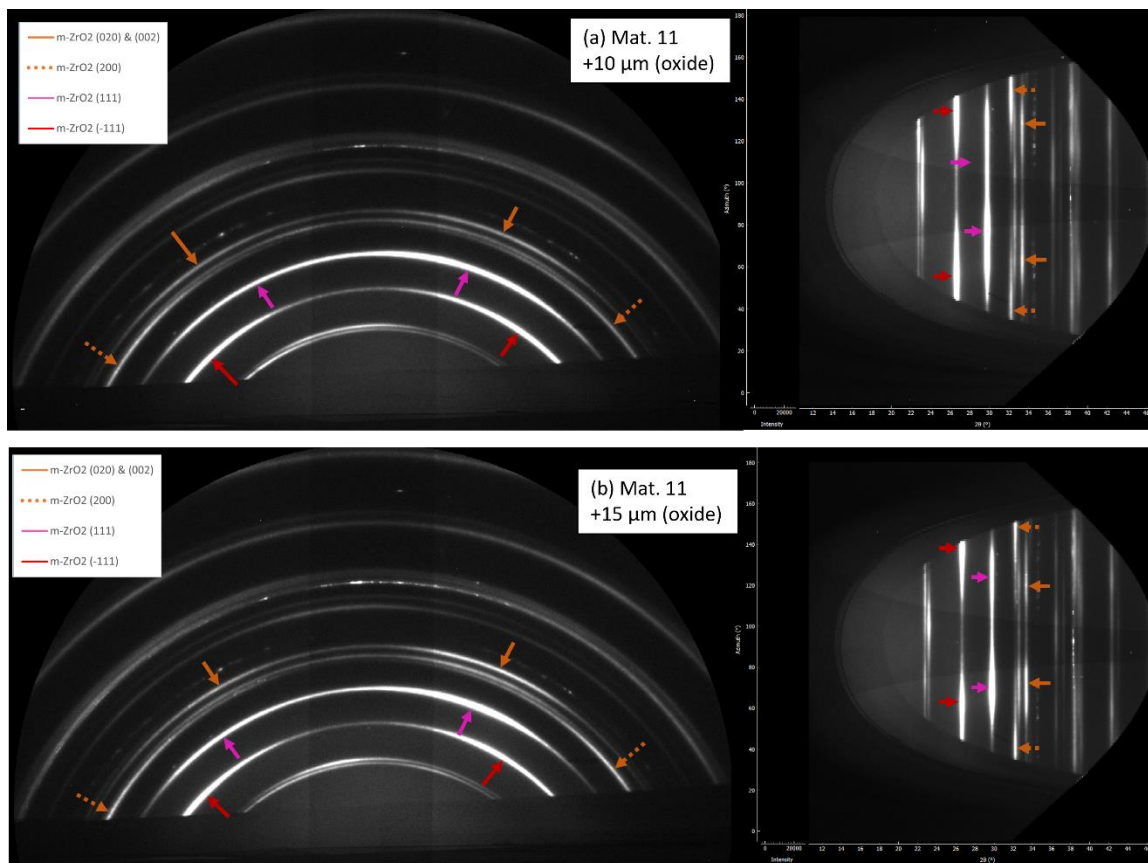


Figure B-7: XRD pattern (image on the left, and “cake” on the right) at two locations in the mid oxide region of material 11: (a) +10 μm ; (b) +15 μm . The high intensity region for the main peaks of $\alpha\text{-Zr}$ and $m\text{-ZrO}_2$ are indicated by the colored arrows.

