Experimental evaluation of oxide growth in binary zirconium alloys along with pure zirconium and Zircaloy-2 by steam corrosion testing

BHADRI NARAYANAN LALGUDI SRINIVAS

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Royal Institute of Technology (KTH)
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Abstract

In the nuclear power industry the wide use of zirconium-based alloys as construction materials in fuel cladding and other internal reactor components has led to the continuous development and upgrading of new robust alloys. At present the demands for better performing nuclear fuel cladding materials are increasing. Also the new nuclear reactor designs which have been proposed would require materials which must be able to resist even more rigorous operating conditions.

One of the important factors that limit the duration of use of zirconium alloys as fuel cladding is uniform corrosion and the resulting hydriding of the fuel. In order to understand the mechanistic role of alloying elements in the growth of a stable thin protective oxide layer, a series of model zirconium binary alloys was tested Zr (1% Cr, 1% Fe, 0.2% Fe, 1% Ni, and 0.6 % Nb) along with pure zirconium and Zircaloy-2.

The alloys were tested for corrosion in an autoclave under the conditions 415 °C at 10.5 MPa for 1 hour, 1 day, and 3 days. This autoclave testing condition was performed according to the ASTM G2 procedure. The short time autoclave tests were performed in order to obtain data on the oxide layer formation during the early stages of oxidation at high pressures. The oxide layers were determined by weight gain and focused ion beam (FIB) measurement techniques. The weight gain and the FIB measurements agree with each other, although the errors were larger for the weight gain method.

A transition in the kinetic trend from approximately cubic to linear behavior is seen in Zr 1%Fe and Zr 1%Cr binary alloys. The protective oxide layer was more uniformly built in Zr 1%Cr compared to Zr 1%Fe. The measured oxide thicknesses for zirconium based alloys were in proximate agreement with previously published experimental results.

Keywords: Waterside corrosion in zirconium alloys, types of corrosion, secondary phase particles (SPPs), ASTM G2 procedure autoclave testing, weight gain/oxide thickness, oxidation kinetics.
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புது காற்றாணல் விளையாட்டு, சீனீயங்கள்
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Glossary

ASTM American Society for Testing and Materials

PWRs Pressurized water reactors

BWRs Boiling water reactors

SPPs Secondary phase particles

Zry-2 Zircaloy-2

Zry-4 Zircaloy-4

FIB Focused ion beam

IAEA International Atomic Energy Agency
Chapter 1

Introduction

Zirconium alloys or Zircalloys are widely used in nuclear power plants as construction materials for example as fuel cladding, fuel channels, pressure and calandria* tubes and also as fuel spacer grids. Zirconium has been chosen in nuclear technology because of their excellent physical properties such as their low capture cross section to neutrons, high hardness and ductile, high melting point, and corrosion resistance to water \([1]\).

Generally, the fuel cladding composition of zirconium based alloys contains approximately 98 weight percent of zirconium and approximately 2 weight percent of alloying elements like iron, chromium, nickel, tin, niobium and some other additional metals, out of which some are soluble in the zirconium matrix and other remaining are insoluble and form precipitates which are known as secondary phase particles (SPPs) \([1,2]\).

The SPPs are either intermetallics formed by alloying elements with zirconium or an alloying element phase with zirconium in solid solution. These precipitates have been shown to be linked to the corrosion resistance property of zirconium alloys. The composition of precipitates is dependent on alloy composition and production parameters, typical precipitate examples in Zircalloys are \(\text{Zr}_2(\text{Fe},\text{Ni})\) and \(\text{Zr}(\text{Fe},\text{Cr})_2\) \([1]\).

The corrosion behaviour of the SPPs in commercial zirconium alloys are well characterized, yet the mechanistic understanding of corrosion behaviour in precipitates and the influence of varied alloying elements is not well understood. The corrosion of zirconium and its alloys is an electrochemical process and it is driven by factors such as time, temperature, microstructure and microchemistry surface, type of oxide layer, chemistry and thermo hydraulics of corroded water and irradiation effects \([1,3]\).

Since significant amount of precipitates in zirconium alloys increases the resistance to corrosion, it is important to understand the behaviour of the precipitates during the oxidation process and their influence on the oxidation behaviour of the entire alloy. In the complex commercial zirconium alloys, the interaction of the alloying elements with each other will cover the behaviour of single alloying element. The extent of this interaction was not known till present due to the absence of data for single alloying element precipitates \([1]\).

A series of short term autoclave testing of zirconium based alloys was performed in this master thesis in order to evaluate and measure the thin protective oxide layer formed during the early stages of oxidation at high pressures. The work provides evaluations on exhibited corrosion rates on zirconium binary alloys (Zr 1%Fe and Zr 1%Cr).

An overview of the renowned facts in the field of zirconium based alloys and their oxidation kinetics is provided in the chapters 1 and 2 of the thesis. In chapters 3 and 4 the investigated material and the experimental methods used are described. Chapter 5 explains the discussions of results and it is divided into the evaluation of the limitations of the experimental results with respect to the understanding the scope of oxidation kinetics. Finally, chapter 6 concludes the used experimental approach and the collective agreement with compared results.

*Calandria – reactor core of CANDU (CANada Deuterium Uranium) reactor.
1.1. Development of zirconium alloys

Selection of right materials is one of the difficult problems associated in building nuclear power plants. Many of the conventional metals capture neutrons which pass through them and thus the neutrons will combine to be a part of metal atoms and are no more accessible for fission reactions. Zirconium is one of the finest transition metals and one special physical property of zirconium is that they allow neutrons to pass through them and will not remove neutrons from the fission reaction inside the nuclear reactor [3].

The materials used in water cooled nuclear reactors have to meet several requirements such as good corrosion resistance, high thermal conductivity, sufficient mechanical strength, and low neutron absorption capture cross-section. None of the conventional construction materials fulfilled all the requirements [1, 3].

Almost six decades before zirconium alloys were developed in the United States of America and were trademarked as Zircalloys, of which Zircaloy-2 (Zry-2) and Zircaloy-4 (Zry-4) exhibited favored properties. Nevertheless, the corrosion properties of zirconium at high temperature water and steam were not adequately known, at that time of material selections for nuclear applications [1].

Consequently the corrosion resistance of pure zirconium and zirconium based alloys is studied to find suitable alloys to exhibit enhanced corrosion resistance. Many of these examinations were mainly targeted on the effect of the alloying elements. They were examined either by varying the concentration of one alloying element in zirconium alloys or by studying the binary alloys containing the alloying element of interest such as Fe, Cr, Ni, Nb etc with zirconium as major composition [1].

The high temperature corrosion property of pure zirconium with oxygen is favorable, though they tend to show increased corrosion rates when tested under steam. Alloying elements such as Cr, Fe and Ni was very well established to enhance the corrosion resistance of zirconium when exposed to steam. Also, the addition of elements such as Sn and Nb were found to counter balance the accelerated corrosion caused by the impurity of nitrogen content. The nitrogen impurity content was very hard to eliminate at the time of the processing of the first zirconium alloys for nuclear applications [1].

Zircalloys were processed with small amount of Cr, Fe in Zry-4, and for Zry-2 with Fe, Cr and Ni in a matrix consisting of Zr, Sn and O. Table 1 exhibit some type of commercial zirconium alloys with Zr balance. Zircalloys exhibited excellent corrosion properties and thermal creep resistance. The alloying elements Fe, Cr and Ni form intermetallic precipitates with zirconium, which are of Zr (Fe, Cr)2 and Zr2(Fe, Ni)-type [1].

Zirconium alloys containing Nb were developed in Canada (Zr 2.5%Nb) and also in the Soviet Union (e.g. E110). Recently developed alloys such as ZIRLO™, MDA (Mitsubishi developed alloy) and the HANA-alloys (high performance alloy for nuclear application) contain Sn, Nb and Fe or Nb and Fe as M5™. Other elements being considered so far as alloying elements with zirconium are V, Ta, Mo and Cu [1].
Table 1: Composition of some of the commercial zirconium alloys \[1\].

