HYDROGEN PICKUP MECHANISM OF ZIRCONIUM ALLOYS

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by
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ABSTRACT

Although the optimization of zirconium based alloys has led to significant improvements in hydrogen pickup and corrosion resistance, the mechanisms by which such alloy improvements occur are still not well understood. In an effort to understand such mechanisms, a systematic study of the alloy effect on hydrogen pickup is conducted, using advanced characterization techniques to rationalize precise measurements of hydrogen pickup. The hydrogen pick-up fraction is accurately measured for a specially designed set of commercial and model alloys to investigate the effects of alloying elements, microstructure and corrosion kinetics on hydrogen uptake. Two different techniques to measure hydrogen concentrations were used: a destructive technique, Vacuum Hot Extraction, and a non-destructive one, Cold Neutron Prompt Gamma Activation Analysis.

The results indicate that hydrogen pickup varies not only from alloy to alloy but also during the corrosion process for a given alloy. For instance Zircaloy type alloys show high hydrogen pickup fraction and sub-parabolic oxidation kinetics whereas ZrNb alloys show lower hydrogen pickup fraction and close to parabolic oxidation kinetics. Hypothesis is made that hydrogen pickup result from the need to balance charge during the corrosion reaction, such that the pickup of hydrogen is directly related to (and indivisible of) the corrosion mechanism and decreases when the rate of electron transport or oxide electronic conductivity $\sigma_{e}^{ox}$ through the protective oxide increases. According to this hypothesis, alloying elements (either in solid solution or in precipitates) embedded in the oxide as well as space charge variations in the oxide would impact the hydrogen pick-up fraction by modifying $\sigma_{e}^{ox}$, which drives oxidation and hydriding kinetics. Dedicated experiments and modelling were performed to assess and validate these hypotheses.
In-situ electrochemical impedance spectroscopy (EIS) experiments were performed on Zircaloy-4 tubes to directly measure the evolution of $\sigma_{e}^{ox}$ as function of exposure time. The results show that $\sigma_{e}^{ox}$ decreases as function of exposure time and that its variations are directly correlated to the instantaneous hydrogen pickup fraction variations. The electron transport through the oxide layer is thus altered as the oxide grows, reasons for which are yet to be exactly determined. Preliminary results also show that $\sigma_{e}^{ox}$ of ZrNb alloys would be much higher compared with Zircaloy-4. Thus, it is confirmed that $\sigma_{e}^{ox}$ is a key parameter in the hydrogen and oxidation mechanism.

Because the mechanism whereby alloying elements are incorporated into the oxide layer is critical to changing $\sigma_{e}^{ox}$, the evolution of the oxidation state of two common alloying elements, Fe and Nb, when incorporated into the growing oxide layers is investigated using X-Ray Absorption Near-Edge Spectroscopy (XANES) using micro-beam synchrotron radiation on cross sectional oxide samples. The results show that the oxidation of both Fe and Nb is delayed in the oxide layer compared to that of Zr, and that this oxidation delay is related to the variations of the instantaneous hydrogen pick-up fraction with exposure time. The evolution of Nb oxidation as function of oxide depth is also compatible with space charge compensation in the oxide and with an increase in $\sigma_{e}^{ox}$ of ZrNb alloys compared to Zircaloys.

Finally, various successively complex models from the well-known Wagner oxidation theory to the more complex effect of space charge on oxidation kinetics have been developed. The general purpose of the modeling effort is to provide a rationale for the sub-parabolic oxidation kinetics and demonstrate the correlation with hydrogen pickup fraction. It is directly demonstrated that parabolic oxidation kinetics is associated with high $\sigma_{e}^{ox}$ and low space charges in the oxide whereas sub-parabolic oxidation kinetics is associated with lower $\sigma_{e}^{ox}$ and higher space charge in the oxide.
All these observations helped us to propose a general corrosion mechanism of zirconium alloys involving both oxidation and hydrogen pickup mechanism to better understand and predict the effect of alloying additions on the behavior of zirconium alloys.
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Chapter 1

Literature review

This chapter presents a literature review to develop relevant aspects of zirconium alloy oxidation and hydrogen absorption by zirconium alloys during corrosion in water.

In the first part, zirconium alloy metallurgy is discussed. The different elements in solid solution and the different kinds of precipitates present in typical zirconium alloys are discussed. Then, different aspects of waterside corrosion kinetics in a reactor and in an autoclave are presented. The influence of different parameters on oxidation kinetics such as alloying element mass fraction and temperature are discussed. The relevant studies on hydrogen pick-up fraction in zirconium alloys, presenting the influences of various parameters as well as different hydrogen uptake mechanisms which have been developed in the literature, are discussed.

1.1. Metallurgy of zirconium alloys

1.1.1. Zirconium alloys used in nuclear industry

The fuel in BWRs and PWRs is in the form of uranium dioxide (UO$_2$) pellets stacked in a tube cladding made of zirconium alloys. These fuels rods (approximately 4 m height and 9.6 mm in diameter) are gathered to form fuel assemblies composed of 64 to approximately 300 fuel rods. Several such assemblies compose the nuclear core (Figure 1-1). The alloying element mass fraction in zirconium alloys is usually very low (a few wt%), but strongly impacts the behavior of the alloys. Table 1-1 presents the chemical composition of the different zirconium alloys used in the nuclear industry today.
The optimization of mechanical properties and resistance to corrosion of zirconium alloys led to the development of Zircaloy-1 (Zr-Sn), more than 50 years ago. Tin is an alloying element, which was initially introduced to neutralize detrimental effects of nitrogen on corrosion [1].

![Figure 1-1. Fuel assembly and rod cross section](image)

The presence of nitrogen was due to the fabrication process used at that time. Later, Zircaloy-1 was replaced by Zircaloy-2 (Zr-Sn-O-Fe-Ni-Cr) which showed a significant improvement in resistance to corrosion and is still used in BWRs. However, nickel has been associated with high hydrogen absorption and thus Zircaloy-2 was not a good candidate for PWR fuel cladding [2].
Consequently, Zircaloy-4 (Zr-Sn-O-Fe-Cr) was developed, in which the nickel was removed and replaced by iron. Zircaloy-2 and Zircaloy-4 have similar characteristics. They are composed of an αZr matrix with precipitates. The αZr structure is hexagonal compact (hcp) with $a = 0.323$ nm and $c = 0.515$ nm, and a $c/a$ ratio of 1.593. The space group is $P6_3/mmc$. At 865°C, Zr undergoes an allotropic transformation from hcp α phase to a bcc β phase and finally melts at 1860°C [3].

Table 1-1: ASTM Specifications for Zircaloy-2, Zircaloy-4 and Zr-Nb [4]. The normal choice of compositions for the advanced ZIRLO™ and M5™ alloys used nowadays in the nuclear industry (wt%) [5] are also shown.

<table>
<thead>
<tr>
<th></th>
<th>Zircaloy-2</th>
<th>Zircaloy-4</th>
<th>Zr-Nb</th>
<th>ZIRLO™*</th>
<th>M5™*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn</td>
<td>1.2-1.7</td>
<td>1.2-1.7</td>
<td>-</td>
<td>0.96</td>
<td>-</td>
</tr>
<tr>
<td>Fe</td>
<td>0.07-0.20</td>
<td>0.18-0.24</td>
<td>-</td>
<td>0.1</td>
<td>-</td>
</tr>
<tr>
<td>Cr</td>
<td>0.05-0.15</td>
<td>0.07-0.13</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ni</td>
<td>0.03-0.08</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Nb</td>
<td>-</td>
<td>-</td>
<td>2.4-2.8</td>
<td>0.99</td>
<td>1.0</td>
</tr>
<tr>
<td>O</td>
<td>1000-1400 wt.ppm</td>
<td>1000-1400 wt.ppm</td>
<td>To be specified</td>
<td>1430 wt.ppm</td>
<td>1250 wt.ppm</td>
</tr>
<tr>
<td>Utilization</td>
<td>BWR and CANDU</td>
<td>PWR</td>
<td>VVER (Russian equivalent to PWR)</td>
<td>PWR</td>
<td>PWR</td>
</tr>
</tbody>
</table>

*ZIRLO™ and M5™ are trademarks of Westinghouse Electric Co. and Areva, respectively.

The microstructure of the alloys largely depends on the heat treatment they undergo during fabrication and processing. Figure 1-2. Zircaloy cladding manufacturing sequence [6] shows a typical manufacturing procedure for Zircaloy cladding. Generally in the recrystallized condition, the microstructure consists of equiaxed (α-phase) grains with precipitated second phase particles. This precipitation is both inter-granular and intra-granular.
1.1.2. **Alloying elements in common zirconium alloys**

The morphology of second phase particles as well as the content of alloying elements supersaturated in the αZr solid solution have been found to correlate well with the corrosion resistance of the alloys. However, there is no general agreement on the cause and impact of these two factors on the corrosion performance. It is thus necessary to detail the different alloying elements and their associated microstructure.

In the αZr matrix of Zircaloy-2 and Zircaloy-4 both Sn and O are found in solid solution, in substitution and insertion respectively [3]. Figure 1-3 presents the phase diagram for Zr-O and Zr-Sn. The Zr-Sn phase diagram shows three compounds: SnZr₃, Sn₂Zr₅, Sn₃Zr, which should be present at room temperature. However, even if thermodynamics predict their formation, they are not observed in normal Zr alloys because of their slow kinetics of formation. Recent thermodynamic studies have shown that there is a possible deviation from stoichiometric ZrO₂ towards sub-stoichiometric ZrO₂ at operating temperatures [7]. However, even though the
protective oxide is likely sub-stoichiometric because of its dark color different from the white stoichiometric ZrO₂, the exact amount of sub-stoichiometry has never been directly measured by Atom Probe Tomography (APT).

The other alloying elements (Fe, Cr, Ni) have a very low terminal solid solubility in αZr and thus precipitate as hexagonal Zr(Fe,Cr)₂ (C14), cubic Zr(Fe,Cr)₂ (C15) and tetragonal Zr₂(Fe,Ni) in Zircaloy-2 and as Zr(Fe,Cr)₂ in Zircaloy-4. The phase diagrams of Zr-Fe, Zr-Cr and Zr-Ni are presented in Figure 1-4, Figure 1-5 and Figure 1-6. The first precipitates to form are of ZrCr₂ and Zr₂Ni types. Zr₃Fe precipitates at a slightly lower temperature so substitutes in the Cr and Ni sublattices Zr(Cr,Fe)₂ or Zr₂(Ni,Fe) instead [3]. The precipitate size and distribution are controlled by the thermal treatment and processing of the alloys, and can influence the corrosion rate of zirconium alloys [8]. It has been shown that the optimal precipitate size to improve resistance to corrosion in PWRs was around 150 nm [9], while finely distributed small precipitates improve the nodular corrosion resistance in BWRs [4]. Indeed, it has been found in PWRs that improved uniform corrosion resistance can be obtained with large precipitates, but in BWRs, better resistance to localized corrosion (nodular corrosion) is seen in materials having finely distributed small precipitates [4]. Charquet [10] studied the solubility limit of iron and chromium in Zr-1.4%Sn-0.1%O matrix. The maximum solubilities in the α phase are 120 wt-ppm for iron at 820°C, 200 wt-ppm for chromium at 860°C, and 150 wt-ppm for iron plus chromium at 810°C (and Fe/Cr = 2).
Depending on the heat treatments (and more specifically on the cumulative annealing parameter, $\text{CAP} = \sum t_i e^{-Q/RT_i}$, where $t_i$ is the time spent at the temperature $T_i$ and $Q/R = 40,000$), different contents of Fe and Cr in the $\alpha$ phase have been reported. For instance, using synchrotron fluorescence measurements, Yilmazbayhan et al. reported a content of approximately

Figure 1-3. Phase diagrams: a) Zr-O [7] b) zoom around the ZrO$_2$ region and c) Zr-Sn [11]
290 wt·ppm of Fe in the $\alpha$ phase of Zircaloy-4 (CAP = $2.1 \times 10^{-16}$h) [12], whereas Wadman et al. reported a Fe content of 400 wt·ppm [13] (CAP = $4.5 \times 10^{-14}$h).

Figure 1-4. Phase diagram Zr-Cr [14]

Figure 1-5. Phase diagram Zr-Fe [14]
Niobium is also found in zirconium-based alloys and acts as a β-stabilizer. The Zr-Nb phase diagram is shown in Figure 1-7. The niobium forms solid solution in αZr up to 0.4 at%–0.5 at% at which point β-Nb precipitates are formed. These precipitates are rich in Nb (approximately 85% of Nb) and have an average diameter of 50 nm which is usually smaller than Zr(Fe,Cr)\textsubscript{2} and Zr\textsubscript{2}(Fe,Ni) precipitates present in Zircalloys. At about 620°C and around 18.5 at% Nb, a monotectoid transformation takes place. By water quenching from the β or upper α and β regions, the β-Zr grains transform by martensitic decomposition into a needle-like α' niobium supersaturated hcp phase. If this is followed by heat treatment below the monotectoid temperature, the niobium will diffuse out of the α' phase and precipitation of β'-Nb occurs at twin boundaries of the α' needles [15].

Figure 1-6. Phase diagram Zr-Ni [14]
The last element of interest in zirconium alloys is hydrogen. Hydrogen is normally present to a level close to 10 wt·ppm after processing of the zirconium alloys. Due to hydrogen pick-up during waterside corrosion, the hydrogen concentration can reach values of hundreds of wt·ppm at the end of life cycle. However, the terminal solid solubility limit of hydrogen in zirconium alloys is generally low: from approximately 65 wt·ppm at 300°C, it decreases to 0.1 wt·ppm at room temperature [17]. The terminal solid solubility (TSS) of hydrogen in αZr, Zircaloy-2 and Zircaloy-4, below 550°C, is given by Kearns et al. as:

$$C_H = 9.9 \times 10^4 e^{-\frac{8250}{RT}} \text{ ppm}$$  \hspace{1cm} (1-1)

where T is the temperature in Kelvins and R the universal gas constant. At 500°C (and probably at lower temperatures) during the oxidation of zirconium in oxygen, the solution of high oxygen content in zirconium displaces the hydrogen previously present in the region, thus, indicating low

Figure 1-7. Phase diagram of Zr-Nb [16]
solubility of hydrogen in the zone containing a high concentration of oxygen [18]. The hydrogen solubility is thus different in the zirconium metal compared to the zirconia.

In the zirconium oxide, extremely low levels of hydrogen were measured using nuclear beam techniques to obtain the hydrogen profile as function of the oxide depth [19]. Assuming the oxide is free of pores and fully dense, Stern et al. found little levels of hydrogen in the oxide film (hydrogen/metal atom < 0.01) in agreement with previous autoradiographic studies [18] on preoxidized samples exposed to tritium. This low solubility of hydrogen in zirconia is also confirmed by Miyake et al. [20] where the hydrogen concentration ranged between 1 wt·ppm and 0.1 wt·ppm and decreases with increasing temperature. This situation might be quite different in porous oxide films [21]. The authors also observed a significantly higher concentration of hydrogen just below the oxide/metal interface. Whether this higher concentration is due to a hydrogen (in tetrahedral sites)-oxygen (in octahedral sites) interaction at the oxidation temperature, to favored hydride precipitation sites during the cooling process (stress effect of the oxide), or to the presence of water into pores has not been clarified yet.