Material 11 (high elevation, low HPUF): far oxide region

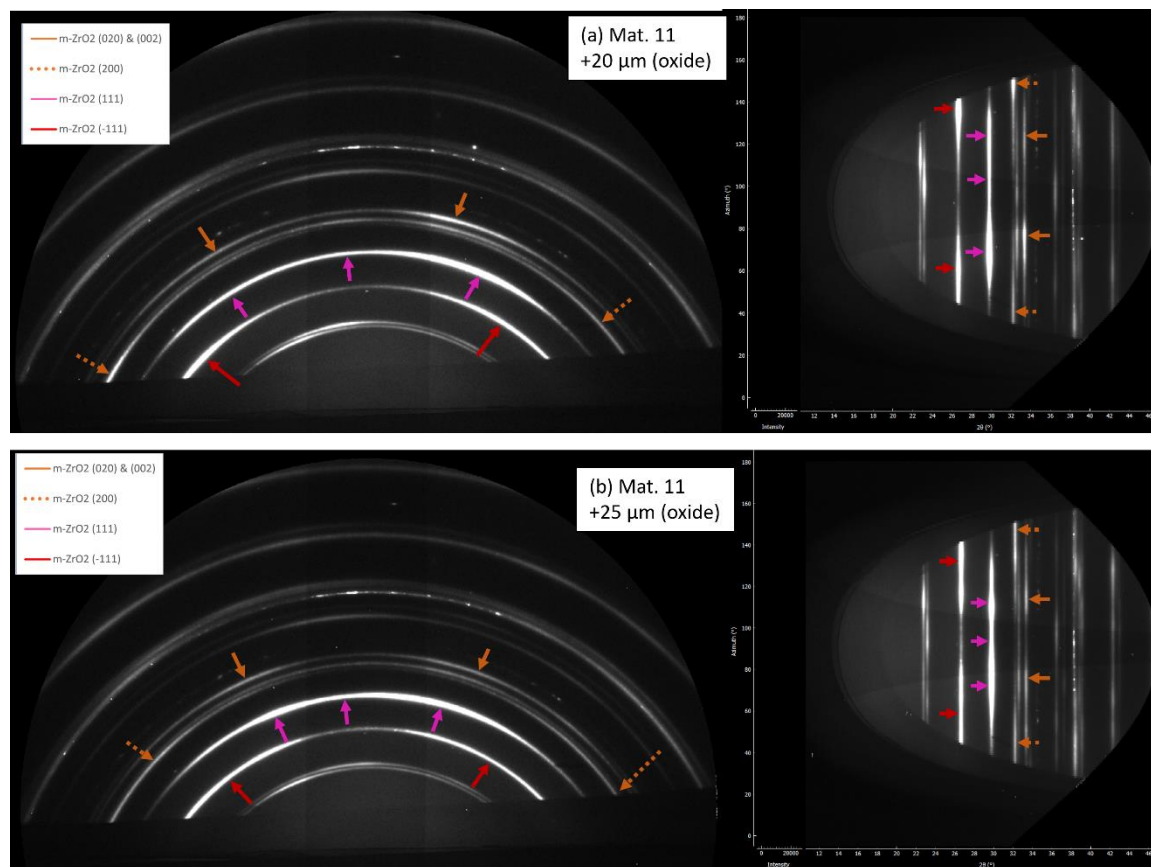


Figure B-8: XRD pattern (image on the left, and "cake" on the right) at two locations in the far oxide region of material 11: (a) +20 μm; (b) +25 μm. The high intensity region for the main peaks of $\alpha\text{-Zr}$ and $m\text{-ZrO}_2$ are indicated by the colored arrows.