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Sn / wt.%</th>
<th>Nb / wt.%</th>
<th>Fe / wt.%</th>
<th>Cr / wt.%</th>
<th>Ni / wt.%</th>
<th>O / wt.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zircaloy-2 (Zry-2)</td>
<td>1.20-1.70</td>
<td>---</td>
<td>0.07-0.20</td>
<td>0.05-0.15</td>
<td>0.03-0.08</td>
<td>---</td>
</tr>
<tr>
<td>Zircaloy-4 (Zry-4)</td>
<td>1.20-1.70</td>
<td>---</td>
<td>0.18-0.24</td>
<td>0.07-0.13</td>
<td>&lt; 70 ppm</td>
<td>0.09-0.13</td>
</tr>
<tr>
<td>Zircaloy-4 high tin</td>
<td>1.5</td>
<td>---</td>
<td>0.2</td>
<td>0.1</td>
<td>---</td>
<td>0.09-0.16</td>
</tr>
<tr>
<td>Zircaloy-4 low tin</td>
<td>1.3</td>
<td>---</td>
<td>0.2</td>
<td>0.1</td>
<td>---</td>
<td>0.11-0.16</td>
</tr>
<tr>
<td>Zircaloy-4 (extra low tin)</td>
<td>0.8</td>
<td>---</td>
<td>0.2</td>
<td>0.1</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>E 110</td>
<td>---</td>
<td>0.9-1.1</td>
<td>0.014</td>
<td>&lt;0.003</td>
<td>---</td>
<td>0.06</td>
</tr>
<tr>
<td>E 125</td>
<td>---</td>
<td>2.5</td>
<td>0.015</td>
<td>---</td>
<td>0.007</td>
<td>0.05</td>
</tr>
<tr>
<td>Zr 2.5% Nb</td>
<td>---</td>
<td>2.5</td>
<td>&lt;0.15</td>
<td>---</td>
<td>---</td>
<td>0.09-0.13</td>
</tr>
<tr>
<td>E 635</td>
<td>1.10-1.40</td>
<td>0.9-1.1</td>
<td>0.30-0.50</td>
<td>---</td>
<td>---</td>
<td>0.05-0.07</td>
</tr>
<tr>
<td>ZIRLO™</td>
<td>0.9-1.2</td>
<td>0.9-1.13</td>
<td>0.1</td>
<td>---</td>
<td>---</td>
<td>0.09-0.13</td>
</tr>
<tr>
<td>optimised ZIRLO™</td>
<td>0.67</td>
<td>1</td>
<td>0.015-0.06</td>
<td>---</td>
<td>0.08</td>
<td>0.1</td>
</tr>
<tr>
<td>M5™</td>
<td>---</td>
<td>0.8-1.2</td>
<td>0.015-0.06</td>
<td>---</td>
<td>0.120</td>
<td>---</td>
</tr>
<tr>
<td>MDA</td>
<td>0.8</td>
<td>0.5</td>
<td>0.2</td>
<td>0.1</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>HANA-4</td>
<td>0.4</td>
<td>1.5</td>
<td>0.2</td>
<td>0.1</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>HANA-5</td>
<td>0.8</td>
<td>0.4</td>
<td>0.35</td>
<td>0.15</td>
<td>0.1</td>
<td>---</td>
</tr>
</tbody>
</table>

1.2. Corrosion of zirconium and its alloys

Zirconium and its alloys do not react with water under normal conditions, but do react with steam at elevated temperatures. The oxidation process in steam produces two hydrogen atoms per consumed oxygen atom as shown in the following reaction \[1\].

\[ \text{Zr} + 2\, \text{H}_2\text{O}_{(\text{steam})} \rightarrow \text{ZrO}_2 + 2\, \text{H}_2(\text{g}) \]

![Figure 1: Schematic representation of oxidation reactions taking place during corrosion in zirconium and its alloys.](image)
The overall oxidation reaction of zirconium with steam is a four step reaction process where oxygen ions from the $H_2O$ molecules react and merge with zirconium. This four step oxidation process starts at the water/oxide interface. The four steps (see figure 1) are:

1. **Chemical adsorption:**

   *Surface reaction and exchange of charge:* Oxygen is dissolved in water and adsorbed on to the oxide layer surface. The two hydrogen atoms produced in the reaction either dissolve in $H_2O$ or are absorbed in the metal,

   $$2e^- + H_2O \rightarrow O^{2-} + H_2$$

2. **Diffusion process:**

   The absorbed oxygen atoms will undergo charge exchange with electrons and by vacancy mechanisms the oxygen ions will diffuse through the oxide layer,

   $$O^{2-} (\text{surface}) \rightarrow O^{2-} (Zr/ Zr0_2 \text{ interface})$$

3. **Oxidation reaction:**

   When the oxygen atoms arrive at the oxide/metal interface they can react with Zr atoms and transfer electrons, thus adding to the protective oxide layer.

   $$Zr \rightarrow Zr^{4+} + 4e^- (Oxidation)$$

   $$[Zr^{4+}] + [2O^{2-}] \rightarrow ZrO_2$$

4. **Transport of electrons in the oxide:**

   The released electrons will migrate through the oxide to react with more oxygen atoms at the water/oxide interface.

   $$e^- (Zr/ Zr0_2 \text{ interface}) \rightarrow e^- (\text{surface})$$

Any one of aforementioned step detailed above can be a rate-limiting step i.e. the slowest of the above mentioned four processes should directly control the corrosion kinetics \[^1\]. The corrosion in zirconium based alloys reduces the life time of the material and therefore the achievable fuel burn-up which can be safely used. The reduction of fuel cost by increased average burn-up puts higher requirements on the materials, due to their longer stay in the reactor. To achieve increased thermal efficiency of the reactor, increased coolant temperatures could also be necessary. For such scenario, higher corrosion resistance is desirable, as the corrosion kinetics is accelerated at elevated temperatures. Improved requirements for zirconium alloys include uniform corrosion resistance and lower hydrogen uptake \[^1\].

Since there is no direct mechanistic relationship between corrosion properties and alloy composition the underlying corrosion mechanism needs a detailed attention. Several models have been proposed to satisfy enhanced corrosion resistance for zirconium alloys in water and steam, which will most likely turn out to be parts of a reasonable description of the fundamental mechanism. A general description of the water side corrosion problem in water
cooled reactors has been published by Cox and during 1998 in a technical review by the International atomic energy agency (IAEA) \(^{[1,4]}\).

### 1.3. Microstructure of zirconium alloys

The microstructure of zirconium alloys consists of two characteristics: the matrix and SPPs. The presence of precipitates in zirconium alloys is of significance for the excellent corrosion properties. The size and the distribution of the SPPs in the zirconium alloys can be very important for the corrosion rate in zirconium alloys. For example it has been reported that improved uniform corrosion resistance can be obtained with large SPPs in pressurized water reactors (PWRs) but in boiling water reactors (BWRs) superior corrosion resistance to localized corrosion is seen in alloys with finely distributed small SPPs\(^{[1,4]}\).

### 1.4. Zirconium matrix oxidation

When zirconium and its alloys are exposed to air (oxygen) at room temperature they always form a thin protective oxide layer preventing from further corrosion. However, at elevated temperatures the oxidation continues and a thicker protective oxide is formed \(^{[1]}\). The kinetics of this oxide formation is investigated in the present work. Earlier works have reported kinetics of cubic to parabolic form with a transition to a linear behaviour at longer exposure times.

A barrier layer concept has been proposed (i.e. the protective oxide layer is retained even when the oxide film break down with progressing oxidation time) at the metal-oxide interface. Their presence was investigated and clearly indicated using SEM and impedance measurements by authors \(^{[5]}\) \(^{[6]}\). The thickness and structural variations of this barrier layer are however under debate, as different measurement techniques gave oxide thickness variations in between 10 nm \(^{[6]}\) to 2 \(\mu m\) \(^{[5]}\). More importantly, it has been widely accepted for the presence of dense oxide layer close to the metal-oxide interface restricting the access of the oxidizing species to the metal interface \(^{[7]}\).

### 1.5. Secondary phase particles (SPPs)

Alloys of zirconium contain precipitate forming elements such as Fe, Cr, Ni and Nb. All these precipitates show a low solubility in the zirconium matrix, and elements being present in solid solution such as tin and oxygen. The alloying elements Fe, Cr and Ni present in the form of secondary phase particles (SPPs) in zirconium alloys were well studied \(^{[1]}\).

### 1.6. Types of corrosion in zirconium alloys

The corrosion associated with zirconium alloys are reliant on a number of parameters which can be associated either to the type of alloy or the type of power plant and occasionally both \(^{[1]}\). The corrosion of zirconium alloys in water and steam can been seen as three different types of corrosion categories as shown in table 2.
Table 2: Types of corrosion in zirconium alloys \(^\text{[3]}\).