In steam at 300-400°C, the rate of hydrogen uptake decreases when the TSS in the metal is exceeded during the oxidation of zirconium alloys [22]. This is interpreted to mean that the uptake process was so local that the uptake rate at the uptake site was high enough to precipitate hydrogen locally at the entry site and to counter-effect the hydrogen diffusion in the bulk. The active sites at the surface were observed to be small cracks or pores that develop in the oxide film even during pre-transition oxidation and were not apparently associated with second-phase particles.

At operating temperatures, with respect to plasticity, precipitated hydrides with hydrogen in solid solution induce a decrease of the yield stress in cold work stress relieved Zircaloy-4 [23]. According to the authors, this behavior might be explained by considering the hydrided Zircaloy-4 material as a composite of a ductile metallic phase containing relatively brittle hydride platelets,
but the role of hydrogen in solid solution at high temperatures is not clear. At high temperatures, hydrogen also induces an increase in creep resistance.

At room temperature, hydrogen precipitates as zirconium hydride, which embrittles the metal by lowering the ductile/brittle transition temperature (DBTT) [24]. Furthermore, hydrogen is also known as a $\beta$-stabilizer, which can have various consequences. For instance, in the case of a Loss Of Coolant Accident (LOCA), high hydrogen content lowers the $\alpha \rightarrow \beta$ transition. The presence of hydrogen increasing the oxygen solubility in the $\beta$ phase, and high oxygen content being known to embrittles the $\beta$ phase, for a given oxygen content, the hydrided $\beta$ phase would be more fragile compared to the non hydrided one. Finally, since the $\beta$ phase is very susceptible to creep, high hydrogen content can lead to a problematic local swelling of the cladding hampering the circulation of water between the fuel rods. The phase diagram of Zr-H is presented in Figure 1-8.

1.2. Zirconium alloys oxidation

1.2.1. Waterside corrosion of zirconium alloys

In this section the oxidation of zirconium and zirconium-based alloys in water environment at 360°C is discussed. A native thin layer of so called air-formed oxide film is present in all zirconium alloy surfaces. At these early stages of oxidation, three suboxides (solid solution of oxygen in the zirconium matrix) of Zr$_2$O were reported to be seen (ZrO, Zr$_3$O and Zr$_3$O$_{1-x}$) accompanied by the oxide of ZrO$_2$ [25]. These suboxides are formed on surfaces at different water vapor atmosphere pressures. Also, it has been reported that at elevated temperatures in an oxidizing environment, where thermally activated thickening of the initial
oxide film occurs, not all the oxygen that reacts forms oxide, some of the oxygen dissolves in the metal matrix [26].

Figure 1-8. Phase diagram of Zr-H [27]
Three phases of stable ZrO\textsubscript{2} exist at atmospheric pressure: monoclinic, tetragonal and cubic. In reactor or autoclave oxidation conditions (below 500ºC), the most stable phase is monoclinic ZrO\textsubscript{2}. However, the tetragonal phase is often observed in zirconium oxides, especially close to the oxide/metal interface. It has been reported that this metastable phase could be stabilized by stress, sub-stoichiometry and alloying elements (especially iron) [28].

The driving force for the zirconium oxidation is the high free energy of the zirconium oxide formation reaction (~965 kJ mol\textsuperscript{-1} at 360ºC [29, 30]). As a consequence of the thermodynamics of the zirconium oxidation system and the environmental conditions to which the material is exposed, different activities will be established at the two interfaces of the oxide layer (oxide/water and oxide/metal interfaces). These activity gradients are the primary driving force for the transport of the species across the oxide film.

The zirconium oxide formed on Zr alloys is mostly protective, such that after the formation of the oxide there is no direct contact between the metal and the water, and the corrosion reaction cannot happen directly. Instead the oxidizing species have to diffuse through the oxide layer. For the zirconium oxidation to occur, it requires either the zirconium cations or the oxygen anions to diffuse through the oxide layer. From the observation of the zirconium oxide system it has been confirmed that the oxide thickening in high temperature environment occurs by oxygen anion migration through the oxide film, with the formation of new oxide taking place at the metal/oxide interface [31, 32]. However, reports of some Zr mobility under Loss Of Coolant Accident (LOCA) conditions showed that there might be some small zirconium ion migration at these high temperatures [33]. The observed sub-stoichiometry gradient of the zirconium oxide would be the primary driving force for the oxygen anion diffusion. However, the amount of sub-stoichiometry in the zirconium oxide in equilibrium with a saturated oxygen solid solution in zirconium metal at reactor temperatures has not been precisely determined. Recent thermodynamic studies of the ZrO\textsubscript{2} system have been performed and report that the amount of
sub-stoichiometry $x$ in ZrO$_{2-x}$ could be as high as 0.0152 at 633K [7]. However no sub-stoichiometry has ever been experimentally measured at the oxide/metal interface of zirconium oxide layers.

The oxidation process can be conceptually divided into several steps as presented in Figure 1-9. First, oxygen in the water molecule dissociates and is adsorbed onto the oxide layer surface (eq.1-2):

$$2\text{H}_2\text{O}^\text{dissociation} \rightarrow 4\text{H}^+ + 2\text{O}_\text{adsorbed}^{2-}$$

(1-2)

and absorbed by a vacancy (eq.1-3):

$$\text{O}_\text{adsorbed}^{2-} + \text{V}_\text{O}^\text{absorption} \rightarrow \text{O}_\text{adsorbed}^{2-}$$

(1-3)

Because of the defect concentration gradient, the oxygen anions diffuse either through the bulk of the oxide or along the oxide grain boundaries via solid state diffusion. When the oxygen anion reaches the oxide/metal interface it reacts with Zr cations to form new oxide (eq.1-4):

$$\text{Zr}^\text{oxidation} \rightarrow \text{Zr}^{4+} + 4\text{e}^-$$

(1-4)

and zirconium cations react with oxygen anions to form new oxide (eq.1-5):

$$\text{Zr}^{4+} + 2\text{O}_\text{absorbed}^{2-} \rightarrow \text{ZrO}_2$$

(1-5)

The formation of this new oxide releases electrons, which then migrate through the oxide to reduce the hydrogen ions at the cathodic site (eq.1-6):

$$4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2$$

(1-6)

Some hydrogen atoms (under the form of protons, water, or neutral hydrogen atom) do not recombine with electrons at the oxide/water interface but are instead absorbed by the oxide layer. These atoms diffuse through the oxide layer to the metal, where they are found either in solid solution of $\alpha$Zr or as hydride precipitate. This phenomenon is called hydrogen pick-up and is the subject of this thesis.
Figure 1-9. Schematic of the reactions taking place during uniform corrosion of Zr.
It is well known that the corrosion rate of zirconium alloys *decreases* as the thickness of the oxide layer increases [34]. Because of this, it is considered that either oxygen anion diffusion or electron diffusion is the rate-limiting step. This assumption leads to the parabolic scaling law for the oxidation kinetics: \( \delta = K \tau^n \), with \( n = 0.5 \) [35, 36]. However, it has been observed that oxidation of zirconium alloys is frequently sub-parabolic [28, 37-39].

In the absence of externally applied potentials on the specimen, the net current through the oxide is zero, which means that the negative and positive oxidation currents must be equal and opposite. In the case of a deviation from this balance, an electrical potential develops across the oxide thickness that equalizes these currents. If the transport of electrons through the oxide is the rate-limiting step, a positive electric gradient through the oxide layer (potential is negative at the metal/oxide interface relative to the oxide/water interface, \( (\nabla \cdot \mathbf{N}) > 0 \)) would appear and induce a negative electric field across the oxide layer (see Figure 1-10). This field would slow down the diffusion of the positively charged oxygen vacancies and increase the diffusion of electrons toward the oxide/water interface through the Coulomb force \( \mathbf{F} \)
\[
\mathbf{F} = -eZ_e (\nabla \cdot \mathbf{N})
\]
where \( Z_e = -1 \) and \( Z_{V_0} = 2 \). Hence this negative electric field will tend to decrease the corrosion rate. Thus, a negative electric field tends to increase the transport of electrons and decrease the transport of oxygen vacancies. By these effects, the magnitude of the negative electric field is, in turn, reduced, so that the variations effected by the electric field are in the direction to decrease the rate of change in the field. Therefore, a stable situation in which the currents produce no further changes in the field is reached, and the net transport of charges at any location in the oxide is zero. Of course, the opposite is observed if the transport of oxygen vacancies is the rate limiting step (and thus the electric field across the oxide is positive, increasing the corrosion rate).
Many studies have observed negative potential at the metal/oxide interface relative to the oxide/water interface (the electric potential across the oxide being then positive) [40-47]. From measurement of that potential as function of exposure time, it also appears that electronic and ionic resistivity are more balanced as the oxide thickens, but the electric potential normally remains positive. This indicates that the transport of electrons is normally slower than the transport of oxygen vacancies, making it the rate limiting step in most circumstances.

Figure 1-10. Schematic of the potentials and electric field if electron transport is considered rate limiting step of the corrosion process
Although the mechanism of electron transport is still unclear [42, 43, 48, 49], it seems reasonable to consider that both bulk and localized electron conduction can contribute to the overall oxidation rate [49-52]. For instance, attempts to image the sites of electronic conduction by using evaporated CuI layers suggested that this process was localized at second phase particles incorporated into the oxide, at least in the thin film region [53]. Also, from anodic oxidation experiments, it was concluded that the equations that best fit the anodic (ionic transport) and cathodic (electron transport) processes are different [41]. Some studies have shown that the former fits a diffusion-controlled process and the latter best fits to a Schottky emission process [51] with the emission taking place at a few localized sites in the oxide [54]. In any case, the preceding arguments indicate that oxide electronic conductivity is a key parameter to partially control zirconium alloy oxidation [55, 56], since, in such a situation, neither diffusion process can be said to uniquely control oxidation.

*Clearly, if electron transport has a significant role in the oxidation kinetics, the precipitates embedded into the growing oxide and the intrinsic or extrinsic compensating defects due to aliovalent cations in solid solution could have a significant impact on the corrosion kinetics by affecting the oxide electronic conductivity* [47, 57, 58].

### 1.2.2. Oxidation of alloying elements relative to the zirconium oxidation

It was found that the size, chemical composition and distribution of precipitates (and so their equilibrium with alloying element concentrations in solid solution) have a profound impact on the corrosion resistance and the hydrogen pickup of zirconium alloys [59-64]. However, despite extensive research, the influence of the alloying elements in precipitates and in solid solution on the mechanisms of corrosion and its associated hydrogen pickup are not well understood [22, 61-63].
The free energy of oxide formation of the intermetallic phases has been calculated for the different binary and ternary precipitates present in zirconium alloys [65]. The comparison of the calculations and the oxidation behavior of individual precipitates has shown that the thermodynamic approach rather than the kinetic approach explains most clearly the behavior of precipitates in the oxidation of binary precipitates, and even in more complex phases. The transition between delayed and simultaneous oxidation occurs at molar oxidation free energy of 760–780 kJ mol⁻¹. According to this theoretical study, delayed oxidation of ZrCr₂, βNb, Zr(Fe,Cr)₂ and Zr(Fe,Nb)₂ should be observed whereas βZr, Zr₃Fe, Zr₂Ni, Zr₂Cu, Zr₂(Fe,Ni) and (Zr,Nb)₂Fe should be oxidized at a lower oxidation potential as zirconium.

Experimentally, potential sweeps of pure binary alloys (ZrFe, ZrNi and ZrCr) have confirmed that the intermetallic compounds are more noble than the alloy [66]. Thus, due to galvanic coupling between the precipitates and the alloy, the oxidation of precipitates is delayed relative to the matrix. Delayed oxidation of Fe, Cr and Nb in second phase precipitates compared to the zirconium phase has also been previously reported from transmission electron microscopy (TEM) examinations [67, 68]. The delayed oxidation of Zr(Fe,Cr)₂ precipitates has been studied more extensively and it has been shown that during the oxidation of Zr(Fe,Cr)₂ precipitates, metallic αFe is segregating at the edge of the precipitates and after complete oxidation, most of the Fe is rejected from the precipitate into the zirconium oxide matrix [67, 69, 70]. Similar Fe phases have been observed using Mossbauer spectroscopy of Fe in Zircalloys [71]. Using this technique, the chemical state of Fe in the oxide layer was also investigated and a combination of Fe²⁺, Fe³⁺ and Fe₃O₄ in the zirconium oxide layer was observed. Depth profiles of Fe and Cr chemical states have been performed by Sakamoto et al using X-Ray Absorption Near Edge Spectroscopy (XANES) [72, 73] and they observed that the fractions of oxidized Fe and Cr slowly increase as a function of distance from the oxide/metal interface, reaching 100% at the outer oxide interface. Similar observations have been made with Nb in ZrNb alloys, the Nb
chemical state and the fraction of oxidized Nb increasing respectively from 0 to +2 to +5 for the former and from 0% to 100% for the later as the distance from the oxide/metal interface increases [74].

The oxidation of alloying elements in solid solution relative to the zirconium oxidation has been less studied over the years due to a lack of sensitivity of experimental methods. Using Mossbauer spectroscopy on Zircaloy-4 samples, Sn$^{2+}$ and Sn$^{4+}$ were clearly identified in the oxide with varying relative concentrations as the oxide thickens [71]. In addition to the oxidized Sn, the presence of metallic βSn in the oxide was greatly suspected which is consistent with simple thermodynamic considerations [30]. However, despite many previous conventional TEM studies, no tin compounds were detected in the oxide and their presence has only been confirmed by two recent high resolution TEM studies [75, 76]. Using Atom Probe Tomography (APT) on Zircaloy-2 oxide/metal interfaces, it has been shown that Fe and Ni in solid solution close to the oxide/metal interface are segregated at sub-grain boundaries inherited from the metal as the advancing oxide layer consumes the metal during corrosion [77].

1.2.3. Weight gain kinetics

It can be easily shown that if the rate limiting step is the diffusion of species across the oxide (either oxygen anions or electrons) a parabolic law for the oxide thickness $\delta$ is obtained [35]:

$$\delta = Kt^{1/2}$$

(1-7)

However, it has often been reported that the zirconium alloy corrosion kinetics are closer to a cubic law (or lower) instead of a parabolic law [38, 45], which is not common in metal oxidation for oxide layers of the micron scale. Assuming that oxygen diffusion is the rate limiting step, some explanations of the sub-parabolic kinetics have been proposed such as grain boundary
diffusion combined with a linear change in the grain size with oxide thickness [37], build-up of compressive stress in the oxide layer as the oxide thickens [78], or emergence of cracks in the oxide layer impeding oxygen diffusion [79]. However, assuming that electron transport is non-negligible in the control of the oxidation kinetics, space charge has been identified as a possible explanation of sub-parabolic kinetics [80, 81]. These points will be more detailed in the chapter 6 on theory of metal oxidation.