Material 12 (low elevation, high HPUF): near metal region

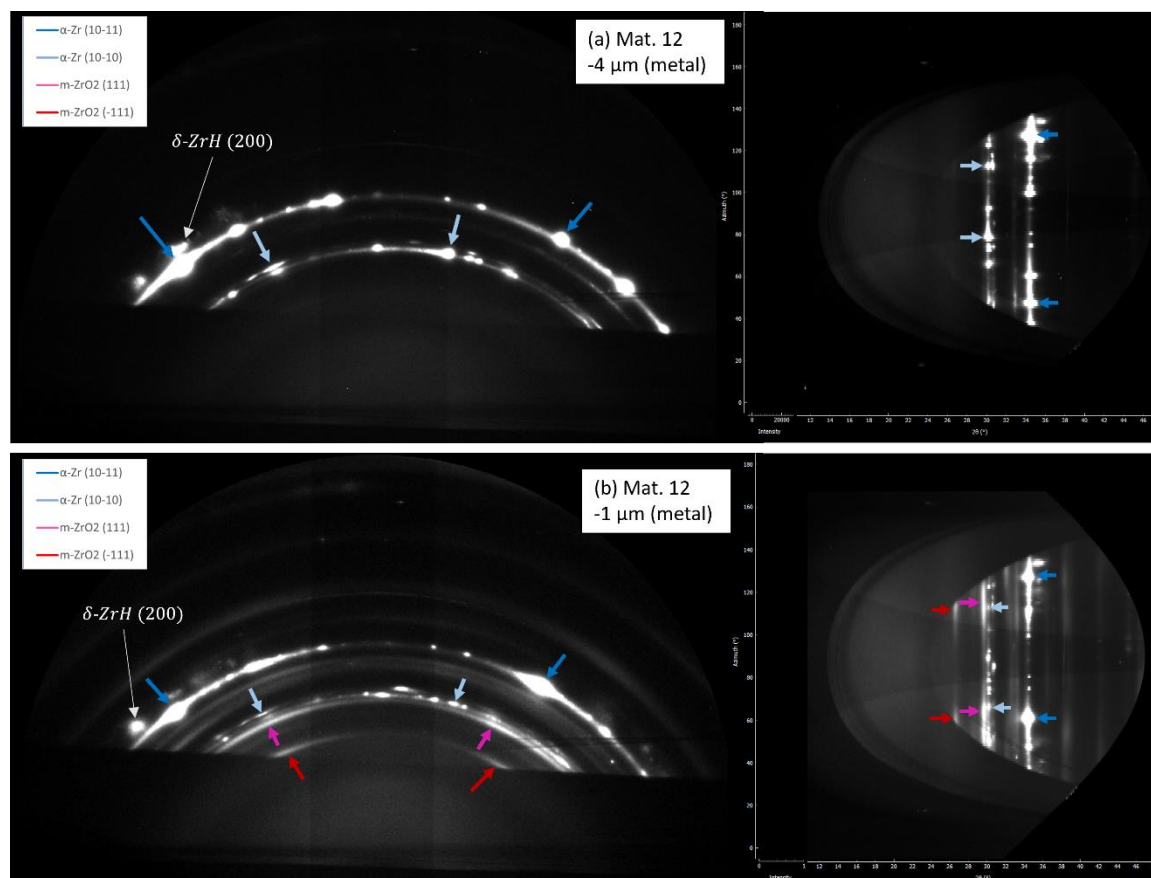


Figure B-9: XRD pattern (image on the left, and “cake” on the right) at two locations in the near metal region of material 12: (a) $-4\ \mu\text{m}$; (b) $-1\ \mu\text{m}$. The high intensity region for the main peaks of α -Zr and m-ZrO₂ are indicated by the colored arrows.