<table>
<thead>
<tr>
<th>Type of corrosion</th>
<th>Reactor type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uniform</td>
<td>All types of light water reactors (LWRs)</td>
</tr>
<tr>
<td>Nodular</td>
<td>Almost occurs only in (BWR/RBMK*)</td>
</tr>
<tr>
<td>Shadow</td>
<td>Mostly occurs in (BWR/RBMK*), is increased zirconium oxide thickness which can appear as (nodular corrosion or as increased uniform corrosion)</td>
</tr>
</tbody>
</table>

RBMK*- Reaktor Bolshoi Mozhnosti Kanalov or high-power channel reactor.

1.6.1. Uniform corrosion

Uniform corrosion is the normal type of corrosion in zirconium alloys and it is seen in all types of light water reactors (LWRs). The oxide itself is uniform and it consists of several different layers. The uniform corrosion in PWRs may occur under non-boiling and hydrogenated conditions. During reactor exposure, the oxide of the Zircaloy in BWRs is constantly growing due to irradiation damage and dissolution of secondary phase particles (SPPs). These changes in oxide will encourage an acceleration of uniform corrosion \(^\text{[3]}\).

Patches of white oxide appears on the surface subsequently a black or grey uniform background is identified for accelerated uniform corrosion in BWRs. These white oxide patches stay very thin as same as the black lustrous uniform corrosion film. At some point these patches will cover almost entire surface and the oxide thickening emerges at a faster rate, and is known as ‘late increased corrosion’. At the same time BWRs will also experience an increased hydrogen pick-up fraction. This type of hydriding is likely a more serious issue than corrosion addition \(^\text{[3]}\).

1.6.2. Nodular corrosion

The nodular corrosion in BWRs can be distinguished by much dense, thick oxide patches emerging as white spots. Generally the small SPPs in zirconium alloys do not form nodules. But in the large SPPs the nodules initiate at the very early stages and grow at a decreasing rate. The nodular corrosion in BWRs does not usually accompany with performance problems, although, it has been published that in extreme cases spalled nodular oxides can be a source of ‘grit’ in control drive mechanisms \(^\text{[3]}\).

1.6.3. Shadow corrosion

Shadow corrosion in zirconium alloys is mainly induced at locations when they are in close proximity to many non-zirconium alloys. For example such as stainless steel or nickel-chromium based alloys such Inconel \(^\text{[3]}\) appearing as a shadow of these components. Shadow corrosion is an increased ZrO\(_2\) appearing either as nodules or as increased uniform oxide. The shadow corrosion in BWRs is induced by stainless steel fuel cladding present in control blade bundle. The thickness of the oxide observed in shadow corrosion is unusually large, dense and un-cracked \(^\text{[3]}\).

Shadow corrosion has always been present in BWRs and not in PWRs because of their high hydrogen concentration, which successively reduces the galvanic potentials between dissimilar alloy components. In BWRs shadow corrosion has caused no performance issues.
Although, recent publications reveals that shadow corrosion is associated with BWRs channel bow problems \(^3\).

In *Figure 2* some types of corrosion existing in zirconium alloys related to this work is presented.

**Figure 2: Some types of corrosion existing in zirconium alloys** \(^3\).

### 1.7. Autoclave testing conditions in water and steam

In order to simulate the short and long-term corrosion behaviour to be predicted for reactor conditions, higher temperatures and pressures than encountered in the reactor can be used in autoclave testing. This testing is performed in order to compensate for the shorter exposure time to be able to compare different materials for in reactor corrosion results.

The 415°C steam autoclave testing do not exactly replicate the PWR operating conditions as shown in *table 3*. In fact, their operating conditions are *more severe* than the ones found in the PWR operation, in terms of temperature and pressure, but the behavior of the alloys in this environment shows a relationship considered with in-reactor behavior, i.e. alloys that perform well in this test perform well in-reactor conditions.

The normal procedure for testing corrosion properties of zirconium alloys in water and steam is carried out according to the ASTM G2 procedure \(^8\). This test procedure recommends different testing conditions in autoclave for zirconium alloys to predict their in-reactor behaviour, which is different for BWR and PWR environments. Some of the design parameters of western type PWR and BWR corresponding to autoclave testing conditions are provided in *table 3*.

*Table 3: Design parameters of BWR and western type PWR corresponding to autoclave corrosion testing conditions* \(^1,9\).

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Western type PWR</th>
<th>BWR</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coolant</td>
<td>Pressurized H(_2)O</td>
<td>Boiling H(_2)O</td>
</tr>
<tr>
<td>Fuel cladding materials</td>
<td>Zry-4, ZIRLO,DUPLEX, M5,Inconel, SS(^*)</td>
<td>Zry-2, Zry-4, Inconel, SS(^*)</td>
</tr>
<tr>
<td>PWR coolant inlet temperature</td>
<td>279-294 °C</td>
<td>272-278 °C</td>
</tr>
<tr>
<td>PWR coolant outlet temperature</td>
<td>313-329 °C</td>
<td>280-300 °C</td>
</tr>
<tr>
<td>Autoclave testing (temperature range)</td>
<td>350-370 °C (water), 400-420 °C (steam)</td>
<td>450-520 °C</td>
</tr>
<tr>
<td>PWR Coolant pressure</td>
<td>155-158 bar</td>
<td>70 bar</td>
</tr>
<tr>
<td>Autoclave testing (pressure range)</td>
<td>100-110 bar</td>
<td>Above 60 bar</td>
</tr>
<tr>
<td>Coolant flow, (m/s)</td>
<td>3 to 6</td>
<td>2 to 5</td>
</tr>
</tbody>
</table>

\(^*\) SS- Stainless steel
The oxidation rate in alloy samples is usually measured as weight gain. This usual procedure is carried out by removing the samples from the autoclave, weighted and put back into autoclave again in periodic intervals. This procedure results in thermal cycling of samples for each time the samples are taken out for measurements. However, the standard in-reactor conditions does not result in so many thermal cycles and more practical testing would involve a temperature gradient over the tube wall, as existent over the tube wall from fuel pellets to cooling water [1].
Chapter 2

Corrosion kinetics

The initially formed oxide layer in zirconium and its alloys is a thin adherent protective black oxide film growing with a cubic or parabolic rate equation as in \( \text{equation 1} \). The two regimes of corrosion kinetics in zirconium are termed as pre-transition and post-transition. This initial protective oxide layer varies with oxidation time to an approximately linear behaviour \((n=1)\), observe from the weight gain curves in Figure 3. The critical thickness for the transition is reached with an oxide thickness exceeding the range of \((\sim 2-3 \, \mu m)\) and a color change from black to white, indicates the non-protective stoichiometric \( \text{ZrO}_2 \) \([1,10]\).

![Figure 3: Corrosion kinetics in zirconium alloys. Kinetic transitions are denoted with ‘T’ on weight gain curves of Zircaloy-4 and Ozhenite (these denotations have been added in this work for clarification) \([1]\).](image)

\[
\Delta w = A \cdot t^{1/n}
\]

\( \Delta w \) - Weight gain in \( \text{mg/dm}^2 \),
\( A \) - Pre-exponential constant,
\( t \) - Oxidation time in \textit{hours}
\( n \) - Exponential factor ranging from 3 to 2 for cubic to parabolic oxidation kinetics \([1,9]\).

The oxidation kinetics classifications in zirconium alloys are based on three factors: \( A, n \) and time to transition. The average oxide thickness from weight gain data is usually calculated to be \( 1 \, \mu m \) oxide for \( 15 \, \text{mg/dm}^2 \) of weight gained, this excludes the probable oxygen and hydrogen diffusion into the metal, sub-stoichiometry of the formed oxide layer and oxide spalling\(^*\). The main corrosion product of zirconium alloys is zirconia \( (\text{ZrO}_2) \), which is known to exist in seven crystallographic polymorphs \([11]\) out of which the monoclinic, tetragonal and cubic have been reported for the oxide films \([1,12]\).