It has been reported that depending on the alloying elements chosen, the general oxidation kinetics follow [8, 38]:

$$\delta = Kt^n$$  \hspace{1cm} (1-8)

The exponent $n$ has been carefully measured in various zirconium alloys at the beginning of the corrosion by fitting weight gain data as function of exposure time and the results are presented in Table 1-2 ($\bar{n}$ being the average exponent over the various alloys of the group).

Table 1-2: Model alloys pre-transition kinetics constants in 360°C water autoclave experiments [8].

<table>
<thead>
<tr>
<th>Alloys group</th>
<th>$K$</th>
<th>$\bar{n}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr-Fe-Cr</td>
<td>9.9</td>
<td>0.21</td>
</tr>
<tr>
<td>Zr-Cr-Fe</td>
<td>10.9</td>
<td>0.19</td>
</tr>
<tr>
<td>Zircaloy-4</td>
<td>10.2</td>
<td>0.22</td>
</tr>
<tr>
<td>Zirconium</td>
<td>7.6</td>
<td>0.22</td>
</tr>
<tr>
<td>Zr-Sn</td>
<td>9.5</td>
<td>0.29</td>
</tr>
<tr>
<td>Zr-Cu</td>
<td>14.1</td>
<td>0.18</td>
</tr>
<tr>
<td>Zr-Sn-Nb</td>
<td>6.5</td>
<td>0.41</td>
</tr>
<tr>
<td>Zr-Nb</td>
<td>5.9</td>
<td>0.45</td>
</tr>
<tr>
<td>ZIRLO</td>
<td>6.7</td>
<td>0.37</td>
</tr>
<tr>
<td>Zr-2-5Nb-0.5Cu</td>
<td>8.4</td>
<td>0.31</td>
</tr>
</tbody>
</table>

The reasons why $n$ varies from 0.18 to 0.45 are not clear and are one of the subject of this study. It is important to point out that the parameter $n$ in this case is probably not derivable from a given metal oxidation theory, but is clear phenomenological evidence of a different oxidation mechanism than the one derived by Wagner [82], as discussed in Chapters 3 and 6.
1.2.4. Oxide transition

The corrosion kinetics of zirconium alloys in aqueous solutions is usually described as having two regimes: an initial pre-transition regime with approximate parabolic or cubic oxidation rate (see Table 1-2) and a post-transition regime, approximately linear in autoclave [4, 28, 29, 83, 84]. The change from the parabolic or cubic kinetics to faster regimes (approximately linear) is called the oxide transition, defined as the oxide thickness at which the change in corrosion kinetics occurs. This change usually occurs at an oxide thickness of 2 to 3 µm. The inner oxide layer may remain dense, and protects the metal.

With a closer observation of the post-transition, it can be distinguished that instead of being completely linear with time, it is composed of several periods of corrosion that reproduces the pre-transition regime, in a cyclical way as it is presented in Figure 1-11. The periodic nature of post-transition corrosion has been observed and noted for some time [85] and this nature of corrosion is common among Zr alloys. After approximately 70-100 µm, the oxide can start to spall off. Not all zirconium-based alloys follow this oxidation behavior. While protective alloy oxides such as formed in Zircaloy-4 follow this cyclical behavior, other alloys can show initial protective behavior and after the oxide growth to a particular thickness they undergo a rapid acceleration of the weight gain with no recovery: this phenomenon is called breakaway and is displayed in Figure 1-12.
When breakaway occurs, the oxide becomes white (grey for transition) which is characteristic of a porous, non-protective oxide and which would allow stoichiometric ZrO$_2$ (white in color and very powdery in aspect) to form and oxide spallation occur. Some models
have been proposed [3, 87-89] but a complete understanding of the oxide transition and of the parameters leading to breakaway is still lacking.

Recent studies using Focused Ion Beam (FIB) sectioning have shown that there is a gradual nucleation of cracks throughout the periods of parabolic/cubic oxide growth both before and after the first transition in kinetics, rather than a sudden burst of crack nucleation at transition as has frequently been assumed from observation of the characteristic layered crack morphology in thicker oxides [90]. The transition would be due to the development of interlinked porosity down to the metal–oxide interface [91, 92].

1.3. Hydrogen pick-up

1.3.1. Definition

To compare the hydrogen pickup of different alloys, it is necessary to quantify the amount of hydrogen picked up relative to the amount of corrosion. To accomplish this, the amount of hydrogen picked up by the metal during reactor or autoclave exposure is normalized to the total amount of hydrogen generated in the corrosion reaction. The hydrogen pickup fraction $f_H$ is defined as the ratio of the hydrogen absorbed by the metal over the total hydrogen generated in the corrosion reaction:

$$f_H = \frac{H_{\text{absorbed}}}{H_{\text{generated}}} \quad (1-9)$$

As a function of exposure time, it was initially reported that the absorption kinetics of hydrogen follow the oxidation kinetics: cubic in the pre-transition regime and quasi linear in the post transition regime [93]. However, since this time, a significant spread of the pick-up fraction results exists in the literature. In particular, for a given alloy, we still do not clearly know if the
pick-up fraction is a constant [34], if it varies as a function of exposure time following the cyclical behavior of oxidation kinetics [94] or not [95]. This spreading of the results is due to a lack of a precise technique to detect hydrogen and to the numerous parameters that influence hydrogen absorption. This literature review on hydrogen pick-up will aim at referring the different important conclusions that have been found in the past.

There has been evidence that $f_H$ depends strongly on the alloying element additions [61, 62], the alloy microstructure and microchemistry [2, 96] and the corrosion conditions [97]. The addition of alloying elements generally decreases hydrogen pickup with the exception of Ni, which increases pickup and Sn which was reported to have little effect [62, 98]. In addition, there is evidence that $f_H$ changes during the corrosion process, such that different fractions of hydrogen are picked up at different stages of oxide film growth [95].

**Before going further one has to note that the pick-up fraction is not enough to characterize the hydrogen absorption behavior of an alloy.** Indeed, the single measure of $f_H$ to compare hydrogen absorption of different alloys is pertinent only if they have similar oxidation kinetics. However, often in the literature, the overall pick-up fractions are integrated over long exposure times after several transitions have occurred or the alloy has undergone breakaway. Regarding the different oxidation kinetics of these different regimes, the determination of $f_H$ is not enough to characterize of the hydrogen absorption behavior of a given alloy. Consequently in this study, the author tried as much as possible to simultaneously provide results on hydrogen pick-up and weight gain. To easily compare alloys with different oxidation kinetics, another way to display the results is to plot the hydrogen content in mg dm$^{-2}$ as a function of the weight gain in mg dm$^{-2}$. Regarding the different mass of hydrogen and oxygen, it is assumed that the total weight gain is due to oxygen absorption. However, one has to keep in mind that for $f_H = 100\%$, the weight gain due to hydrogen will be equal to 11.1% of the corrosion weight gain! A “normal” pickup fraction of $\sim 15\%$ would result in an increase of $\sim 1.5\%$. 
1.3.2. Hydrogen pickup in Zirconium alloys

Many techniques have been traditionally used to measure hydrogen content in zirconium. Destructive techniques, which preclude further analyses on the sample, such as Vacuum Hot Extraction (VHE) or Inert Gas Fusion (IGF) have been widely used in past research [61-63, 99]. Hence, sister samples (identical samples coming from the same batch of material) must be used to evaluate the hydrogen pick-up variation as a function of corrosion time, which inherently spreads the results and makes the induced error difficult to evaluate. Also, the sample size analyzed in VHE and IGF (a piece of approximately 4 mm x 8 mm) is much smaller than a standard corrosion coupon (25 mm x 20 mm). Thus, spot-to-spot hydrogen concentration variations within the coupon may falsify the results. Finally the precision of these destructive techniques at these low hydrogen concentration levels is not well established.

Various non-destructive techniques have been used for evaluating hydrogen content in zirconium alloys. The EMAR method (electromagnetic acoustic resonance) [100] is ideal for in situ measurement but is not very precise. Also ultrasonic measurement coupled with eddy current testing [101], or neutron transmission technique [102] have been applied to this problem. However none of these techniques have the level of reliability and precision required to detect low hydrogen mass fractions in zirconium alloys. We have previously demonstrated the reliability of the Cold Neutron Prompt Gamma Activation Analysis (CNPGAA) technique to analyze low levels of hydrogen in zirconium [103]. As will be shown, this technique is non-destructive, precise, measures the average hydrogen concentration in the whole sample, can detect very low levels of hydrogen (as low as 5 wt-ppm) [104]). However, it has not been routinely used to detect hydrogen in zirconium alloys, as it is time consuming and can only be performed in a specialized facility.
Although, in most environments, the oxidation kinetics of Zircaloy-2 and Zircaloy-4 are comparable, it is well established that Zircaloy-2 absorbs generally more hydrogen than Zircaloy-4 [2]. Autoclave tests made between 280°C and 400°C have shown that the Zircaloy-4 hydrogen pick-up fraction was in the range of 20-40% while Zircaloy-2 exhibited a hydrogen pick-up fraction in the range of 40-60% [61, 93].

In Zr-Nb alloys containing up to 2.5% of niobium mass fraction, the hydrogen absorption kinetics are comparable to the Zircaloy family, but their hydrogen pick-up fraction is much lower [64, 105].

This wide range of results shows how the hydrogen pick-up can vary among the different zirconium alloys and the different environments. Hence, it is important to identify the effect of the different factors on hydrogen pick-up. Those have been precisely reviewed in [106] and only updated conclusions will be recalled in that document.

1.3.2.1. External parameters

The effect of temperature has not been completely characterized and previous research does not agree on its influence on hydrogen pick-up [2, 93, 107]. For instance, although in autoclave steam corrosion at temperatures lower than 420°C, Zircaloy-2 absorbs more hydrogen than Zircaloy-4, at higher temperatures the two alloys show similar hydrogen absorption behavior [2]. This temperature dependence could be directly related to the catalytic effect of Ni as it has been shown that the activation energy for hydrogen absorption by zirconium is reduced in the presence of Ni up to a temperature of approximately 310°C (48 kJ·mol⁻¹) before reaching a higher value comparable to the one of pure zirconium at higher temperatures (71 kJ·mol⁻¹) [108].

Regarding the dissolved gases in solution, it was concluded that the presence of oxygen in the aqueous phase is relatively innocuous to the Zircaloy corrosion behavior although slightly
higher weight gains are obtained in the oxygenated environment [97]. But, without exception, the hydrogen pick-up value at any given weight gain is higher for the hydrogenated environment [97, 109].

Irradiation seems to slightly accelerate the oxidation kinetics when compared to an identical experiment performed in out-of-pile autoclaves [110]. However, studies on Zr-2.5Nb alloys under irradiation have shown that irradiation does not seem to have a strong effect on hydrogen pick-up [111]. In irradiated samples, after the first transition, a second transition appears where oxidation kinetics and hydrogen absorption increase (however the hydrogen pick-up fraction decreases) [110].

The conclusion that can be drawn from this review on external parameters is that the surface reaction governing hydrogen absorption should not be neglected in the study of hydrogen pickup; especially the effects of getters such as Ni or Cu and of the hydrogen pressure at the cathodic site.

1.3.2.2. Intrinsic parameters

The effect of Fe is more ambiguous, but the sizes, types, and distributions of ZrFe types of precipitates definitely play a role in the hydrogen absorption behavior of a given alloy [59, 61, 63, 99, 112]. Adding either iron or chromium increases the amount of intermetallic precipitates in the alloy since their solubility limits are very low. However, their effects on hydrogen pick-up are totally different: addition of Fe seems to increase $f_H$, whereas addition of Cr seems to reduce it. Thus, the various intermetallics do not play a consistent and general role in determining hydrogen pick-up fraction [63, 113]. Baur et al. have studied the mechanism for hydrogen pick-up in water at 350°C using electrochemical techniques [55] to clarify the influence of the precipitate size on the oxide layer electrical resistivity. They found that one important
The parameter for the hydrogen pick-up is the potential gradient formed over the oxide layer. Zircaloy-4 with large SPP’s (160 nm diameter) and high iron content (0.22%) create a lower electrical resistance in the oxide layer and hydrogen pick-up than Zircaloy-4 with small SPP’s (130 nm diameter) and low iron content (0.20%). Also Zr-2.5Nb has the lowest oxide layer electrical resistance and hydrogen pick-up. These results on precipitate size effects (lower hydrogen pick-up related to bigger precipitate sizes) do not agree with the work done by Hatano et al. [60] on which bigger precipitates are supposed to increase the hydrogen uptake. There seemed to be a relationship between electrical resistance and hydrogen pick-up but the effect of precipitate size or iron content on electrical resistance is not obvious. However, the authors concluded that the increased corrosion rate generally observed for Zircaloy-4 with very fine precipitates is due to the lack of the contribution from the precipitates to the electrical conductivity. A recent theoretical thermodynamic study has shown that ZrCr$_2$ and ZrFe$_2$ (the boundary phases of the Zr(Cr,Fe)$_2$ solid solution) are unfavorable for hydrogen accommodation compared to αZr [114]. Conversely, the end members of the Zr$_2$(Fe,Ni) solid solution accommodate hydrogen readily, even compared to αZr. They propose that the presence of partially metallic Zr(Cr,Fe)$_2$ SPPs will aid the transport of hydrogen through the oxide, while Zr$_2$(Fe,Ni) SPPs are not helpful to hydrogen diffusion through the oxide, trapping the migrating hydrogen until these SPPs are dissolved or oxidized. These results do not support the model from Hatano et al. [60] based on Zr$_2$(Fe,Ni) SPPs acting as pathways for hydrogen diffusion.

From deuterium diffusion experiment and XANES analysis, Une et al. [115] proposed that the observed improvement of hydrogen absorption property with increasing iron contents in the alloys [59] would be due to the decreased diffusivity of hydrogen ions. Indeed, when trivalent Fe$^{3+}$ ions are dissolved substitutionally in ZrO$_2$, it changes the lattice defect structure. In addition to the iron dissolution effect on lattice structure, delayed oxidation of SPPs in the oxide layer would work to maintain a higher compressive stress state, impeding hydrogen diffusion.
According to them, this would explain the superior hydrogen absorption performance of alloys containing the SPPs with larger size and number density in their study.