Material 12 (low elevation, high HPUF): near oxide region

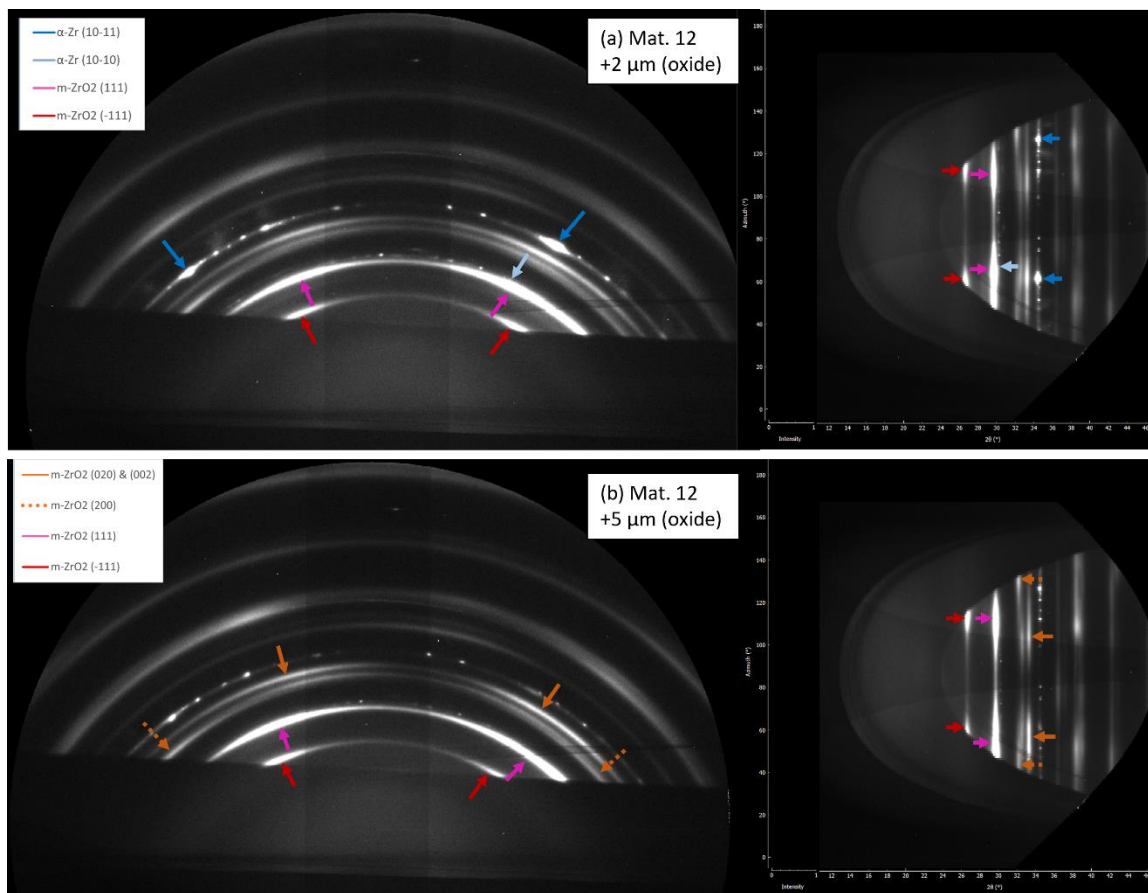


Figure B-10: XRD pattern (image on the left, and "cake" on the right) at two locations in the near oxide region of material 12: (a) +2 μm ; (b) +5 μm . The high intensity region for the main peaks of $\alpha\text{-Zr}$ and $m\text{-ZrO}_2$ are indicated by the colored arrows.