\(^*\)Oxide spalling – refers to breaking up of oxide into smaller pieces.
2.1. Transition of oxidation kinetics

The oxidation kinetic transition from a parabolic/cubic to linear or cyclic oxidation behaviour has been shown to be linked to the formation of cracked layers in the oxide\[13\] and a variation of the thickness of the critical oxide layer\[14\]. A cyclic variation of the tetragonal zirconia content has been observed in the oxide scale, which illustrates that besides cracks, the oxide structure is changing with proceeding oxidation and kinetic transitions\[13\]. The connection between these characteristics in the oxide scale and the kinetic transitions is still not fully understood. The relationship between the time to transition of different alloys and the spacing between the cracked oxide layers is important to understand the nature of this effect\[15\].

2.2. Corrosion kinetics from previous studies

The chemical reaction of zirconium with oxygen at high and low temperatures in steam has been studied by several investigators\[16-24\] and comparison of results shows wide range of discrepancies concerning the activation energies, rate laws such as linear, cubic or parabolic, etc; which best describes the oxidation kinetics. While contradictory results exist, most authors are in agreement more or less on the oxidation mechanisms\[2\]. The large number of studies has produced a number of rate laws depending on the temperature, oxygen pressure and exposure time (equivalent to thickness of oxide film given under set of conditions).

As mentioned before, the weight gain kinetics of zirconium and its alloys in steam usually fall in two periods, referred to as pre and post transition regimes. During the initial pre-transition oxidation, the kinetic growth rate is usually closer to cubic or parabolic kinetics predicted by Wagner/Haufe theory\[25\]. In the post-transition regime during which the oxide scale breaks down and transition to linear kinetics\[26\]. The two widely observed cubic and parabolic rate laws during early stages of oxidation will depend upon the surface preparation of specimen.

Some examples of previous observations in initial oxide growth rate of zirconium and zirconium alloys are stated below:

- The cubic rate law was observed from mechanically abraded samples provided if an initial deviation was disregarded; an approximate fit to the parabolic rate law was observed by Gulbransen and Andrew\[16\], Bradhurst\[17\], Belle and Mallet\[18\], Porte\[19\], Westerman\[20\], and Pemsler\[21\]. On contrary Hillner\[22\] noted parabolic rate law on chemically polished samples. In spite of obeyence of parabolic law Hillner\[22\] observed white spots on the chemically polished sample surface which are indicative of a localized break down of the oxide scale.

- The parabolic rate law appeared to describe the oxidation behaviour of chemically polished samples and was reported by Gulbransen and Andrew\[16\], Hillner\[22\], Cubiciotti\[23\], Debuigne, and Lehr\[24\].

- Gulbransen and Andrew\[27\] studied reaction on zirconium foil specimens between (200 - 425°C) and they reported parabolic rate law fit their data. On contrary, Belle and Mallet\[18\], reported cubic rate law with the same data in different fashion, implying that the understanding of the data can be somewhat arbitrary in some cases.

- From another study Gulbransen and Andrew\[16\] found in between (400 – 600°C), the surface preparation method will influence the reaction kinetics. They reported,
chemically polished foils obeyed parabolic rate law and mechanically polished foils react much faster than chemically polished and obeyed cubic rate law.

- A study by Charles, Barnartt, and Gulbransen [28] on prolonged oxidation up to 500 hours, oxidation of zirconium foils at 350°C and 450°C established cubic rate law for mechanically polished samples.

- There are some reasons to suspect the size and shape of samples might influence the reaction kinetics. Belle and Mallett [18] studied reaction kinetics on rod specimens with different sizes in between (575 - 950 °C), and fitted their data to cubic rate law.

- At same temperature range from Debuigne and Lehr [24], Garibotti, Green and Baldwin [29] observed parabolic rate law on foil specimens.

- Gulbransen and Andrew [16] observed oxide failure at the transition point and this behaviour was responsible for the change to linear law. The same authors concluded that the weight gain to transition should not be converted to an oxide thickness unless the weight gain due to oxygen dissolution has been subtracted first.
Chapter 3

Experimental methods

The corrosion testing of zirconium alloys was carried out in a Limbo 350-type autoclave. These autoclave tests were scaled up to simulate the temperature and pressure conditions similar to nuclear reactors and therefore formation of oxide on the alloys under those conditions. This short term autoclave experiments were conducted to simulate current PWR fuel cladding materials (refer to table 3).

Focused ion beam (FIB) technique was used in this thesis to prepare cross sections of the oxide. The zirconium alloy samples surface were pickled before oxidation in autoclave, as per ASTM G2 procedure resulting in increased surface roughness. The selected environment gives an idea about the influence of steam, temperature and pressure as well as oxidation time. However for the used samples several parameters are changed concurrently, so that they cannot be used to identify the particular influence of certain parameter.

The autoclaved binary alloys (1 wt. % Fe, Cr, and Ni, 0.6 wt. % Nb), pure zirconium and Zircaloy-2) were of the same material composition as those used in the previous study by Barberis et al. The oxide layers in the previous study were examined by metallographic techniques such as atomic force microscope (AFM), scanning electron microscope (SEM) and energy dispersive spectroscopy (EDS). The results from Barberis et al. are published in an ASTM special technical publication and used in this master thesis work.

3.1. Materials

3.1.1. Binary alloys

The chemical compositions of the binary alloys studied in the present work are included with type of alloy, average metal grain size and their precipitate (composition, type, and density) as presented in table 4.

Table 4: The chemical analysis of the zirconium binary alloys (in ppm or wt. %) and precipitate data is provided from a previous study.

<table>
<thead>
<tr>
<th>Binary alloy</th>
<th>Cr (ppm)</th>
<th>Fe (ppm)</th>
<th>Ni (ppm)</th>
<th>O (ppm)</th>
<th>Nb</th>
<th>Average metal grain size (µm)</th>
<th>SPP type</th>
<th>SPP density (g/ cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr 1% Cr</td>
<td>1.04 wt.%</td>
<td>247</td>
<td>37</td>
<td>760</td>
<td>-</td>
<td>5.2</td>
<td>ZrCr₂</td>
<td>6.98</td>
</tr>
<tr>
<td>Zr 1% Ni</td>
<td>46</td>
<td>205</td>
<td>1.17 wt.%</td>
<td>755</td>
<td>-</td>
<td>4.6</td>
<td>Zr₂Ni</td>
<td>7.21</td>
</tr>
<tr>
<td>Zr 1% Fe</td>
<td>44</td>
<td>0.99 wt.%</td>
<td>28</td>
<td>720</td>
<td>-</td>
<td>3.1</td>
<td>Zr₃Fe</td>
<td>6.82</td>
</tr>
<tr>
<td>Zr 0.2% Fe</td>
<td>45</td>
<td>0.44 wt.%</td>
<td>35</td>
<td>650</td>
<td>-</td>
<td>6.2</td>
<td>Zr₁Fe</td>
<td>6.82</td>
</tr>
<tr>
<td>Zr0.6%Nb</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.6 wt.%</td>
<td>-</td>
<td>β-Nb(20%Zr)</td>
<td>8.49</td>
</tr>
</tbody>
</table>

3.1.2. Pure zirconium and Zircaloy-2

Samples of pure zirconium and the commercial alloy Zircaloy-2 were also included in the autoclave corrosion testing. They were included in order to allow the comparison of their oxide growth with binary alloys. The chemical composition of pure zirconium and Zry-2 are given in table 5.
### Table 5: Chemical analysis of pure zirconium and Zry-2 (in ppm or wt. %) \(^{[1, 31]}\)

<table>
<thead>
<tr>
<th>Type of Alloy</th>
<th>Cr (ppm)</th>
<th>Fe (ppm)</th>
<th>Ni (ppm)</th>
<th>O (ppm)</th>
<th>Sn (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure zirconium</td>
<td>-</td>
<td>150</td>
<td>-</td>
<td>300</td>
<td>-</td>
</tr>
<tr>
<td>Zry-2</td>
<td>0.05 - 0.15</td>
<td>0.07 - 0.20</td>
<td>0.03 - 0.08</td>
<td></td>
<td>1.20 - 1.70</td>
</tr>
</tbody>
</table>

### 3.2. Alloy sample preparation

A precision diamond wire saw (size 0.17 mm) was used to cut fine samples of alloys. The size of binary and pure zirconium alloy samples were (4 mm × 6 mm) and (10 mm × 10 mm) for Zry-2. In order to suspend the alloy samples inside the autoclave a small 1 mm perforation was drilled in the samples.