Concerning the Zr-Nb alloys corroded in autoclave, Zr-2.5Nb and Zr-1.0Nb show much less hydrogen pick-up than Zircaloy-4 [116-118]. However, it seems that depending on the thermal treatments of the alloys, the hydrogen pick-up could increase [64] such that Zr-Nb aged alloy pick-up more hydrogen than quenched Zr-Nb alloy. The XANES analysis performed by Sakamoto et al. [74] shows that the Nb oxidation state increases from 0 to +5 as the distance from the oxide/metal interface increases as shown in Figure 1-13. The authors believe that these defects act mainly as acceptors and thus would generate oxygen vacancies by the substitutional dissolution of the lower valences of Nb$^{3+}$ and Nb$^{2+}$ in the bulk oxide layer, which would trap hydrogen and form a stable defect complex. The dissolution of the higher valence Nb$^{5+}$ restricted in the surface oxide region would promote the reduction of dissociated hydrogen ions at the oxide surface by the increased concentration of electrons [119].

![Figure 1-13](image)

Figure 1-13 Depths profiles of niobium oxidation states in zirconium oxide layer (corroded in steam at 400°C) reproduced from [74].
From the literature, it is also clear that the addition of nickel in zirconium as a single alloying element significantly increases the hydrogen pick-up fraction [2], but the role of Ni or Zr₂(Fe,Ni) precipitates, or indeed of any of the alloying elements on hydrogen pick-up fraction has not been clearly clarified yet.

Besides alloying element additions, the metallurgical state of the alloy also influences its hydrogen pickup. In the case of Zircaloy-4, alpha annealed material absorbs greatest amount of hydrogen while the beta-quenched material absorbs less amount of hydrogen [1]. The differences between different thermal treatments could be due to the intermetallic precipitates since a β quench could result in more alloying elements in super saturation relative to the matrix and to less coarse precipitates compared to a recrystallized state [120].

In conclusion, even very small additions of alloying elements have a significant impact on hydrogen pickup. It is generally believed that the presence of metallic precipitates in the oxide layer reduces hydrogen uptake by increasing oxide electronic conductivity and/or increasing the oxide compressive state. However, the influence of precipitate chemistry, size and volume fraction on hydrogen pickup is not well understood. On the other hand, alloying elements in solid solution may dope the oxide and affect the oxide electronic conductivity and electrical potential gradient across the oxide.

1.4. Objective of the study

In an effort to understand the hydrogen pickup mechanism, a systematic study of the alloy effect on hydrogen pickup is conducted, using advanced characterization techniques to rationalize precise measurements of hydrogen pickup. Since the external parameters do not vary significantly at operating conditions, this study will focus more on the influence of internal rather
than external parameters on hydrogen pickup. The overall structure of the thesis is depicted in Figure 1-14 and explained in the following.

In Chapter 2, the hydrogen pick-up fraction is accurately measured for a specially designed set of commercial and model alloys to investigate the effects of alloying elements, microstructure and corrosion kinetics on hydrogen uptake. Two different techniques to measure hydrogen concentrations were used: a destructive technique, Vacuum Hot Extraction (VHE), and a non-destructive one, Cold Neutron Prompt Gamma Activation Analysis (CNPGAA) [103]. The hydrogen pickup fraction results are rationalized to a general hypothesis on hydrogen pickup mechanism in Chapter 3. To assess that hypothesis, both experimental and modeling tools are needed.

According to this hypothesis, alloying elements (either in solid solution or in precipitates) would impact the hydrogen pick-up fraction. Because the mechanism whereby these alloying elements are incorporated into the oxide layer is critical to hydrogen pickup, the evolution of the oxidation state alloying elements when incorporated into the growing oxide layers of zirconium alloys is investigated using X-Ray Absorption Near-Edge Spectroscopy (XANES) using microbeam synchrotron radiation on cross sectional oxide samples. This study is the subject of Chapter 4.

Following the general hypothesis, the oxide electronic conductivity would be a critical parameter to control hydrogen pickup in zirconium alloys. Thus, in-situ electrochemical impedance spectroscopy (EIS) technique is developed to directly measure the oxide electronic conductivity on a set of samples archived at different exposure times for various alloys and the results are presented in Chapter 5.

Eventually, the physics behind the general hypothesis are verified in Chapter 6 using an oxidation model based on the diffusion of charged species across an oxide with a net current null everywhere in the oxide. To finish with, in Chapter 7, both the experimental and modeling results
are analyzed to check if they support the general hypothesis and the hydrogen pickup fraction results.

Figure 1-14 Overall thesis structure.
Chapter 2
Hydrogen pickup fraction characterization

This chapter reviews the experimental procedures to determine hydrogen content in zirconium alloys used in this study. Before explaining these experimental procedures, a detailed description of the zirconium alloys used in this study is provided. Then, the hydrogen pick-up fraction parameter is presented and the weight gain and hydrogen pickup results on various zirconium alloys are detailed and discussed.

2.1. Zirconium alloys studied

Alloys currently used in the nuclear industry such as Zircaloy-4 and ZIRLO were selected for this study along with Zr-2.5Nb, Zr-2.5Nb-0.5Cu, and three model alloys: pure Zr, Zr-0.5Cu and Zr-0.4Fe-0.2Cr to help understand the specific effect of alloying microstructure and composition on hydrogen pickup. All alloys were in the recrystallized state (RX) except for Zircaloy-4 tube which was tested in a cold-worked stress relieved state (CWSR). The full list of samples is shown in Table 2-1. Model alloys were investigated to understand the specific effect of alloying microstructure and composition on hydrogen pickup. The initial hydrogen concentrations in the alloys prior to autoclave testing were 10 to 15 wt·ppm.

The zirconium model alloy samples were processed in laboratory and are in the form of corrosion sheet coupons (25 mm x 20 mm x 0.8 mm) [39]. They were processed following the sequence detailed in [121]. The buttons were rolled at different temperatures depending on the desired final microstructure. The sand blasted and pickled hot rolled strip was then vacuum annealed, which was followed by two iterations of cold rolling and vacuum annealing to produce
a final strip in a fully recrystallized condition with a thickness of about 0.8 mm. The majority of the model alloys were processed with a final heat treatment at 580°C. This was required in order to minimize grain growth for commercially pure zirconium (sponge) and to maintain small precipitates in Zr-0.4Fe-0.2Cr (L) and Zr-0.5Cu alloys. A higher final heat treatment temperature of 720°C was used to grow larger precipitates in the Zr-0.4Fe-0.2Cr (H) alloy.

The grain structure of the resulting alloys revealed by etching was observed using polarized light microscopy in reflection mode (see Figure 2-1). The average grain size was determined to be approximately 10 µm, with predominantly equiaxed grains and a homogeneous microstructure, as would be expected from a recrystallizing heat treatment. The average diameter of the precipitates in Zr-0.4Fe-0.2Cr (L) alloy was previously determined by synchrotron X-Ray diffraction and is equal to 40 nm, whereas it is equal to 110 nm in Zr-0.4Fe-0.2Cr (H) alloy [39].

Table 2-1: Chemical composition, geometry, process temperature and origin of alloys used in this study [8].

<table>
<thead>
<tr>
<th>Alloy system</th>
<th>Alloy composition (wt%)</th>
<th>Sample geometry</th>
<th>Process temperature °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure Zr</td>
<td>Zr sponge</td>
<td>Sheet</td>
<td>580</td>
</tr>
<tr>
<td>Zr-Fe-Cr</td>
<td>Zr-0.4Fe-0.2Cr (L)</td>
<td>Sheet</td>
<td>(L): 580</td>
</tr>
<tr>
<td></td>
<td>Zr-0.4Fe-0.2Cr (H)</td>
<td></td>
<td>(H): 720</td>
</tr>
<tr>
<td>Zr-Cu</td>
<td>Zr-0.5Cu</td>
<td>Sheet</td>
<td>580</td>
</tr>
<tr>
<td>Zr-Nb</td>
<td>Zr-2.5Nb</td>
<td>Sheet and tube</td>
<td>580</td>
</tr>
<tr>
<td>Zr-Nb-Cu</td>
<td>Zr-2.5Nb-0.5Cu</td>
<td>Tube</td>
<td>580</td>
</tr>
<tr>
<td>ZIRLO</td>
<td>Zr-1.0Nb-1.0Sn-0.1Fe</td>
<td>Sheet and tube</td>
<td>580</td>
</tr>
<tr>
<td>Zircaloy-4</td>
<td>Zr-1.45Sn-0.2Fe-0.1Cr</td>
<td>Sheet and tube</td>
<td>580</td>
</tr>
</tbody>
</table>

The processing of the ZIRLO and Zircaloy-4 sheet material was similar to that used for the model alloys described above, featuring multiple iterations of cold rolling and annealing to final size. ZIRLO, Zircaloy-4, Zr-2.5Nb and Zr-2.5Nb-0.5Cu tube extrusions were processed in production facilities following the procedure in [122]. The production of Zircaloy-4 tubing from
an extrusion involved $\alpha$-annealing in vacuum prior to cold pilgering followed by tube reduction extrusions (TREXs). ZIRLO, Zr-2.5Nb and Zr-2.5Nb-0.5Cu extrusions were $\beta$-annealed, air cooled, conditioned to remove the native oxide film, and then pilgered to TREXs. All TREXs were $\alpha$-annealed to induce recrystallization of the material prior to further working. TREXs were reduced to final size tubing by an alternating sequence of cold pilgering and vacuum annealing. The same four-pass reduction schedule was utilized for all the chemistries. Each vacuum anneal was performed in the $\alpha$ range to recrystallize the tubing, with the exception of the final stress-relief anneal. Final conditioning of the tubes included straightening, pickling, polishing of the tube outside diameter using 400 grit silicon carbide belts, and grit blasting the inside diameter surface. After ultrasonic inspection, the tubes were cut to length and cleaned for fabrication into fuel rods.

The final microstructure of the alloys was studied by polarized light microscopy and scanning electron microscope (SEM) using secondary electron mode (Figure 2-1 to Figure 2-8) after polishing and etching of cross sectional samples using a 50mL $H_2O$/45mL $HNO_3$/5mL HF solution. Energy Dispersive Spectroscopy (EDS) was performed to confirm precipitate type.
Figure 2-1. Polarized light microscopy and scanning electron microscope micrographs of Zircaloy-4 sheet cross section with the following normal direction: a) longitudinal POL, b) transverse SEM and c) longitudinal SEM.

Figure 2-2. Polarized light microscopy and scanning electron microscope micrographs of Zircaloy-4 tube cross section with the following normal directions: a) longitudinal POL, b) transverse SEM and c) longitudinal SEM.
Figure 2-3. Polarized light microscopy and scanning electron microscope micrographs of ZIRLO sheet cross section with the following normal directions: a) longitudinal POL b) longitudinal SEM.
Figure 2-4. Polarized light microscopy and scanning electron microscope micrographs of ZIRLO tube cross section with the following normal directions: a) longitudinal POL, b) longitudinal SEM.
Figure 2-5. Polarized light microscopy and scanning electron microscope micrographs of Zr-2.5Nb tube cross section with the following normal directions: a) longitudinal POL, b) longitudinal SEM.
Figure 2-6. Polarized light microscopy and scanning electron microscope micrographs of Zr-2.5Nb-0.5Cu tube cross section with the following normal direction: a) longitudinal POL, b) transverse SEM and c) longitudinal SEM.

Figure 2-7. Polarized light microscopy micrograph of pure sponge zirconium cross section [8].
The etching reveals the precipitates (white dots in the SEM pictures) as well as the grain structure. The grains are better seen in Zircaloy-4 since the etching solution used was developed for that alloy. Nevertheless, the optical micrographs from the alloys show predominantly equiaxed grains and a homogeneous microstructure (Figure 2-1), as would be expected from a recrystallizing heat treatment, except for Zircaloy-4 tube in a cold work stress relieved state (Figure 2-2). ZIRLO and Zr-2.5Nb alloys show microstructure similar to that observed in Figure 2-1 with a higher precipitate volume fraction. The precipitates appear to be distributed homogeneously and are generally equiaxed except for the elongated precipitates observed in Zr-2.5Nb-05Cu and Zr-0.5Cu (Figure 2-6), which are parallel to the surface. The consistent presence of copper in these elongated precipitates has been confirmed by EDS.

By comparing Figure 2-4 and Figure 2-5, the size of the β-Nb particles in Zr-2.5Nb are similar to those in ZIRLO, however, the volume fractions of these precipitates are greater than the volume fractions of precipitates in ZIRLO [5]. From optical micrographs of Zr-0.4Fe-0.2Cr annealed at 580°C and 720°C (Figure 2-8), it is clear that the grain size of the Zr-0.4Fe-0.2Cr alloy annealed at 580°C is smaller than in the alloys heat treated at 720°C.
2.2. Corrosion procedure

All the alloys were corroded in 360°C pure water in a single 4-liter static autoclave in saturated pressure condition at 2708.6 psi (18.7 MPa) according to ASTM G2-88 [123] (Standard Test Method for Corrosion Testing of Products of Zirconium, Hafnium, and Their Alloys in Water at 680°F [360°C] or in Steam at 750°F [400°C]). Autoclave corrosion studies were conducted to simulate temperature and pressure conditions similar to those seen in nuclear reactors and thus form oxide scales on the alloys under those conditions. The 360°C water autoclave experiments do not exactly reproduce the PWR operating conditions (the mean coolant temperature is approximately 310°C at a pressure of 2250 psi [15.5 MPa]), but the behavior of the alloys in this environment correlates well with in-reactor behavior, i.e. alloys that behave well in this test normally behave well in-reactor.

These corrosion tests were performed at Westinghouse Electric Co. in Monroeville, PA. The autoclave was periodically opened to measure the sample weight gains as a function of exposure time and to archive specimens for subsequent measurement of hydrogen. The periodic opening of the autoclave helped maintain low dissolved hydrogen levels (less than 50 cc H₂/kg H₂O) in the autoclave throughout the experiment by refreshing the autoclave solution at the start of each corrosion interval. Hydrogen levels in water less than 25-50 cc of H₂/(kg of H₂O) should have no impact on the corrosion process [24].

2.3. Weight gain kinetics

The weight gains from the corrosion experiments are plotted as a function of exposure time for the different alloys in Figure 2-9. The weight gain measurements are also displayed in tables in Appendix A-I. The weight gains are the average weight gain from all the duplicate
(sister) samples at each corrosion interval. The standard deviation of the weight gain measurements was less than 0.5 mg/dm² for the production alloys (a) to (f). The production alloys show the Zircaloy-4 and ZIRLO corrosion behaviour featuring a transition, as has often been observed in zirconium alloys [28].