Material 12 (low elevation, high HPUF): mid oxide region

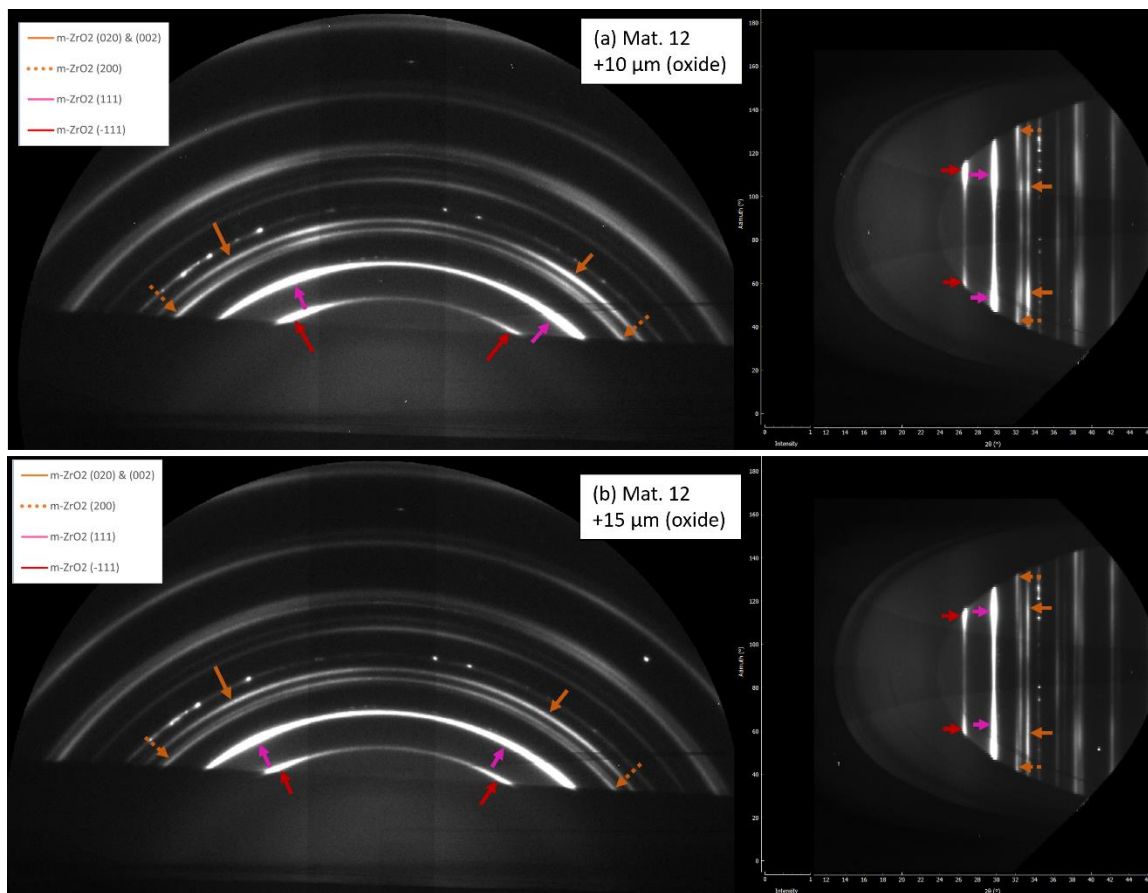


Figure B-11: XRD pattern (image on the left, and "cake" on the right) at two locations in the mid oxide region of material 12: (a) +10 μm ; (b) +15 μm . The high intensity region for the main peaks of $\alpha\text{-Zr}$ and $m\text{-ZrO}_2$ are indicated by the colored arrows.