For obtaining smooth and flat surface, the alloy samples were grinded in a disc grinder GATAN (max. 6 x 6 mm). The material used for grinding was silicon carbide grits of size grades 1000, 1200 and 4000. The surface polishing of alloys is done using 1 and 3 μm diamond suspensions in Struers Tenupol-5 polishing machine \(^{[32]}\). The samples were polished to remove the mechanical damage from previous grinding steps. In order to prevent scratches while polishing, the samples surfaces were examined cyclically under an optical Olympus CX41 microscope.

Some alloy samples were also polished using the basic slurry (pH 9.5) containing silica particles in the vibratory polishing machine (VibroMet 2) \(^{[33]}\). This method resulted in more smooth, scratch free surfaces compared to the diamond slurry polishing technique. Finally the alloy samples were cleaned in acetone or ethanol in an ultrasonic bath to remove all traces of polishing slurry and to reduce the surface layer contamination. Figure 4 shows the pure zirconium alloy sample before grinding and polishing and figure 5 shows the prepared samples for oxidation tests.

![Figure 4: Sample of pure zirconium alloy before grinding and polishing](image)

![Figure 5: Samples of Pure zirconium and Zircaloy-2 prepared for oxidation experiments.](image)
3.3. Autoclave setup

The oxidation of small test specimens of pure zirconium, binary zirconium alloys and Zry-2 was performed in a Limbo 350 type autoclave \textsuperscript{[30]}. Figure 6 shows the autoclave with a TC 450 type PID controller set up. A detachable sample holder was prepared from stainless steel and fixed inside the autoclave vessel. The sample holder is enclosed in a zirconia pipe. Figure 7 shows the prepared sample holder. Small hooks about 0.3 mm was prepared from Zry-2 and suspended on the zirconia pipe. The prepared alloy samples were carefully suspended using Zry-2 hooks (0.3 mm wire) and 0.1 mm drilled holes in the samples, see figure 8. The autoclave consists of a k-type thermocouple for the automated temperature control connected through a TC 450 type microprocessor PID controller.

The pressure in the autoclave was observed using digital manometer from WIKA (DG-10-S, 0-600 bar). A safety pressure vent was present on the top of autoclave to be used for manual pressure release. The PID controller can automatically programmable for temperature close to 25 steps. The controller is also equipped with a safety thermostat (analog output, interface RS - 485) which can be independently programmed for safe automatic shutdown. The heating of the autoclave vessel is achieved by an electrical coil with a maximum heating power up to 2000 W. The system can operate safely at temperatures ranging from -10 to +450 °C and at maximum pressure of 350 bar at 350°C.

![Figure 6: Autoclave with TC 450- PID controller set up](image)
3.4. Autoclave operation

Before closing the autoclave, all the sealing parts of autoclave were cleaned. The autoclave cylinder was filled with 50 ml of de-ionized water (0.05-0.1 μS). At first, in order to achieve the desired temperature and pressure conditions, the TC controller was programmed to maximum possible heating of 450°C. The pressure was manually reduced in regular intervals to 100 bar and set within the target pressure condition of about 100-110 bar range before exceeding 110 bar.

When the autoclave temperature was close to 400°C the target temperature of the automated TC control was reduced to 415-420°C range from 450°C. At the same time the pressure was also regulated manually between 100 and 110 bar at 415°C. After the planned exposure at the oxidation conditions (1 h, 24 h and 72 h) the heating was shutdown and the autoclave was allowed to cool down to room temperature without external cooling. Figure 9 represents typical temperature and pressure profile in the autoclave for oxidation constrains of 1 hour at 415 °C and 100 bar nominal pressure for Zr 0.2% Fe binary alloy.

![Autoclave oxidation conditions](image)

**Figure 9: Autoclave oxidation conditions (P, T vs. time).**
3.5. Cross sectional analysis (FIB)

The cross sectional analysis of the autoclaved samples in this master project was performed using a dual beam (FIB/SEM) microscope (NVision 40 series by Carl-Zeiss™). The FIB technique is chiefly used for cross sectional analysis of the oxide at specific site of interest. The cross sections were prepared perpendicular to the oxide surface. Observing the cross sections, the oxide thickness and variations were determined by sectional ion milling at different positions on the samples. This ion milling was performed by a liquid metal gallium source. The source was accelerated to generate gallium ions applied with an acceleration voltage of 30 kV for sputtering some small amount of material [1].

The cross sections of oxide (15-20 µm width) were cut and polished with smaller ion beam current (300 pA) and imaged by the scanning electron microscope (SEM).

Due to the tilt angle between FIB and the SEM columns in the device, the measured values should be corrected for the tilt to obtain their real length. This is done by the following equation:

\[ Y_{\text{real length}} = Y_{\text{image}} \times \left( \frac{1}{\sin 54^\circ} \right) \quad (\text{equation 2}) \]

This correction is done because the tilt axis of the sample was present along the x-axis of the image and the images along the x-axis were undistorted. Distances along the y-direction on the images acquired were to be multiplied by \( \left( \frac{1}{\sin 54^\circ} \right) \) in order to obtain the real length. The sample orientation during milling is shown with respect to SEM and FIB column in shown in Figure 10.

![Figure 10: Sectional geometry of SEM & FIB column in the NVision 40 series workstation. The orientation of the sample is shown for polishing of cross sections.](image)

3.6. Micrograph Analysis

The quantitative micrograph analysis for oxidized alloys for optimizing the thickness of oxide is done by the ‘Lince’ [34] a useful digital image manipulating software. As this method gives only the local oxide thickness, the results does not represent of the overall oxide thickness; however they give good estimation of what is to be expected as oxide thickness, especially if several sections are performed on the micrograph.
The procedure is done after creating the line segments representative of the oxide thickness at the metal-oxide interface, the micrographs were calibrated with respect to length (micron bar) in pixels from the micrograph and actual length of FIB micro-graphing scale, which can be viewed from the left side bottom of all the micrographs and then corrected with the (equation 2) to obtain the average, maximum, minimum and standard deviation of the oxide thickness. Around 2-3 micrographs per autoclaved sample was used in measuring oxide thickness.
Chapter 4

Weight gain

The oxide growth for autoclaved samples is characterized by corrosion weight gain. The relative weight gain was measured after the samples were air dried. The mass of sample before and after the oxidation was measured using an analytical balance provided with a high precision (± 0.02 mg). The change in mass of the sample should correspond to the amount of oxygen transformed into oxide at the surface \(^1\). A simple formula is then used to convert the mass of oxygen into oxide. The weight gain conversion into an oxide thickness was performed under the following assumptions:

- The oxidation process is identical and the oxide thickness is homogeneous over the whole surface of alloy.
- The surface area of the sample can be evaluated precisely.
- All the weight gain of the sample is due to the oxide build up and no other element has been involved in the reaction.
- No correction was made to local dissolution of oxygen in metal.
- No loss of oxide formed occurs by any process such as spall, dissolution, etc., and that all the weight change measured comes from only the oxygen reacted \(^9\).

This conversion from weight gain to oxide thickness can be either done by dividing the weight gained mass per unit area, generally in \((mg/dm^2)\) by the theoretical density change due to the access of the oxygen. The other way of conversion is the transformation of zirconium (Zr\(^{4+}\)) to ZrO\(_2\) (mass/volume increase, \(\sim 1.4746 \text{g/dm}^3\)), thus permitting a kinetic evaluation of different alloys as described \(^9\):

\[
\text{Weight gain, } (\Delta W) = \frac{(M_o - M_i)}{\text{volume}} \left( \frac{mg}{dm^2} \right) \quad (\text{equation 3})
\]

Where, \(M_o\) - mass after (mg), \(M_i\) - mass before (mg)

\[
\text{Theoretical density of ZrO}_2 (\rho) = 5.68 \left( \frac{g}{cm^3} \right)
\]

\[
\frac{(mO_2)}{(mZrO_2)} = \frac{31.988}{(91.224 + 31.988)} = 0.259
\]

So the density change due to oxygen access in ZrO\(_2\) is given by:

\[
5.68 \cdot 0.259 = 1.4746 \left( \frac{g}{cm^3} \right) = 14.746 \left( \frac{mg}{dm^2 \cdot \mu m} \right)
\]

We see that 1 \(\mu m\) of formed oxide is equivalent to 14.746 mg (\(\approx 15 \text{mg}\)) of weight gained per \(dm^2\) during oxidation. The weight gain is only representative of the oxygen uptake of the sample provided no spalling has occurred. This should be confirmed by examining the sample surface. The partition of the oxygen in the oxide and the subjacent metal should be identified to be able to convert the weight gain into average oxide thickness, as with increasing temperature more oxygen is dissolved in the zirconium metal. We can now summarize,
Oxide thickness from weight gained = $\Delta W / \rho / (m_{\text{ZrO}_2} / m_{\text{ZrO}_2}) / S \cdot 10^3 \, (\mu m)$ \hspace{1cm} (equation 4)

Where, $S$ – Surface area of alloy (mm$^2$).