The weight gains of the four model alloys as function of exposure time are also plotted in Figure 2-9 from (g) to (j) (note the different exposure time scales). The two Zr-0.4Fe-0.2Cr alloys (i) and (j) do not show any transition during the exposure time used and their oxides are still protective after an exposure of 463 days. The corrosion data of Zr-0.5Cu (respectively pure Zr) are only shown in the protective regime in Figure 2-9 (g) and (h).
Figure 2-9. Weight gain as a function of exposure time for the following production alloys: a) Zircaloy-4 sheet, b) Zircaloy-4 tube, c) ZIRLO sheet, d) ZIRLO tube, e) Zr-2.5Nb, f) Zr-2.5Nb-0.5Cu (CONTINUED NEXT PAGE).
After 233 days Zr-0.5Cu alloy undergo corrosion breakaway (respectively 14 days for pure Zr) after which their oxide layers ceased to be protective, and the corrosion rate suddenly increases (not shown here). The loss of protectiveness of Zr-0.5Cu and pure Zr has been confirmed by SEM characterizations of the oxide layers. Figure 2-10 shows SEM micrographs of before (c) and after (a-b) the loss of protectiveness for pure Zr. Lateral and longitudinal cracks as well as significant preferential oxide growth in the zirconium metal (under the form of dendrites) have been observed [39]. However, before breakaway, the oxide layers do not show any cracks and are still adherent to the metal as seen in Figure 2-10.c.
As previously mentioned, it has been reported that the general oxidation kinetics follow a power law: $\delta = Kt^n$ [39]. By fitting the weight gain data to a power law, the exponent $n$ has been determined for the various zirconium alloys used in this study. The $R^2$ of the power law fit was kept above 0.999%. An example of this fit is displayed in Figure 2-11 and the values of $n$ are displayed in Table 2-2 for the other alloys. All the fits are plotted in Appendix A-II.

![Figure 2-10. SEM micrographs of pure Zr after a) and b) 69 days of exposure [8] and c) 14 days of exposure [124].](image)

The oxide thicknesses at the first transition $\delta_t$ for the production alloys were determined by extrapolation of the weight gain measurements ($1\mu m = 14.77mg/dm^2$) by fitting the pre-transition and the 1st transition regime to power laws. An example (ZIRLO sheet) is displayed in

![Figure 2-11. Power law fit of the pre-transition regime of ZIRLO sheet alloy. The grey area on the plot represents the error associated to the power law fit to enclose all experimental data points and is equal to ±5% in this case.](image)
Figure 2-12 and the oxide thicknesses at transition $\delta_t$ are displayed in Table 2-3 for the different alloys.

Table 2-2: Exponent $n$ from pre-transition (or pre-breakaway) power law fits of the different alloys [39].

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Exponent $n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure Zr</td>
<td>0.20</td>
</tr>
<tr>
<td>Zr-0.4Fe-0.2Cr (L)</td>
<td>0.21</td>
</tr>
<tr>
<td>Zr-0.4Fe-0.2Cr (H)</td>
<td>0.22</td>
</tr>
<tr>
<td>Zr-0.5Cu</td>
<td>0.17</td>
</tr>
<tr>
<td>Zr-2.5Nb</td>
<td>0.37</td>
</tr>
<tr>
<td>Zr-2.5Nb-0.5Cu</td>
<td>0.36</td>
</tr>
<tr>
<td>ZIRLO sheet</td>
<td>0.41</td>
</tr>
<tr>
<td>ZIRLO tube</td>
<td>0.37</td>
</tr>
<tr>
<td>Zircaloy-4 sheet</td>
<td>0.29</td>
</tr>
<tr>
<td>Zircaloy-4 tube</td>
<td>0.32</td>
</tr>
</tbody>
</table>

The extrapolation of the oxide thickness at the 2nd transition is of course less obvious because less samples were available at long exposure times, but it was possible to determine this transition for some of the alloys as seen in Table 2-3.

Table 2-3: Extrapolated oxide thickness at the 1st transition $\delta_t$ and 2nd transition for different alloys.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Oxide thickness at the 1st transition (µm) $\delta_t$</th>
<th>Oxide thickness at the 2nd transition (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr-2.5Nb</td>
<td>3.5</td>
<td></td>
</tr>
<tr>
<td>Zr-2.5Nb-0.5Cu</td>
<td>3.2</td>
<td></td>
</tr>
<tr>
<td>ZIRLO sheet</td>
<td>2.9</td>
<td>5.7</td>
</tr>
<tr>
<td>ZIRLO tube</td>
<td>3.1</td>
<td></td>
</tr>
<tr>
<td>Zircaloy-4 sheet</td>
<td>2.1</td>
<td>4.5</td>
</tr>
<tr>
<td>Zircaloy-4 tube</td>
<td>2.6</td>
<td>4.9</td>
</tr>
</tbody>
</table>
2.4. Hydrogen concentration measurements

Vacuum Hot Extraction (VHE) measurements were performed by LUVAK, Inc. in Boylston, MA. An NRC Model 917 apparatus [125] was used for VHE as described in detail in [103]. Although VHE technique is fast and reasonably accurate, it is also destructive. To measure the hydrogen content as a function of time, it is necessary to perform measurements on sister samples from the same alloy, which is a potential source of measurement dispersion. Duplicate measurements from the same coupon confirmed that the average measurement error is approximately ±10%, as confirmed by other studies [95, 126]. The total analyzed sample size was 8 mm x 8 mm for sheet coupons and 3 mm-long tube sections for tube coupons. The analyzed samples were made as large as possible to minimize any local area-to-area variations of hydrogen content which is another potential source of measurement dispersion.

In addition to the measurements of hydrogen in the archived samples by VHE, some additional samples were used for hydrogen measurements by Cold Neutron Prompt Gamma

Figure 2-12. Extrapolation of the weight gain at transition for the ZIRLO sheet alloy.
Activation Analysis (CNPGAA). Since this experiment measures hydrogen content non-destructively, these samples were returned to the autoclave for additional exposure followed by further CNPGAA measurements of hydrogen concentrations. This provided results on the evolution of hydrogen pickup fraction as a function of exposure time on a single sample.

CNPGAA measurements in zirconium alloys have been discussed in detail elsewhere [103, 106]. CNPGAA was performed at National Institute of Standards and Technology (NIST), Gaithersburg, MD, in one of the cold neutron beam lines on ZIRLO and Zircaloy-4 sheet samples. The background noise at the hydrogen gamma ray energy at this beamline is very low so that concentrations of hydrogen in zirconium alloys as low as 5 to 10 wt·ppm are detectable. The gamma-ray spectra were fit using two different programs: an algorithm for hand fitting of peaks (SUM) written at NIST [127] and the standard commercial peak search program Genie2000®.

The hydrogen content in wt·ppm measured as function of exposure time in days for the different alloys is plotted in Figure 2-13. The sample weight gains from which the hydrogen content is measured are also plotted on the same graph.

As can be inferred from the weight gains in Figure 2-13, the sister samples of a given alloy behave similarly, following the averaged weight gain curves plotted in Figure 2-9 except for the alloy Zr-0.4Fe-0.2Cr (L), which shows more scattered weight gains especially at long exposure times. It is possible that the reason for the data scatter is that the alloy is close to breakaway [8]. Another conclusion from these measurements is that CNPGAA gives reliable hydrogen content results (squares in Figure 2-13 (a) and (c), as detailed in [103].

The hydrogen content as function of exposure time can also be fitted. However, because no developed hydrogen pickup kinetics theory exist, it has been decided to fit the hydrogen content data using a polynomial of the lowest degree possible to best fit the data [128]. The hydrogen content measurements are also displayed in tables in Appendix A-III.
Figure 2-13. Hydrogen content and weight gain of sample as function of exposure time of a) Zircaloy-4 sheet, b) Zircaloy-4 tube, c) ZIRLO sheet, d) ZIRLO tube, e) Zr-2.5Nb, f) Zr-2.5Nb-0.5Cu (CONTINUED NEXT PAGE).
This polynomial has no physical significance but is only used to fit the data and carry out the hydrogen pickup fraction calculation. After trial and error, a 4th degree polynomial function was used for every alloy and transition regime as, a 3rd degree or lower polynomial does not reproduce either the hydrogen content variations as function of exposure time or $f_{H}$ measured experimentally, as detailed next. On the other hand, a 5th degree or higher polynomial does not significantly modify the fit and would rather induce unphysical variations of the hydrogen content.
as function of exposure time. An example of this fit is displayed in Figure 2-14 for ZIRLO sheet alloy. All the fits are plotted in Appendix A-IV.

![Figure 2-14](image)

Figure 2-14. Fit of the hydrogen pickup kinetics using a 4th polynomial function for the case of the ZIRLO sheet alloy in pre-transition regime. The gray area represents the error associated to the polynomial fit to enclose all experimental data points and is equal to ±10% in this case.

The hydrogen content at the 1st transition (see Table 2-3) for the production alloys were determined by extrapolation of the hydrogen content measurements by fitting the pre-transition and the 1st transition regimes to 4th degree polynomials. An example (ZIRLO sheet) is displayed in Figure 2-15. These fits were performed only on the production alloy data and not for the model alloys because of the lack of archived samples in the latter.
2.5. Total hydrogen pickup fraction

The total hydrogen pickup fraction $f_{H}^{t}$ is defined as the ratio of the hydrogen absorbed from the beginning of the corrosion test to the total amount of hydrogen generated by the corrosion reaction:

$$f_{H}^{t} = \frac{\Delta \tilde{f}_{H}^{p}}{\Delta \tilde{f}_{H}^{generated}}$$

The hydrogen pickup fraction of a sample was calculated from measurement of both weight gain and hydrogen content. The assumptions made for calculations of hydrogen pickup fraction are the following:

- The oxide formed during autoclave exposure did not spall, so that the measured weight gain was a valid measurement of the extent of oxide formation. This was confirmed by Figure 2-15. Extrapolation of the hydrogen content at transition in the case of ZIRLO sheet alloy. Figure 2-12 is also plotted on the same graph.

The hydrogen pickup fraction of a sample was calculated from measurement of both weight gain and hydrogen content. The assumptions made for calculations of hydrogen pickup fraction are the following:

- The oxide formed during autoclave exposure did not spall, so that the measured weight gain was a valid measurement of the extent of oxide formation. This was confirmed by
visual inspection of the specimens, and also by the fact that the oxide layer thickness
determined by SEM investigations corresponds well to the measured weight gain.

- The weight gain is assumed to be only due to oxygen and does not take into account the
  hydrogen uptake. This is a good assumption for low hydrogen pickup fraction but it
  should be kept in mind that the hydrogen uptake resulting from a theoretical hydrogen
  pickup fraction of 100% would account for 11.1% of the weight gain.

- Finally the hydrogen that enters the sample comes only from the hydrogen generated
during the corrosion reaction. This assumption is mostly valid in autoclave corrosion,
since no radiolysis of water occurs, in contrast to in-reactor conditions. Also, since the
autoclave was opened at least every 30 days, no significant build-up of hydrogen gas is
observed in the autoclave (the concentration was kept below 50 cc H₂/kg H₂O) so that
hydrogen evolved from one sample does not enter the other samples as confirmed in
[129]. At the early stages of corrosion when corrosion rates are higher and hydrogen gas
releases are more significant, the autoclave was opened more frequently.

According to these assumptions, the concentration (in wt·ppm) of hydrogen in the sample
$C_H$ is given by the following equation:

$$C_H = 10^6 \frac{m^i_H + m^c_H}{m^f_s}$$  \hspace{1cm} (2-2)

where $m^f_s$ is the mass of the sample at the time of the measurement, $m^i_H$ is the initial mass of
hydrogen in the sample and $m^c_H$ is the mass of hydrogen picked up by the sample during
corrosion. $m^i_H$ is equal to:

$$m^i_H = \frac{2N_A f^i_H}{N_A} M_H$$  \hspace{1cm} (2-3)

where $N_A$ is Avogadro’s number, $M_H$ the atomic mass of hydrogen and $N_O$ the number of oxygen
atoms absorbed during corrosion. $N_O$ is equal to:
\[ N_0 = \frac{(m_s^t - m_s^i)}{M_O} N_A \]  

(2-4)

where \(m_s^i\) the initial sample mass and \(M_O\) the atomic mass of the oxygen atom.

The initial mass of hydrogen (in grams) in the sample is given by \(m_H^i = C_H^i m_s^i \times 10^{-6}\) where \(C_H^i\) is the initial concentration of hydrogen in the sample in wt·ppm. If \(C_H^t\) is the concentration of hydrogen at the time of measurement in wt·ppm, \(f_H^t\) is equal to:

\[ f_H^t = \frac{10^{-6}(m_s^t C_H^t - m_s^i C_H^i)}{2 \left( \frac{m_s^t - m_s^i}{M_O} \right) M_H} \]  

(2-5)

Using error propagation formula, the total hydrogen pick-up fraction error is given by:

\[ \Delta f_H = f_H \sqrt{A + \frac{B + C}{D}} \]  

(2-6)

where:

\[ A = \frac{\Delta m_s^2 + \Delta m_s^i}{(m_s - m_s^i)^2} \]  

(2-7)

\[ B = (m_s C_H)^2 \left( \frac{\Delta m_s}{m_s} \right)^2 + \left( \frac{\Delta C_H}{C_H} \right)^2 \]  

(2-8)

\[ C = (m_s^i C_H^i)^2 \left( \frac{\Delta m_s}{m_s^i} \right)^2 + \left( \frac{\Delta C_H^i}{C_H^i} \right)^2 \]  

(2-9)

\[ D = (m_s C_H - m_s^i C_H^i)^2 \]  

(2-10)

The total hydrogen pickup fraction can be determined at given exposure times using the experimental data from archived samples, but also, continuously using the functions from the weight gain and hydrogen content fits. The hydrogen content fits were not carried out on the model alloys because of the sparseness of the data, so only the experimentally measured \(f_H^t\) are plotted for these alloys. The results of total hydrogen pickup fraction are plotted in Figure 2-16.
Firstly, the experimental $f_{H}^L$ is contained within the error bounds of the continuous $f_{H}^L$ determined from the weight gain and hydrogen content fits. Thus the fits appear to give reliable results in terms of total hydrogen pickup fraction.

Secondly, looking at the production alloys (a) to (f), a **common general trend, independent of the alloy can be observed**. At the very start of the corrosion process, $f_{H}^L$ increases markedly before reaching a plateau. Then, approximately halfway before transition, $f_{H}^L$ starts steadily increasing again up to transition and showing an apparent decrease just before the transition. This evolution repeats itself in the next transition regime, suggesting that the **hydrogen pickup kinetics follow the periodicity of the oxidation kinetics periodicity but with different behaviour** [39, 85].

Finally, it is noted that $f_{H}^L$ increases from one transition regime to the next, suggesting that although the protective oxide behaves similarly from one period to the next, the non-protective oxide present after the first transition affects the hydrogen pickup process. Although it is not expected that the $f_{H}^L$ will keep increasing indefinitely with successive periods it is not possible to determine the final steady state value because of the lack of archived samples at long exposure times.