Material 12 (low elevation, high HPUF): far oxide region

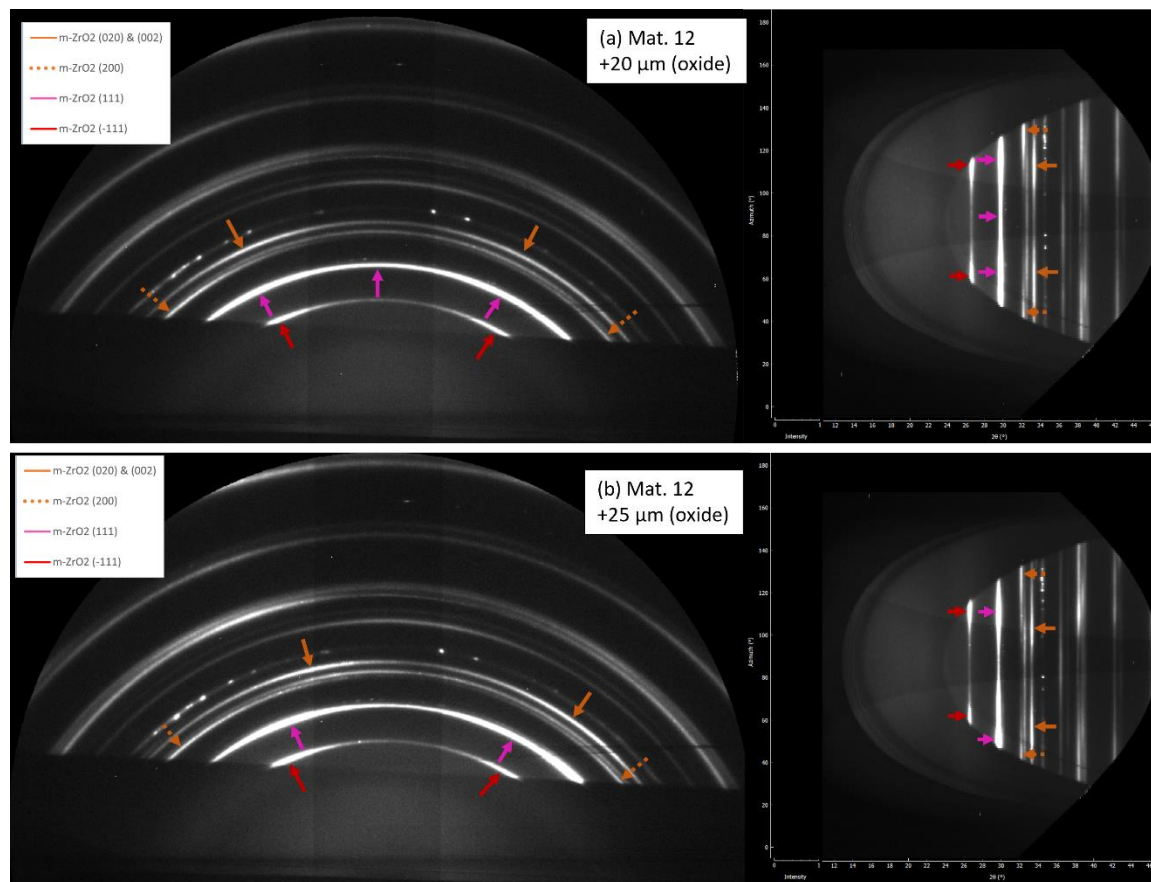


Figure B-12: XRD pattern (image on the left, and “cake” on the right) at two locations in the near oxide region of material 12: (a) +20 μm; (b) +25 μm. The high intensity region for the main peaks of $\alpha\text{-Zr}$ and $m\text{-ZrO}_2$ are indicated by the colored arrows.

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Curriculum Vitae

Pierre BOUHADDANE

<i>Skills Summary</i>	
▪ Multidisciplinary background in both nuclear and materials engineering, with distinctive knowledge on zirconium alloys. ▪ Experimental techniques: synchrotron X-ray absorption spectroscopy (fine structure), synchrotron X-ray diffraction, electron microscopy, metallography, and sample preparation; familiar with focused ion beam and atom probe tomography. ▪ Programming techniques: MATLAB, C/C++ (GEANT4), HTML, EXCEL (macro)	
<i>Education</i>	
The Pennsylvania State University , State College, Pennsylvania, USA	2017-2024
PhD in Nuclear Engineering , Mai 2024 Dissertation title: “Examinations of BWR-corroded Zircaloy-2 water rods with XANES and XRD to investigate the role of nickel in enhancing hydrogen pickup at high burnup”	
École Centrale de Lyon , Écully, France	2015-2018
Diplôme d’Ingénieur (M.S. in Engineering)	
Classes Préparatoires Lycée Stanislas , Paris, France	2013-2015
MPSI, MP* (B.S. in Mathematics and Physics)	
<i>Research Experience</i>	
Graduate Research Assistant , The Pennsylvania State University, USA	2018-2024
Nuclear Materials Group Advisor: Dr. Arthur T. MOTTA Investigating the role of nickel in enhancing hydrogen pickup at high burnup in BWR Zry-2 materials with synchrotron radiation (XANES, XRD).	
Undergraduate Internship , CEA (Atomic Energy Commission), France	Summer 2017
Department of Particle Physics (DPhP) Advisor: Dr. Matthieu VIVIER Modeling of neutron background and shielding for experiments on coherent elastic neutrino-nucleus scattering with GEANT4.	
Undergraduate Research , INL (Nanotechnology Institute of Lyon), France	Fall 2016
Light Engineering and Conversion Group Advisors: Dr. Hai Son Nguyen, Dr. Sébastien Cueff Modeling and characterization of photonic crystals for use in semiconductors.	