### 4.1. Weight gain uncertainty

The uncertainties due to the weight gain method are listed below,

i. The uncertainties of the balance accuracy have to be taken in account. However the weight gains can be measured with balance scales of high precision ($\pm 0.02 \, mg$). This uncertainty error due to balance accuracy is used in figure 11.

ii. The second concern is the increase of the uncertainty due to the sample size. Since the precise dimensions of a sample cannot be determined, the surface area is a source of error in the weight gain method. This error is however small compared to the error in weight measurement.

iii. The autoclaved samples were only air dried and the presence of hydrated water might influence on the weight gain.
Chapter 5

Discussion of results

In this chapter the results obtained from the autoclave measurements are discussed with the motive of developing an understanding of the relationship between the microstructure of oxide film formed and exhibited corrosion rates. The autoclave experimental results from weight gain and observed oxide are presented and compared to show the overall characteristics of the examined oxide layers on model binary alloys. The multiple corrosion kinetic trends from cubic to linear are shown for the model binary zirconium alloys (1% Fe and 1% Cr). The remaining (failed) autoclave tests are also presented and discussed in connection to oxide spalling.

5.1. Weight gain measurements

The evaluated weight gain to oxide thickness measurement results during the corrosion testing of the various model alloys are summarized in table 6. A selection of results is presented in figure 11. The growth of the oxide layer over time is clearly seen in the figure.

<table>
<thead>
<tr>
<th>Alloy type</th>
<th>Weight before (mg)</th>
<th>Weight after (mg)</th>
<th>Weight gained (mg)</th>
<th>Oxide thickness from weight gained (µm) (refer chapter 4)</th>
<th>σ, (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr 0.2%Fe</td>
<td>164.20</td>
<td>164.20</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Zr 1%Fe</td>
<td>147.93</td>
<td>148.04</td>
<td>0.11</td>
<td>0.89</td>
<td>±0.18</td>
</tr>
<tr>
<td>Zr 1%Ni</td>
<td>151.92</td>
<td>151.98</td>
<td>0.06</td>
<td>0.57</td>
<td>±0.19</td>
</tr>
<tr>
<td>Zr 1%Cr</td>
<td>175.56</td>
<td>175.64</td>
<td>0.08</td>
<td>0.66</td>
<td>±0.16</td>
</tr>
<tr>
<td>Zr 0.6%Nb</td>
<td>65.78</td>
<td>65.90</td>
<td>0.12</td>
<td>1.08</td>
<td>±0.18</td>
</tr>
<tr>
<td>Pure Zr</td>
<td>122.48</td>
<td>122.54</td>
<td>0.05</td>
<td>0.49</td>
<td>±0.19</td>
</tr>
<tr>
<td>Zry-2</td>
<td>1364.56</td>
<td>1364.99</td>
<td>0.43</td>
<td>0.76</td>
<td>±0.035</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Alloy type</th>
<th>Weight before (mg)</th>
<th>Weight after (mg)</th>
<th>Weight gained (mg)</th>
<th>Oxide thickness from weight gained (µm) (refer chapter 4)</th>
<th>σ, (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr 0.2%Fe</td>
<td>148.67</td>
<td>148.78</td>
<td>0.11</td>
<td>0.95</td>
<td>±0.17</td>
</tr>
<tr>
<td>Pure Zr</td>
<td>99.93</td>
<td>100.06</td>
<td>0.12</td>
<td>1.26</td>
<td>±0.21</td>
</tr>
<tr>
<td>Zry-2</td>
<td>1461.06</td>
<td>1461.67</td>
<td>0.60</td>
<td>0.98</td>
<td>±0.032</td>
</tr>
<tr>
<td>Zr 1%Fe</td>
<td>154.22</td>
<td>154.22</td>
<td>0.12</td>
<td>1.30</td>
<td>±0.21</td>
</tr>
<tr>
<td>Zr 1%Cr</td>
<td>145.77</td>
<td>145.86</td>
<td>0.09</td>
<td>0.83</td>
<td>±0.18</td>
</tr>
<tr>
<td>Zr 1%Cr</td>
<td>149.92</td>
<td>150.06</td>
<td>0.14</td>
<td>1.38</td>
<td>±0.14</td>
</tr>
<tr>
<td>Zr 1%Fe</td>
<td>88.82</td>
<td>88.96</td>
<td>0.13</td>
<td>1.28</td>
<td>±0.15</td>
</tr>
</tbody>
</table>

σ-standard deviation (µm).
Figure 11: Oxide layer thickness (weight gain) versus time for zirconium based alloys exposed to steam at intervals 1, 24 and 72 hours. The uncertainty in the weight balance is included in the plot. The data points of each set are connected by lines for clarity and with respect to time (in X-axis) they are slightly separated to show error bars clearly.

5.2. Oxide cross-section measurements

As explained in section 3.6, large number of measurements was performed on each electron micrograph. An example of image mapping in Zr 0.2% Fe alloy oxidized for 24 hours is shown in figure 12. The results of the evaluated average, minimum, maximum and standard deviation oxide thicknesses measurements using cross sections are presented in table 7. The results are illustrated in the plot of figure 13. As in the case at the weight gain measurements, the oxide growth over time is clearly seen here.

Figure 12: Micrograph of Zr 0.2% Fe alloy metal-oxide layer exposed. The green lines in the figure depict the mappings for oxide thickness evaluations.
Table 7: Average, maximum, minimum and standard deviation of oxide thicknesses, calibrated from the electron micrographs, for oxidized alloys in autoclave (415°C and 10-11 MPa) during all exposures.

<table>
<thead>
<tr>
<th>Autoclave Exposure</th>
<th>Binary-Alloy</th>
<th>Avg, X (µm)</th>
<th>Max, X (µm)</th>
<th>Min, X (µm)</th>
<th>σ, X (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 hour</td>
<td>Zr 0.2%Fe</td>
<td>0.42</td>
<td>0.57</td>
<td>0.26</td>
<td>± 0.06</td>
</tr>
<tr>
<td></td>
<td>Zr 1%Fe</td>
<td>0.62</td>
<td>1.19</td>
<td>0.36</td>
<td>± 0.22</td>
</tr>
<tr>
<td></td>
<td>Zr 1%Ni</td>
<td>0.49</td>
<td>0.79</td>
<td>0.41</td>
<td>± 0.08</td>
</tr>
<tr>
<td></td>
<td>Zr 1%Cr</td>
<td>0.52</td>
<td>0.61</td>
<td>0.46</td>
<td>± 0.03</td>
</tr>
<tr>
<td></td>
<td>Zr 0.6%Nb</td>
<td>0.40</td>
<td>0.49</td>
<td>0.32</td>
<td>± 0.05</td>
</tr>
<tr>
<td></td>
<td>Pure Zr</td>
<td>0.62</td>
<td>0.84</td>
<td>0.32</td>
<td>± 0.17</td>
</tr>
<tr>
<td></td>
<td>Zry-2</td>
<td>0.40</td>
<td>0.77</td>
<td>0.26</td>
<td>± 0.09</td>
</tr>
<tr>
<td>1 day</td>
<td>Zr 0.2%Fe</td>
<td>1.08</td>
<td>1.33</td>
<td>0.79</td>
<td>± 0.13</td>
</tr>
<tr>
<td></td>
<td>Pure Zr</td>
<td>0.88</td>
<td>1.26</td>
<td>0.54</td>
<td>± 0.23</td>
</tr>
<tr>
<td></td>
<td>Zry-2</td>
<td>1.15</td>
<td>1.56</td>
<td>0.88</td>
<td>± 0.13</td>
</tr>
<tr>
<td></td>
<td>Zr 1%Fe</td>
<td>1.14</td>
<td>1.54</td>
<td>0.93</td>
<td>± 0.11</td>
</tr>
<tr>
<td></td>
<td>Zr 1%Cr</td>
<td>0.94</td>
<td>1.17</td>
<td>0.78</td>
<td>± 0.09</td>
</tr>
<tr>
<td>3 days</td>
<td>Zr 1%Fe</td>
<td>1.53</td>
<td>1.84</td>
<td>1.15</td>
<td>± 0.16</td>
</tr>
<tr>
<td></td>
<td>Zr 1%Cr</td>
<td>1.28</td>
<td>1.52</td>
<td>1.03</td>
<td>± 0.12</td>
</tr>
</tbody>
</table>

where, X-Oxide thickness (µm), σ-standard deviation (µm)