It is emphasized that the full lines in Figure 2-16 are not the actual fit of the experimental $f_{H}^L$. They represent the $f_{H}^L$ **calculated from the hydrogen content and weight gain fits** in Figure 2-11 and Figure 2-15. These calculations could not be carried out on model alloys because of the lack of systematic archiving of samples.
Figure 2-16. Total hydrogen pickup fraction as function of exposure time of a) Zircaloy-4 sheet, b) Zircaloy-4 tube, c) ZIRLO sheet, d) ZIRLO tube, e) Zr-2.5Nb, f) Zr-2.5Nb-0.5Cu, g) Pure Zr (CONTINUED NEXT PAGE). The full lines are not the actual fit of the experimental $f_H$- They represent the $f_H$ calculated from the hydrogen content and weight gain fits in Figure 2-11 and Figure 2-15. These calculations could not be carried out on model alloys because of the lack of systematic archiving of samples.
Even though the data are more scattered, a similar $f_H^t$ evolution can be observed in the model alloys (g) to (j), at least for the Zr-0.4Fe-0.2Cr alloys. A marked increase in $f_H^t$ of Zr-0.4Fe-0.2Cr (L) alloy (see Figure 2-16 (i)) is observed. Comparing the total hydrogen pickup fraction of different alloys using Figure 2-13 is not an easy task since all the alloys have different oxidation kinetics.

Thus, it is useful to plot the results in a manner that allows easier comparison of $f_H^t$ of different alloys with similar oxide thickness, but different kinetics. The hydrogen contents (in mg/dm$^2$) of zirconium alloys are plotted in Figure 2-17 to Figure 2-20 as function of weight gain (the oxide thickness is also indicated). An expanded view of low weight gain results is provided in Figure 2-17 and Figure 2-18. Results obtained with CNPGAA are indicated by a star. It is
interesting to note that a constant hydrogen pickup fraction during corrosion would mean that in these plots the points would follow straight lines, which is clearly not the case. The dashed lines represent the hydrogen content as function of weight gain for constant values of $f_H^t$ of 10%, 20%, 30% and 40%. Plotting the results in this manner allows comparison of the pickup fraction of different alloys with the same oxide thickness, but different kinetics. **The results clearly show that the total hydrogen pickup fraction changes from alloy to alloy, and for a given alloy increases with increasing exposure time.**

Figure 2-17 shows that the $f_H^t$ of pure Zr at 1µm (before breakaway) is approximately equal to 18%. This pickup fraction is higher than that of any other alloys in the protective regime before the transition or breakaway, except Zr-0.5Cu (see Figure 2-19). In the pre-transition regime Zircaloy-4 exhibits a much lower $f_H^t$ (~8%) than pure Zr, and Zircaloy-4 reaches $f_H^t = 18\%$ only after growing an oxide of 5.5µm. These observations suggest that the presence of alloying elements generally reduces hydrogen pickup. In the case of Zircaloy 4 this effect is likely ascribed to precipitates since Sn is thought to have limited effect on hydrogen pickup [62]. In Figure 2-19, for an oxide thickness of approximately 3µm, the $f_H^t$ for Zr-0.5Cu is equal to 25% compared to 15% for Zr-2.5Nb-0.5Cu and 5% for Zr-2.5Nb. **It appears that the addition of Cu in zirconium alloys increases $f_H^t$, whereas Nb addition decreases it.** The $f_H^t$ of Zircaloy-4 and ZIRLO lies between the $f_H^t$ of Zr-2.5Nb and the $f_H^t$ of Zr-2.5Nb-0.5Cu, with a constantly lower $f_H^t$ for ZIRLO compared to that of Zircaloy-4 at a given weight gain.
Figure 2-17. Hydrogen content (in mg/dm$^2$) as a function of weight gain (and oxide thickness) for the Zircaloy-4 sheet and tube. The straight dashed lines correspond to constant total hydrogen pickup fraction of 10%, 20% and 30%. An expanded view at early exposure time is displayed. Results obtained with CNPGAA are marked by a star on the upper left of the symbol.

Figure 2-18. Hydrogen content (in mg/dm$^2$) as a function of weight gain (and oxide thickness) for the ZIRLO sheet and tube. The straight dashed lines correspond to constant total hydrogen pickup fraction of 5%, 10% and 20%. An expanded view at early exposure time is displayed. Results obtained with CNPGAA are marked by a star on the upper left of the symbol.
Figure 2-19. Hydrogen content (in mg/dm$^2$) as a function of weight gain (and oxide thickness) for the Zr-0.5Cu, Zr-2.5Nb-0.5Cu and Zr-2.5Nb alloys. The straight dashed lines correspond to constant total hydrogen pickup fraction of 10%, 20%, 30% and 40%.

Figure 2-20. Hydrogen content (in mg/dm$^2$) as a function of weight gain (and oxide thickness) for the Zr-0.4Fe-0.2Cr (L) and Zr-0.4Fe-0.2Cr (H) alloys. The straight dashed lines correspond to constant total hydrogen pickup fraction of 10%, 20% and 30%. Results obtained with CNPGAA are marked by a star on the upper left of the symbol.
It also appears that the $f_{H}^{T}$ increases with oxide thickness (or exposure time). At the end of the corrosion test (after 375 days of corrosion), there is some indication that the $f_{H}^{T}$ of Zircaloy-4 and ZIRLO may start to stabilize around 25% for Zircaloy-4 and 19% for ZIRLO. At the end of the corrosion test, Zr-2.5Nb alloy shows the lowest $f_{H}^{T}$ (around 15%) whereas Zr-2.5Nb-0.5Cu shows the highest $f_{H}^{T}$ (around 35%). The $f_{H}^{T}$ increases significantly from the 1$^{st}$ transition to the 2$^{nd}$, and, to a lesser extent, from the 2$^{nd}$ to the 3$^{rd}$.

The microstructure of the alloy also affects $f_{H}^{T}$. In Figure 2-20, the hydrogen content as function of weight gain is plotted for the Zr-0.4Fe-0.2Cr model alloys. Before reaching a thickness of approximately 3µm (~44 mg/dm$^2$), the alloys show a similar $f_{H}^{T}$ (between 10% and 15%). Interestingly after that oxide thickness and even though the corrosion kinetics are unchanged, an increase in $f_{H}^{T}$ is observed in both alloys, and the increase is more marked in the alloy with smaller precipitates. At the end of the corrosion test, even though both alloys have approximately the same oxide thickness, the $f_{H}^{T}$ of Zr-0.4Fe-0.2Cr (H) is equal to 20% whereas the $f_{H}^{T}$ of Zr-0.4Fe-0.2Cr (L) is above 30%. SEM micrographs of the oxide of one sample of each alloy with similar oxide thickness (δ~3.3µm) are shown in Figure 2-21 (a) and (b). The oxide scales have similar appearance and no difference in oxide crack density is noticed.

This suggests that for Zr-0.4Fe-0.2Cr alloy type, for a given volume fraction and corrosion rate, alloys with larger precipitates tend to pick up less hydrogen than alloys with smaller precipitates.

Not only the precipitate size, but also the general microstructure can affect the results. It is observed that the tube geometry delays the oxide transition compared to the sheet geometry, probably because of a better stress accommodation. However, the geometry or the metallurgical state of the alloy (recrystallized or not) do not seem to affect the hydrogen pickup fraction.
2.6. "Instantaneous" hydrogen pickup fraction

It is clear from Figure 2-17 to Figure 2-20 that hydrogen pickup fraction varies within a transition regime. Accordingly, the instantaneous hydrogen pickup fraction was calculated in order to more precisely characterize this evolution as function of corrosion kinetics. The \textit{instantaneous hydrogen pickup fraction} $f_H^t$ is defined as the ratio of the hydrogen absorbed from a time $t$ to a time $t + \Delta t$ to the total amount of hydrogen generated by the corrosion reaction during the same time interval.
Mathematically it is the time derivative of the hydrogen absorbed divided by the time derivative of the amount of hydrogen generated:

\[ f_H^i = \frac{dH_{absorbed}}{dt} \left/ \frac{dH_{generated}}{dt} \right. \sim \lim_{\Delta t \to 0} \frac{\Delta t^{+} \Delta t H_{absorbed}}{\Delta t^{+} \Delta t H_{generated}} \quad (2-11) \]

We can notice that \( f_H^i \) is actually proportional to the derivative of the hydrogen absorbed as a function of the oxide thickness (and not as a function of time):

\[ f_H^i \propto \frac{dH_{absorbed}}{d\delta} \quad (2-12) \]

*For clarity it is emphasized that \( f_H^i \) is not the time derivative of \( f_H^i \): \( f_H^i \neq df_H^i / dt \), but it does reflect the hydrogen pickup fraction over a smaller time increment rather than the total time as in \( f_H^i \). Also it is emphasized that throughout this study, the term instantaneous is defined on a time increment (or an oxide thickness increment) and is not really instantaneous but depends on the defined increment. The mathematical relationship between \( f_H^i \) and \( f_H^i \) is displayed in Appendix A-V to verify the coherency of these derivations.

The instantaneous pickup fraction \( f_H^i \) is given by:

\[ f_H^i = \frac{10^{-6} (m_s^{t+\Delta t} C_H^{t+\Delta t} - m_s^{t} C_H^{t})}{2 \left( m_s^{t+\Delta t} - m_s^{t} \right) M_H} M_H \quad (2-13) \]
Figure 2-22. Instantaneous hydrogen pickup fraction from the fit (plain line), of the 1st set of sister samples (black circles), of the 2nd set of sister samples (open circles) of a) Zircaloy-4 sheet, b) Zircaloy-4 tube, c) ZIRLO sheet (CONTINUED NEXT PAGE)
Figure 2-22. Instantaneous hydrogen pickup fraction from the fit (plain line), of the 1st set of sister samples (black circles), of the 2nd set of sister samples (open circles) of a) Zircaloy-4 sheet, b) Zircaloy-4 tube, c) ZIRLO sheet, d) ZIRLO tube, e) Zr-2.5Nb, f) Zr-2.5Nb-0.5Cu. The data points corresponding to experimental data are at the middle of the time increment. The full lines are not the actual fit of the experimental $f_H^i$. They represent the $f_H^i$ calculated from the hydrogen content and weight gain fits in Figure 2-11 and Figure 2-15.
$f^i_H$ can be approximated from experimental data either by VHE on sister samples or by CNPGAA on a given sample. These calculations have only been performed on the production alloys since the model alloys have not been consistently archived at regular time intervals. Regarding VHE measurements, the time steps between two sister sample hydrogen content measurements have not been kept constant throughout the experiment. Two sets of sister samples were used and their time intervals are displayed in Table 2-4. $f^i_H$ can be calculated from the weight gain and hydrogen content fits (see Figure 2-11 and Figure 2-14). The results are displayed in Figure 2-22. Once again it is emphasized that the full lines in Figure 2-16 are not the actual fit of the experimental $f^i_H$. They represent the $f^i_H$ calculated from the hydrogen content and weight gain fits in Figure 2-11 and Figure 2-15. These calculations could not be carried out on model alloys because of the lack of systematic archiving of samples.

Table 2-4: Time intervals between two VHE measurements and archiving of sister samples.

<table>
<thead>
<tr>
<th>1st set of sister samples</th>
<th>2nd set of sister samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>0→19 days</td>
<td>0→30 days</td>
</tr>
<tr>
<td>19→45 days</td>
<td>30→60 days</td>
</tr>
<tr>
<td>45→75 days</td>
<td>60→90 days</td>
</tr>
<tr>
<td>75→105 days</td>
<td>90→120 days</td>
</tr>
<tr>
<td>105→135 days</td>
<td>120→150 days</td>
</tr>
<tr>
<td>135→165 days</td>
<td>150→210 days</td>
</tr>
<tr>
<td>165→225 days</td>
<td>210→240 days</td>
</tr>
<tr>
<td>225→255 days</td>
<td>240→270 days</td>
</tr>
<tr>
<td>225→375 days</td>
<td>270→360 days</td>
</tr>
</tbody>
</table>

The large error bars in $f^i_H$ of sister samples come from the small $\Delta t$ and from errors from the VHE measurements, especially when the corrosion rate is low. However, a general trend can be clearly observed in all these plots. Even though the alloys exhibit different corrosion kinetics they show a similar $f^i_H$ evolution. It is quite clear that $f^i_H$ is not constant with exposure time.
would be expected since $f^i_{H}$ is not constant. At first, when the corrosion rate is high, $f^i_{H}$ is low (around 5% in the pre-transition regime for all the alloys). Then, the corrosion rate slows down, $f^i_{H}$ increases significantly. *This steep increase in $f^i_{H}$ is observed for every alloy.* $f^i_{H}$ keeps on increasing until the sample reaches transition. Just before transition, the $f^i_{H}$ calculated from the fits appear to drop significantly for all the alloys. It is not clear if this is due to real physical phenomena or is due to the errors associated to the fitting functions used. After the 1st transition, the corrosion rate increases again and $f^i_{H}$ returns to the low values observed at the beginning. Because the derivatives of the weight gain and hydrogen content fits are not continuous at transition, the derived instantaneous hydrogen pickup fraction is also not continuous at transition. Then *the process repeats itself in the 2nd transition regime and so on, following the periodicity of the oxidation kinetics.*

In order to evaluate the possible effect of different hydrogen pickup behaviour among sister samples, CNPGAA has been used on two given Zircaloy-4 sheet and ZIRLO sheet samples at different exposure times. These single samples have had their hydrogen content measured at different exposure times by CNPGAA. This was possible because CNPGAA is a precise non-destructive technique to evaluate hydrogen content. The results are plotted in Figure 2-23. $f^i_{H}$ determined by the fit of weight gain and hydrogen content measured by VHE on sister samples is also plotted for comparison (see Figure 2-22). One can conclude that the $f^i_{H}$ on a given sample follow the same pattern as seen on sister samples in Figure 2-22, *confirming that the general experimental conclusions on hydrogen pickup fraction evolution drawn from Figure 2-22 are valid.*

To conclude, it is interesting to calculate the hydrogen uptake of a given sample in wt-ppm per day. Indeed, since $f^i_{H}$ increases as the oxidation rate (proportional to $\Delta^t H_{generated}$) slows down, it could be argued that the overall hydrogen uptake per day ($\Delta^t H_{absorbed}$) might be
a constant (see eq.2-1). The hydrogen uptake in wt·ppm per day is plotted for two given ZIRLO sheet samples in Figure 2-24.

![Graphs showing hydrogen pickup fraction](image)

**Figure 2-23.** Instantaneous hydrogen pickup fraction calculated using CNPGAA as function of exposure time for a) two given Zircaloy-4 sheet and b) two given ZIRLO sheet samples. The “instantaneous” hydrogen pickup fraction from fits plotted in Figure 2-18 are also plotted for comparison and the transitions are also indicated. The data points corresponding to experimental data are positioned at the middle of the time increment. The full lines are not the actual fit of the points in the figure. They represent the calculation from the hydrogen content and weight gain fits in Figure 2-11 and Figure 2-15.
One can directly conclude from Figure 2-24 that \textit{the hydrogen uptake rate is not a constant of exposure time}, but rather follows the variations observed in the instantaneous hydrogen pickup fraction. This makes sense since, for a given transition regime, the oxidation rate is a monotonous function of exposure time, and thus the observed variations in instantaneous hydrogen pickup fraction are governed by similar variations in hydrogen uptake rate. These variations being measured on a given sample, they do not result from data scattering in sister samples and thus give direct and meaningful indications on the hydrogen pickup mechanism of zirconium alloys.