Figure 13 Oxide layer thickness (FIB) results versus time for zirconium based alloys exposed to steam at intervals 1, 24 and 72 hours. The uncertainties from the micrograph analysis are included in the plot. The data points of each set are connected by lines for clarity and with respect to time (in X-axis) they are slightly separated to show error bars clearly.
5.3. Comparison between the two measurement methods

Figure 14 and 15 summarizes the comparison of oxide thickness between weight gain and FIB methods in Zr 1%Fe and Zr 1%Cr alloys. Both the method of oxide measurements does agree with each other. Comparatively, the errors in FIB method was smaller and hence used for kinetic model in section 5.5.

**Figure 14**: Zr 1%Fe alloy. The data points with respect to time (in X-axis) are slightly separated to show error bars clearly.

**Figure 15**: Zr 1%Cr alloy. The data points with respect to time (in X-axis) are slightly separated to show error bars clearly.
5.4. Short and long term data

In the left column of table 8 the results from the present work (1 hour, 1 day and 3 days) is summarized. Here only the result from the cross section measurement (FIB) was used, due to their smaller errors. To be able to evaluate the oxide growth kinetics also for the long term, data from Barberis et al. [31] is included (long term: 3 days – 110 days) as shown in the right column of the table 8. The average oxide thickness for the Barberis et al. [31] is converted from the provided weight gain data at conversion factor of 1 µm oxide thickness corresponding to 14.746 mg/dm² of weight gained (see chapter 4).

<table>
<thead>
<tr>
<th>Present work, Autoclave PSI (µm)</th>
<th>Barberis et al. [31] (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>415 °C, (10-11 MPa)</td>
<td>415 °C, (10-11 MPa)</td>
</tr>
<tr>
<td><strong>Alloy</strong></td>
<td><strong>1 hour</strong></td>
</tr>
<tr>
<td>Pure Zr</td>
<td>0.62</td>
</tr>
<tr>
<td>Zr 0.2%Fe</td>
<td>0.42</td>
</tr>
<tr>
<td>Zr 1%Cr</td>
<td>0.52±0.03</td>
</tr>
<tr>
<td>Zr 1%Ni</td>
<td>0.49</td>
</tr>
<tr>
<td>Zr 0.6%Nb</td>
<td>0.47</td>
</tr>
<tr>
<td>Zr 1%Fe</td>
<td>0.62±0.22</td>
</tr>
<tr>
<td>Zry-2</td>
<td>0.46</td>
</tr>
</tbody>
</table>

5.5. Oxide growth kinetic model

The fitting of model curves for the binary alloys Zr 1%Cr and Zr 1%Fe were performed based on the results from the oxide cross section measurements. The pre-transition oxidation kinetics in zirconium alloys at constant temperature could be approximated by a kinetic model equation (compare with eq.1) with the form:

\[ d = K_c \cdot t^{(1/n)} + m \]  
(equation 5)

where,

- \( d \) – oxide thickness coefficient (µm),
- \( t \) – oxidation time (hours),
- \( K_c \) – Empirical constant
- \( m, n \) – constant parameters.

The model curve was fitted to the experimental data to extract the parameters empirically. Using \( m = 0 \), i.e. \( d = K_c \cdot t^{(1/n)} \), and including all the data points, the resulting values for the parameter \( n \) was \( n_1 (Zr 1\%Fe) = 3.171±0.2686 \) and \( n_2 (Zr 1\%Cr) = 2.627±0.2242 \).

This result is well consistent with approximately cubic model of growth. Upon relaxing the starting condition and allowing significant and fast growth of oxide by rapid linear kinetics (before the first data point at \( t = 1 \) hour) the resulting parameter values were,
Pre-transition: \( d_1 (Zr\ 1\%Fe) = (0.276 \pm 0.0005) \cdot t^{(1/2.919\pm0.0019)} + (0.336 \pm 0.008) \)

\textit{(equation 6)}

Pre-transition: \( d_2 (Zr\ 1\%Cr) = (0.172 \pm 0.0245) \cdot t^{(1/2.452\pm0.0010)} + (0.327 \pm 0.005) \)

\textit{(equation 7)}

We see that result for Zr 1%Fe gives cubic behavior while Zr 1%Cr gives a model curve between \( n=2 \) and \( n=3 \). By including the data from Barberis et al.\textsuperscript{[31]} post-transition linear kinetics was approximated with the polynomial equation of degree 1 (or linear function) as,

Post-transition: \( d_1 (Zr\ 1\%Fe) = a_0 + a_1 \cdot t_1 = 2.092 + 0.001086 \cdot t_1 \) \textit{(equation 8)}

Post-transition: \( d_2 (Zr\ 1\%Cr) = a_0 + a_2 \cdot t_2 = 2.784 + 0.005431 \cdot t_2 \) \textit{(equation 9)}

Where, \( a_1 \neq 0 \), is an angled line with \( d \)-intercept \( a_0 \) and slope \( a_1, a_2 \).

The kinetic growth of the oxide layer is thus approximated with a rate law according to \textit{(eq.5)} for intervals of 1, 24 and 72 hours and with \textit{(eq.8 & eq.9)} linear behavior at longer times. The figures 16 and 17 illustrate the multiple kinetic trends from cubic to linear growth (including data from Barberis et al.\textsuperscript{[31]}) for the mentioned binary alloys.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure16.png}
\caption{Fit of oxide layer versus exposure time curve to the kinetic model of type \( d_1 = K_{c_1} \cdot t_1^{(1/n_1)} + m_1 \) and linear law of type \( d_1 = a_0 + a_1 \cdot t_1 \) for Zr 1%Fe binary alloy. The inlet shows the first three data points scaled up.}
\end{figure}
Figure 17: Fit of oxide layer versus exposure time curve to the kinetic model of type $d_2 = K c_2 \cdot t_2^{\frac{1}{n_2}} + m_2$ and linear law of type $d_2 = a_0 + a_2 \cdot t_2$ for Zr 1%Cr binary alloy. The inlet shows the first three data points scaled up.

In figures 16 & 17 results from Barberis et al. [31] for ($t > 600$ hours) was added. The dotted lines on the both these figures depict the appearance of the model curve connecting data points from a single sample while the dashed lines for the same represent the approximated transition to linear kinetics.

The points on the curves in the figures where near cubic and linear portions of the corrosion kinetics intersection have been called ‘rate transition’ or simply ‘transition’. These are identical to the term ‘breakaway’ used for corrosion of pure zirconium which indicates the point of change from decreasing rate as a function of time to one where in the oxidation rate becomes constant with time Hillner et al. [35].

In 1977, according to Hillner et al. [35], published study results show a corrosion rate transition kinetics occurring in Zry-2 and Zry-4 equivalent to an approximate cubic rate law up to a weight gain of 30 to 40 mg/dm$^2$ i.e. between 2 to 2.7 $\mu$m of oxide thickness, further beyond producing linear set of kinetics.

Although it is difficult to extract the exact point of the cubic - to - linear transition for the present work, the results in figures 16 & 17 indicate that the transition point can be estimated in between 2.5 to 3.5 $\mu$m for Zr 1%Fe and between 2.8 to 3.5 $\mu$m in Zr 1%Cr binary alloys.

It is interesting to see that oxide thickness of the different alloys from 1 hour to 1 day has only increases by about a factor of 2. This shows that the rate of oxidation decreases with time at the early stages of oxidation. Comparison of the oxide thickness of the alloys Zr1%Fe and Zr1%Cr after 3 days with the 1 day oxidation shows that the oxidation rate slows down even more.