Figure 2-24. Hydrogen uptake rate in wt-ppm per day and weight gain as function of exposure time for two given ZIRLO sheet samples. The hydrogen uptake rates averaged on 20 days determined from fits are also plotted for comparison and the transitions are also indicated. The hydrogen uptake rate data points corresponding to experimental data are positioned at the middle of the time increment. The full line is not the actual fit of the points in the figure. It represents the \textit{calculation from the hydrogen content and weight gain fits} in Figure 2-11 and Figure 2-15.
2.7. Conclusions on hydrogen pickup fraction characterization

- Zirconium alloy oxidation kinetics are sub-parabolic ranging from quadratic and cubic for Zr-Cu and Zircaloys to closer to parabolic for Nb containing alloys.

- Hydrogen pickup fraction varies as function of exposure time and presents a common trend to every zirconium alloys (see Figure 2-22 and Figure 2-16):
  - At the very start of the corrosion process, \( f_H^t \) increases markedly.
  - Between 40\% and 70\% of \( \delta_t \), \( f_H^t \) remains constant, reaching a plateau.
  - Then, approximately at 70\% of \( \delta_t \), \( f_H^t \) starts to steadily increase again up to transition. It is not clear if \( f_H^t \) decreases or not before transition point.

- The hydrogen uptake rate is not constant with exposure time and thus \( f_H^t \) variations are directly linked to the corrosion mechanism.

- Hydrogen pickup fraction varies from alloy to alloy.
At a given oxide thickness, Cu additions increases $f_H^t$ whereas Nb additions decreases it.

The presence of precipitates appear to decrease $f_H^t$, and for a given precipitate volume fraction, the presence of coarser precipitates reduces $f_H^t$.

The sample shape (tube or sheet) does not influence the hydrogen pickup but does affect the corrosion rate, tube geometry delaying the transition.

Metallurgical state of the alloy seems to have no effect on the hydrogen pickup mechanism.

Hydrogen pickup fraction evolution is periodic, following the oxidation periodicity but with a different time dependence. $f_H^t$ increases from a transition regime to the next, at least up to the 3\textsuperscript{rd} transition.
Chapter 3

Discussion and hypothesis on hydrogen pickup mechanism

This chapter presents a summary of the results on hydrogen pickup fraction and, after discussion, how they compare with other results in the literature. Then, these results are rationalized into a hypothesis for a general hydrogen pickup mechanism. Finally, this hypothesis is confronted to other existing hypotheses and the experiments chosen in the study to test the hypotheses are briefly presented.

3.1. Summary of hydrogen pickup fraction results

The results detailed in Chapter 2 are summarized and discussed in this section.

3.1.1. Oxidation kinetics

The different alloys in this study present a range of sub-parabolic kinetics from $n \sim 0.2$ for Zr-0.5Cu to $n \sim 0.4$ for ZIRLO sheet (see Table 2-2). Similar variations have been observed in the literature [38]. It is important to notice that Zr-Nb alloys are generally very close to parabolic kinetics [39, 118] whereas Zircalloys are closer to cubic or quadratic [29, 79, 130, 131]. In theory, if diffusion of species is the rate limiting step of the corrosion process (surface reactions are at equilibrium), there is only one possibility to account for sub-parabolic kinetics for thick oxide films: an oxide property related to diffusion of species across the oxide varies with time, increasing the resistance to transport. This variation can either be related to (a) an alteration of one of the diffusion routes during the corrosion process or (b) to the oxidation mechanism by
itself. Several hypotheses to tentatively explain zirconium sub-parabolic kinetics in relation to (a) have been proposed in the literature:

- The oxide grain size progressively increases with time, increasing the resistance to oxygen transport [37]. Even though the zirconium oxide grain size does indeed evolve with time from small tetragonal equiaxed grains to larger monoclinic columnar grains [28], no significant differences in oxide grain size and microstructure have been noticed between alloys with different oxidation kinetics despite many TEM studies.

- There are barriers for the oxygen diffusion that develop in the oxide during oxide growth such as pores or cracks randomly distributed inside the oxide layer. The gradual evolution of crack density reported by Ni et al [90] might indeed be related to the theory of diffusion through imperfect lattices [79, 132] predicting non parabolic kinetics. It is supposed that cracks in the oxide parallel to the interfaces would actually act as resistances to oxygen transport and the departure from the parabolic law would be accounted for by the existence of these diffusion barriers in the layer. If the density of cracks increases linearly with thickness, then cubic kinetics are recovered. However the crack density evolution observed experimentally does not correlate with the oxidation kinetics [92]. Also, the extended microanalysis observations of cracks in oxide layers grown on zirconium alloys with different oxidation kinetics cannot discriminate the alloys.

- The effect of a gradient of compressive stresses in the oxide layer has been one of the hypotheses presented in the literature to account for sub-parabolic kinetics [78, 133, 134]. According to the authors, the oxidation kinetics for oxides which accumulate compressive stress during growth would be lower than parabolic because of changes in migration energy. However, this model is contradicted by Fromhold
[36, 135], who still predicts parabolic kinetics. Also, to fit experimental data with their theory, the authors suppose an oxygen sub-stoichiometry at the oxide/metal interface of ZrO$_{1.96}$ [20], a value rather high compared to thermodynamic studies [7] and which does not convey to Atom Probe Tomography measurements [91]. Also the amount of energy that can be stored in the oxide lattice would only provide very small changes in defect migration energy (less than 0.1eV) as detailed in Appendix B.

- Since alloys with very small differences in alloying contents show wide variations in oxidation kinetics, there has to be an effect of alloying elements on the corrosion mechanism. It has been proposed that the \textit{aliovalent ions with different charge states and ionic radius} than Zr$^{4+}$ perturb the defect population (especially oxygen vacancy densities) and would be responsible for altering oxygen anion migration [57]. However, no oxidation theory correlating sub-parabolic kinetics to defect population or aliovalent ions density has been developed so far.

All former hypotheses are based on a corrosion mechanism controlled by oxygen anion transport (anodic current) and alteration of the oxygen anion transport as the oxide grows to tentatively explain sub-parabolic kinetics. Whereas this has to be proven [26, 41, 43, 48, 49, 52], none of these hypotheses or models deal with the predominant charge state of the oxygen vacancy (or oxygen anion) and thus takes into account the electric field across the oxide and the necessary coupled electron current (cathodic current) to balance the charge. Indeed, despite many experimental efforts, the existence of an oxygen concentration gradient across the oxide acting as a primary driving force for oxygen diffusion and oxide growth has never been reported in the literature, even though the protective oxide color would suggest the presence of a gradient. \textit{Thus it seems reasonable that in order to grow micrometer scale oxides, the effect of charges and electric field has to be considered} [136, 137]. Few experimental studies have actually
concentrated their efforts on the electron transport and on the resistance to electronic transport because measuring the potential developed across the oxide film during oxidation without affecting the oxidation reaction is not easy [138]:

- Attempts to image the sites of electronic conduction suggested that this process would be localized at second phase particles incorporated into the oxide [53]. Thus, it has been proposed that the *conduction is mainly localized at intermetallic particles* in Zircaloy type alloys. Thus, alteration of precipitate chemistry as function of exposure time observed with TEM [67, 139, 140] might lead to sub-parabolic kinetics as it is frequently observed in Zircaloy type alloys [85, 141].

- **Alloying elements in solid solution** also affect the electron transport via localized energy levels in the zirconia band gap [58] and any alteration of the density of aliovalent ions in the oxide would result in non-parabolic kinetics.

These hypotheses are all related to (a). But, **space charge theory** can more readily explain sub-parabolic kinetics [81] without assuming alteration of any diffusion route as function of exposure time and is thus related to (b). The sub-parabolic kinetics would be due to the oxidation mechanism itself rather than to changes in oxide microstructure and/or microchemistry properties as function of exposure time. Very few studies have attempted to apply this theory to zirconium oxidation [46, 80], even though their results are convincing. However, **this general theory has to be rationalized to explain different oxidation kinetics observed for different alloys** with small differences in alloying element contents.

As a conclusion to this section, many hypotheses exist that can explain the variations in oxidation kinetics between alloys as reported in Table 3-1. But, taken alone, **none can account for the magnitude of the effects and the ensemble of the experimental observations**.
3.1.2. **Hydrogen pickup fraction and relation to oxidation kinetics**

One of the main conclusions of Chapter 2 is that *hydrogen pickup fraction is not constant*. We try to correlate its variations with oxidation kinetics. Similar observations have been reported by Harada et al. [95]. A $f_H^i$ evolution common to every alloy has been observed: at first a steep increase in $f_H^i$ is observed, then after approximately 40% of the thickness of the oxide at transition ($\delta_t$) has grown, $f_H^i$ remains constant before steadily increasing again after the oxide thickness has reached approximately 70% of $\delta_t$. A typical $f_H^i$ evolution is plotted in Figure 3-1.

General evolution of the total hydrogen pickup fraction as function of oxide thickness relative to

<table>
<thead>
<tr>
<th>Diffusion of charged species control the oxidation kinetics</th>
<th>Grain size evolution [37]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxide microchemistry and/or microstructure change with time</td>
<td>Gradient of compressive stress [78, 133, 134]</td>
</tr>
<tr>
<td></td>
<td>Crack and/or pores evolution [79, 132]</td>
</tr>
<tr>
<td></td>
<td>Aliovalent ions change oxygen vacancy density [57]</td>
</tr>
<tr>
<td></td>
<td>Oxygen transport control oxidation kinetics</td>
</tr>
<tr>
<td></td>
<td>Evolution of precipitate chemistry [67, 139, 140]</td>
</tr>
<tr>
<td></td>
<td>Localized energy states in the band gap induced by aliovalent ions [58]</td>
</tr>
<tr>
<td>No change in oxide microchemistry and/or microstructure</td>
<td>Space charge theory [81]</td>
</tr>
</tbody>
</table>
δ₁ in a transition regime. Thus the hydrogen pickup mechanism is linked to the corrosion mechanism as evidenced by similar periodicity even though hydrogen pickup kinetics does not follow oxidation kinetics.

![Diagram](image)

Figure 3-1. General evolution of the total hydrogen pickup fraction as function of oxide thickness relative to δ₁ in a transition regime.

It is interesting to determine if there is a correlation between $f_{H}^{δ}$ and oxidation kinetics for different alloys that would suggest a common oxidation and hydrogen pickup mechanism. To compare the different alloys together, since $f_{H}^{δ}$ varies within the protective regime and since δ₁ also varies between alloys, the value of $f_{H}^{δ}$ in the plateau region (see Figure 3-1) has been used for comparison. This value is plotted as function of the parameter $n$ in the power law fit of the weight gain curve (see Figure 2-11 and Table 2-2) in Figure 3-2.
A general trend is observed in Figure 3-2. An inverse relationship between the oxidation kinetics and \( f_H^I \) is observed: the lower the \( n \), the higher the \( f_H^I \). It is observed that the Zr-Fe-Cr and Zircaloy type alloys exhibit quadratic to cubic behaviour and higher \( f_H^I \) compared to the Nb alloys, at the end of the spectrum, which exhibit close to parabolic kinetics (\( n \sim 0.4 \)) and the lowest \( f_H^I \). These results definitely show that the oxidation kinetics variations between alloys are linked to the variations of \( f_H^I \), which indicates that the hydrogen pickup mechanism is linked to the corrosion kinetics: the more the oxidation kinetics tends towards parabolic the lower the hydrogen pickup fraction. This is also in accordance with results reported on binary Zr-Fe alloys [142] and on Zr-Sn-Fe-Cr alloys [143] and with the overall lower hydrogen pickup fraction of Nb containing alloys [144]. A scheme to summarize the influence of the alloying elements on oxidation kinetics and hydrogen pickup is presented in Figure 3-3.
3.1.3. Influence of precipitates and metallurgy on hydrogen pickup

One of the conclusions of Chapter 2 and Figure 3-2, is that $f_H^i$ is also dependent on the microstructure of zirconium alloys. The presence of $\text{Zr(Fe,Cr)}_2$ precipitates appears to reduce $f_H^i$, compared to pure Zr. It is believed that a material with a homogeneous distribution of precipitates has a higher oxide electronic conductivity compared to pure Zr. Indeed, TEM observations [28, 67] and $\mu$XANES experiments [145] have shown that Fe remains metallic (both in solid solution, with possible segregation at grain boundaries [146], and in precipitates) when incorporated into the zirconium oxide layer. Theoretical studies have also supported that $\text{Zr(Fe,Cr)}_2$ precipitates remain metallic in the oxide layer up to a certain oxide depth [65]. Metallic precipitates would likely enhance the electronic conductivity of the oxide layer, which would in turn reduce the hydrogen pickup. This argument assumes that the $\text{ZrO}_2$ which forms between the precipitates is also a relatively good electron conductor due to doping effects from the nearby particles since precipitates are not actually in contact. The differences in corrosion kinetics and $f_H^i$ observed in

![Figure 3-3. Scheme of the influence of the alloying elements on oxidation kinetics and hydrogen pickup fraction.](image-url)
Figure 3-2 for pure Zr and Zr-0.4Fe-0.2Cr alloys with different precipitate sizes but similar precipitate volume fraction might thus be related to SPP’s distribution.

Hatano et al observed an opposite effect of precipitate size on hydrogen pickup but their study does not provide enough oxidation kinetics data and microstructure information to be totally conclusive [96]. On the other hand, electrochemical measurements [55] have shown that Zircaloy-4 with bigger precipitates (~400 nm diameter) has a lower oxide electronic resistivity than Zircaloy-4 with smaller precipitates (~130 nm diameter), which according to the authors resulted in smaller \( f_{\text{H}} \). Even though the precipitate sizes are different in our study, this result tends to confirm our observations. However, since the heat treatment temperature of Zr-0.4Fe-0.2Cr model alloys with large and small precipitates was different, other factors besides SPP size such as the concentrations of alloying elements in the matrix, are likely different. The concentrations of alloying elements in solid solution were not quantified in this study but could also impact \( f_{\text{H}} \).

### 3.1.4. Periodicity of hydrogen pickup kinetics

The last conclusion from Chapter 2 is that the hydrogen kinetics is periodic following the periodicity of oxidation kinetics. This suggests once more that the hydrogen and oxygen uptake mechanisms are part of one main corrosion mechanism. However, it is observed that \( f_{\text{H}} \) increases from a transition regime to the next, at least up to the 3rd transition. Since many microanalysis studies have shown that the oxide microstructure is periodic [85, 141, 147], it is probable that one of the boundary conditions for oxidizing species transport changes after transition. One possibility is that the presence of the outer porous oxide changes the boundary condition at the outer limit of the protective oxide. Previous studies have indicated that hydrogen overpressure increases hydrogen pick-up in zirconium alloys [97, 148]. Following the hypothesis
made by Beie et al.[46], in the pre-transition regime the cathodic site is directly in contact with water, so that the hydrogen pressures at the cathodic site and in the water are equal. However, when a non-protective oxide layer is present on the top of the growing protective oxide, the hydrogen evolved at the cathodic site has to diffuse through these layers to finally reach the water. As a result a hydrogen pressure gradient will be established across the non-protective oxide layers. This would cause a hydrogen overpressure at the hydrogen evolution site to build up leading to an increase in proton concentration at this location. A higher concentration of protons at the interface could lead to an increase in hydrogen pick-up fraction.