This confirms the presence of an oxygen diffusion controlled process at the early stages of oxidation (at least in the pre-transition phase) [36]. Further in binary alloy (Zr 1%Fe) un-uniform corrosion resistance can be clearly visualized through the micrographs provided in section 5.6.
5.6. Results from FIB electron micrographs (oxide-metal layer)

Pure Zr

Zr 0.2% Fe

Zr 1% Cr

Zr 1% Fe

Zr 1% Cr

Zr 1% Cr

Zr 1% Fe

Zr 1% Fe

- 1 hour oxidation, - 1 day oxidation, - 3 days oxidation.
5.6.1. Comments on electron micrograph results

- The electron micrographs presented are scaled to show oxide-metal interface clearly. The micrographs listed in section 5.6 were used in this work for measuring and evaluating oxide thickness as explained in section 5.2.

- The oxide layers formed under autoclave were observed with uniform corrosion resistance in alloys (Zr 1% Cr, Zr 0.6% Nb, pure Zr and Zry-2) except Zr 1%(Ni, Fe) binary alloys. During 1 hour oxidation uneven bulged oxide growth was observed in Zr 1%Ni alloy.

- In Zr 1%Fe, protrusion with pores above the oxide layer and un-uniform oxide growth was observed during 1 hour oxidation. Diffusion of oxygen ions through the oxide is seen during 24 hour oxidation. Uneven oxide growth and cracked oxide layers were observed during 24 and 72 hour exposures.

\[ ^a - 1 \text{ hour oxidation}, ^b - 1 \text{ day oxidation}, ^c - 3 \text{ days oxidation.} \]
5.7. Oxide spalling (72 hour testing)

Some autoclave measurements were not successful. Two failed autoclave batch runs are described here, in spite of the problems some information on oxide formation in these experiments is presented here.

The first failed batch of autoclave experiments with Zry-2, Zr 0.2%Fe and pure Zr were oxidised together in the autoclave on different Zircaloy-2 hooks. Platinum wires were used as spacer to avoid contact of the samples with each other during oxidation. After 3 days of oxidation the Zircaloy-2 hooks were completely disintegrated along with platinum wires and the samples were found at the bottom of the autoclave and spalling occurred on all samples. Patches of white oxides were observed on the corroded samples as shown in figure 18. The evaluated weight gain after oxidation was below the original weight of the sample.

![Spalled white oxide patches on Pure Zr, Zr 0.2%Fe and Zry-2 samples](image1)

![Disintegrated Zry-2 hooks with platinum wires](image2)

*Figure 18: First batch of failed Autoclave tests*

The second failed batch of autoclave tests was performed with Zr 1%Ni and Zr 0.6%Nb samples. Instead of platinum spacer wires, A4 stainless steel screws were used as spacers. After 3 days the outcome was similar to first batch of experiment. Both the samples were completely spalled and suspended on its heavily corroded hook as seen in figure 19. Due to the weight loss from the samples, it was decided to calculate only the approximate amount of oxide formed over the surface during spalling.
Figure 19: Second batch of failed Autoclave tests

The figures 20 and 21 represent the cross sectional micrograph of the spalled oxide surfaces. In order to determine the approximate amount of oxide formed during spalling, the samples were ultrasonically cleaned with distilled water until all the oxides present over the surface were removed. The samples were air dried and weighed. The weight difference ($\Delta w$) between the sample before oxidation and after spalling were used to calculate the approximate amount of oxide formed and oxide deposited (the oxide deposited can no more be determined, as the weight loss and weight gain are now confounded, therefore the weight loss will only determine the minimum oxidation).

Figure 20: Cross section of Zr 0.6% Nb alloy sample. Blue arrows indicate the spalled oxide layer.

Figure 21: Observation of Ni precipitates present in Zr 1% Ni spalled oxide surface after 72 hour oxidation.

The weight of oxide removed by spalling is determined from equation 10. In table 9 the approximate amount of oxide formed due to spalling is presented.
The oxide formed due to spalling of samples (Zr 0.2\% Fe, Zr 1\% Fe, Zr 0.6\% Nb, Pure Zr and Zry-2) were calculated by considering the following,

\[ \Delta w = W_1 - W_2 (mg) \]  

(equation 9)

Where, \( W_1 \) – Weight of the polished sample before oxidation (mg), 
\( W_2 \) – Weight of ultrasonically cleaned spalled sample (mg), 
\( \Delta w \) – Weight loss, (mg).

\[ \frac{m(ZrO_2)}{m(Zr)} = \frac{(91 + 32)}{32} = 1.35 \]

The weight of spalled oxide, \( WO (mg) = \Delta W \times \frac{m(ZrO_2)}{m(Zr)} \)  

(equation 10)

Table 9: Approximate weight estimation of spalled oxide in alloys after 72 hour steam - oxidation.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Unoxidized alloy ( (W_1), mg )</th>
<th>Oxidized alloy(after ultrasonic cleaning), ( (W_2), mg )</th>
<th>Weight loss, ( (\Delta W) ), mg</th>
<th>Weight of spalled oxide sample ( (Wo) ), mg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr 1% Ni</td>
<td>125.72</td>
<td>106.90</td>
<td>18.82</td>
<td>25.42</td>
</tr>
<tr>
<td>Zr 0.2% Fe</td>
<td>155.43</td>
<td>91.426</td>
<td>64.00</td>
<td>86.45</td>
</tr>
<tr>
<td>Zry-2</td>
<td>1446.01</td>
<td>1187.08</td>
<td>258.93</td>
<td>348.93</td>
</tr>
<tr>
<td>Zr 0.6% Nb</td>
<td>57.672</td>
<td>57.12</td>
<td>0.552</td>
<td>0.745</td>
</tr>
<tr>
<td>Pure Zr</td>
<td>132.29</td>
<td>78.29</td>
<td>54.00</td>
<td>72.94</td>
</tr>
</tbody>
</table>
6. Conclusions

A systematic study has been performed on oxide layers formed in model alloys during exposure to steam using weight gain and cross sectional (FIB) methods. From the series of exposure periods during 1h, 1 day and 3 days, it is possible to understand the behaviour of oxide growth transition during early stages of zirconium oxidation.

The oxide growth and corrosion kinetics were observed among the model binary alloys studied, indicating the alloy chemistry and microstructure as major factors determining the corrosion behaviour. The alloy ranking of protective oxide layer was maintained at 415 °C. The oxide layer under 1 hour, 1 day and 3 days varied in between 0.3 to 1.6 µm. The weight gain and the FIB measurements from this work do agree with each other, although the errors were larger for the weight gain method. The transition kinetics in Zr 1%Fe and Zr 1%Cr showed an approximate cubic dependence during the pre-transition regime and proceeded with linear kinetics according to the predicted kinetic model.

The estimated oxide thicknesses for model zirconium binary alloys using both weight gain and FIB were in agreement with the results of Barberis et al. Table 10 compares the two methods of measurements of oxide layer under same oxidation conditions in Zr 1%Cr and Zr 1%Fe alloys.

Table 10: Agreement of relative oxide layer values

<table>
<thead>
<tr>
<th>Alloys</th>
<th>PSI (72 hour autoclave oxidation)</th>
<th>Barberis et al. [31] (µm) (72 hour autoclave oxidation)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Oxide thickness from FIB (µm)</td>
<td>Oxide thickness from weight gain (µm)</td>
</tr>
<tr>
<td>Zr 1%Fe</td>
<td>1.53 ± 0.16</td>
<td>1.28 ± 0.15</td>
</tr>
<tr>
<td>Zr 1%Cr</td>
<td>1.28 ± 0.12</td>
<td>1.38 ± 0.14</td>
</tr>
</tbody>
</table>

6.1. Outlook

So far no reliable prediction of the long-term behaviour of zirconium alloys in the corrosive environment inside a nuclear reactor was performed. Even for short-term oxidation tests in an autoclave the oxidation behaviour of zirconium and its alloys cannot be entirely explained. Considering the diversity of materials, facilities, techniques and other similar factors, the agreement between the current compilation and the previously reported series of corrosion testing appears good.

Although reliability of autoclave long term or short term experiments is a concern, experimental investigations with longer exposure time could be imperative. Such data can develop a better understanding of the oxidation trend with respect to time. In future more short term autoclave experiments between 1 hour and 3 days exposure with fewer test samples can also be suggested so as to obtain more data points for determining more precisely the oxide transition point (near cubic to linear phase).
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