3.2. Hydrogen pickup mechanism hypothesis

In light of these discussions, a hydrogen pick-up mechanism based on the oxide electronic conductivity variations between alloys and as function of exposure time is proposed. The mechanism should account for both oxidation kinetics and \( f_H^t \) at the same time! It is proposed that the electrochemical potential gradient over the oxide layer, mainly governed by the oxide electrical resistance, acts as driving force for \( H^+ \) absorption in the oxide: higher oxide resistivity would result in greater electrical potential across the oxide lowering the activation energy of proton absorption at the cathodic site, increasing hydrogen pickup fraction. By the hydrogen absorption effect, the magnitude of the electrical potential is in turn reduced, so that the variations affected by the electrical potential are in a direction to decrease the rate of change in the potential. Therefore, a stable situation is reached in which the hydrogen uptake produces no further significant changes in the field. Thus, the variations in \( f_H^t \) would result from the need to balance charge during the corrosion reaction, such that the pickup of hydrogen increases when the electrochemical potential gradient (the driving force) across the oxide increases. To
rationalize the sub-parabolic kinetics and the observed variation in $f_H^e$ in a common oxidation mechanism, two hypotheses are proposed:

1. **The oxide electronic conductivity decreases as function of exposure time in a transition regime** (alteration of electron transport, related to (a)) leading to sub-parabolic kinetics and an increase in the electrochemical potential gradient over the oxide layer and thus an increase in hydrogen pickup. This decrease in electronic conductivity would be more significant in Zircaloy type alloys (closer to cubic, higher $f_H^e$) than in ZrNb alloys (closer to parabolic, lower $f_H^e$).

2. Sub-parabolic kinetics are due to **space charge accumulating in the oxide**. The space charge accumulation in the oxide as the oxide grows would result in an increase of hydrogen pickup. Zircaloy type alloys would not accommodate space charge as easily as ZrNb alloys and thus would have a higher tendency to pick up hydrogen.

### 3.3. Experiments and modeling to verify the hypotheses

In both cases oxide electronic conductivity and alloying elements either in precipitates or in solid solution should play key roles in the corrosion mechanism. It is thus of interest to develop experimental techniques to characterize their evolutions as function of exposure time and oxide depth and also the differences between alloys.

As detailed in the previous chapter, precipitate chemistry evolves as function of oxide depth and possibly as a function of exposure time. Most precipitates remain metallic when embedded in the oxide up to a certain distance from the oxide/metal interface where they start oxidizing. This delayed oxidation modifies the oxide electronic properties. Also, the alloying element in solid solution will have different oxidation states acting either as donors or acceptors depending on their energy levels lying in the zirconia band gap, also modifying the oxide
electronic conductivity. Thus, X-Ray Absorption Near Edge Spectroscopy (XANES) experiments have been performed to characterize the oxidation state of alloying elements as function of exposure time and oxide depth (Chapter 4).

Oxide electronic conductivity plays a key role in the corrosion mechanism. In order to verify if the oxide electronic conductivity varies as function of exposure time and if these variations correlate with $f^{\text{eq}}_{\text{H}}$ variations, in-situ Electrochemical Impedance Spectroscopy (EIS) experiments have also been performed (Chapter 5) on archived samples and on different alloys.

There are still two hypotheses to explain sub-parabolic kinetics and hydrogen pickup kinetics: oxide electronic conductivity variations and space charge accommodation in the oxide. Thus, it is also necessary to develop a corrosion model to verify if oxide electronic conductivity and/or space charge accommodation modify the corrosion kinetics and hydrogen pickup and up to which extent. Different corrosion models have been developed to evaluate these hypotheses and they are detailed in the last chapter of this study (Chapter 6).

Finally, the correlations between experimental and modelling results are discussed and the general corrosion mechanism hypotheses made in this chapter are reevaluated in Chapter 7.
Chapter 4

X-Ray Absorption Near-Edge Spectroscopy (XANES) in zirconium alloys

This chapter presents firstly a brief review of the literature and the experimental motivation to perform XANES in zirconium alloys and oxides. Then, the technique and the results obtained are detailed. The chapter ends with a brief discussion of the results in terms of the previously proposed hydrogen pickup mechanism hypothesis.

4.1. Objective of the experiments and principles of XANES

4.1.1. Objective of the XANES experiment

As detailed in the preceding chapters, because very small alloying element differences make large differences in oxidation kinetics and hydrogen pickup of zirconium alloys, it is natural to examine the alloying element behavior in the oxide layer for clues to the origin of the differences between these alloys. In this chapter, we present the results of the study of the evolution of the chemical states of two alloying elements, Fe and Nb, when incorporated into the zirconium alloy oxide layers. As detailed in Chapter 2, the solubility of Fe in the alloys is less than a few hundreds of wt-ppm and thus Fe is mainly found in Zr(Cr,Fe)₂ intermetallic precipitates in Zircaloy-4 and in ZrNbFe precipitates in ZIRLO. In ZIRLO and in Zr-2.5Nb alloys, Nb is found both in solid solution (the Nb solubility limit is approximately 0.5wt% in the α zirconium phase), in βNb and ZrNbFe precipitates.

If we consider the free energy of oxidation, we expect Nb and Fe to oxidize at a higher oxygen potential compared to zirconium [30]. Delayed oxidation of Fe and Nb in second phase precipitates compared to the zirconium phase has been previously reported from TEM
examinations [67, 68]. However, the precise evolution of the chemical state of Fe and Nb, both in second phase precipitates and in solid solution upon incorporation in the zirconium alloy oxide layers as a function of oxide depth is still unknown.

To address this, a microbeam X-Ray Absorption Near-Edge Spectroscopy (XANES) investigation of the evolution of Fe and Nb oxidation states when incorporated into oxide layers formed on Zircaloy-4 sheet, ZIRLO tube, Zr-2.5Nb and Zr-0.4Fe-0.2Cr (H) has been performed using micro-beam synchrotron radiation on cross sectional oxide samples. Previous XANES studies of Fe and Nb oxidation evolution in pre-transition zirconium alloys using synchrotron radiation have focused on either flakes of powdered oxide layer, thus determining only the average element oxidation state [72], or, when some oxide depth resolution was made possible using surface sensitive XANES on sputtered oxide layers, the XANES signal originated from the contributions of both the element in precipitates and the element in solid solution [73, 74]. XANES studies of Nb oxidation in various Zr-Nb alloys have also been reported but the sample geometry did not allow precise oxide depth resolution [149].

In this study, Fe and Nb oxidation states have been determined as function of oxide depth on multiple pre and post transitions archived samples of Zircaloy-4 sheet, ZIRLO tube, Zr-2.5Nb and Zr-0.4Fe-0.2Cr (H). Also, in the case of Fe in Zircaloy-4 sheet, a new sample preparation technique has allowed us to perform studies on FIB’d samples which allows to deconvolute the signals from precipitates and solid solution. Thus, it was also possible to separate the chemical state evolution of Fe in ZrO₂ solid solution from that of Fe in Zr(Cr,Fe)₂ intermetallic precipitates embedded in the oxide layer.
XANES principles

XANES is an experimental technique particularly sensitive to element oxidation state. It is based on the determination of the X-Ray absorption coefficient depending on the incoming photon energy. As the optical excitation of a core level electron requires the binding energy $E_b$ as the minimum photon energy, an increase in absorption coefficient will be observed as the photon energy is greater than $E_b$ (see Figure 4-1 (a)). This increase in absorption coefficient is called absorption edge (see Figure 4-1 (b) and (c)).

![Figure 4-1](image1.png)

Figure 4-1. a) Photo-electric absorption coefficient as function of incoming X-Ray energy (example of lead) [150]. XANES region is shown by a circle. b) Photoelectric effect in which an X-Ray is absorbed and a core level electron is promoted in the continuum. c) Following decay of the excited state by X-Ray fluorescence [151].

As the oxidation-state of the element increases, the absorption edge energy increases correspondingly. Different levels of analysis can explain this phenomenon:

- Using a simple electrostatic model: atoms with a higher oxidation state require more energetic X-ray to excite their core electrons because the nuclei are less-shielded and carry a higher positive effective charge.
An alternative interpretation treats the edge features as continuum resonances. A continuum resonance refers to a short excitation process in which a core electron is excited into a higher energy state usually above the continuum. An example is the potential well created by the absorbing atom and the scattering (between nearest neighboring) atoms (Figure 4-2). As the absorber–scatterer distance gets shorter, the energy of the continuum state increases as \(1/R^2\). Since higher oxidation-states implies shorter bond lengths between atoms, the edge energies increases with the oxidation states.

As stated above, XANES is oxidation sensitive as observed in Figure 4-3 for the case of Fe. Moreover, multiple scattering is particularly important in the XANES region. It is for instance possible to determine the three-dimensional structure of the absorbing atom to its environment from analysis of the XANES and EXAFS features (see Figure 4-2 (a)), since both regions are quite sensitive to small structural variations.

![Figure 4-2](image)

Figure 4-2. a) Absorption coefficient as function of photon energy for Fe K-edge showing the XANES and EXAFS regions. b) Schematic explaining the phenomenon resulting in the fine structure of the absorption edge observed experimentally [151].

Also frequently observed, as in Figure 4-3, weak pre-edge structures usually result from bound state transitions. Although the 1s to 3d transition is forbidden by dipole selection rules, it is nevertheless observed due to metal 3d to oxygen 4p orbital coupling.

Consequently, XANES appears to be the suited experiment to precisely investigate the oxidation of alloying elements as function of oxide depth in zirconium alloy oxides.
4.2. XANES Experimental procedures

4.2.1. XANES experiment

The XANES experiments were performed at the 2ID-D beamline of the Advanced Photon Source (APS) at Argonne National Laboratory. Using zone plate diffraction gratings, the X-ray microprobe in the experimental station produces a monochromatic X-ray beam of size 0.2μm × 0.2μm (FWHM) with a photon flux of 5 × 10⁹ photons/sec with an X-ray energy band width (dE/E) of 0.01%. Figure 4-3 shows a schematic of the scattering and data acquisition geometry for the XANES experiments: the microbeam is placed in frontal incidence on the region of interest of the specimen to keep the probed surface area as small as possible. The XANES signals are recorded in fluorescence, with a fluorescence detector placed at approximately 85º from the incident beam to avoid elastic scattering perturbation of the fluorescence signal. The XANES scan energy step is 0.5eV and the chosen energy windows are 100eV (from 7.09keV to
7.19keV) for Fe (the Fe K-edge is located at 7.12keV), and 140eV (from 18.94keV to 19.08keV) for Nb (the Nb K-edge is located at 18.98keV). In the case of the thin cross sectional sample prepared by focused ion beam (FIB), an ionization chamber was placed at the end of the beamline to detect the transmitted signal. The transmitted signal has only been used to determine the thin sample thickness. No XANES in transmission have been performed because the Fe K-edge in transmission was not detectable, due to the overall low concentration of Fe in the microbeam path. All the measurements were performed at room temperature.

The experimental procedure consisted of first taking a fluorescence scan of the Zr L-edge (in case of XANES on Fe) or Zr K-edge (in case of XANES on Nb), in order to determine the position of the oxide/metal and oxide/water interfaces. Then XANES scans were performed at various distances of the interface, in the oxide and in the metal. The XANES experiment was then conducted by setting the beam at a particular oxide location and varying the energy in small increments within an energy window containing the edge of the element of interest. This was repeated for the entire oxide layer. After each XANES scan, the current beam position was confirmed by running an extra fluorescence scan to rule out specimen drift during the experiment.

Figure 4-4. Schematic drawing of the geometry of data acquisition at the synchrotron beamline.
4.2.2. Samples preparation

A list of the samples investigated using microbeam XANES is shown in Table 4-1 and their weight gain as a function of exposure time is plotted in Figure 4-5. The arrows in Figure 4-5 represent the samples that have been archived and used in the XANES experiments. The exact exposure time and oxide thickness (from the weight gain) for these samples are indicated in Table 4-1.

Table 4-1: List of the samples used for the XANES experiments. Their exposure time (in days) and their oxide thickness (in microns, derived from the weight gain) are indicated.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Before 1st transition</th>
<th>Between 1st and 2nd transitions</th>
<th>Between 2nd and 3rd transitions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe Zircaloy-4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>45</td>
<td>90</td>
<td>120</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>105</td>
<td>135</td>
</tr>
<tr>
<td></td>
<td></td>
<td>150</td>
<td>165</td>
</tr>
<tr>
<td>Zr-0.4Fe-0.2Cr</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>173</td>
<td>463</td>
<td></td>
</tr>
<tr>
<td>ZIRLO</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>60</td>
<td>90</td>
</tr>
<tr>
<td>Nb ZIRLO</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>60</td>
<td>90</td>
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<td></td>
<td></td>
<td>240</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>240</td>
<td></td>
</tr>
<tr>
<td>Zr-2.5Nb</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
4.2.2.1. Thick samples preparation

All samples have been prepared as thick cross-sectional samples. The samples were in the form of small transverse cross-sections (the transverse direction being normal to the cross section) of corroded tube coupons prepared according to the following procedure. A thin segment (2mm x 15mm x 0.8mm) was cut from the corrosion coupon using a low speed diamond saw to expose its cross-section and then ground to a thickness of about 0.25mm on one side to facilitate subsequent mounting into a slotted molybdenum rod. The Mo rod was then inserted into a 3mm
diameter round brass tube which was then filled with copper based epoxy. The Mo-rod and encapsulation help protect the oxide layer during subsequent mechanical polishing. The sample was polished to a mirror finish with 1200 grit sandpaper followed by 3µm diamond paste on Vel-Cloth®, 1µm diamond paste on White-Cloth® and a final polish with a 0.05µm colloidal silica solution. Schemes of the sample tubing and of the final sample preparation are displayed in Figure 4-6 (a) and (b).

Figure 4-6. Thick sample preparation for XANES experiments: a) sample tubing and b) final sample preparation after cutting and polishing. The brass tube is in yellow, the Mo rod in grey, the epoxy in pink, and the sample in white. The oxide is attached on the surface of the rounded side of the cross-section.

The thickness of the samples in the transverse direction is approximately 200µm. The incident beam being parallel to the transverse direction, the detected XANES signal as a function of oxide depth is a combination of contribution from the alloying element (Fe or Nb) in precipitates and in solid solution. Because the X-Ray attenuation lengths in zirconia are approximately 12.5µm at 7.12keV and 28µm at 18.98keV [152], the sampled volume is tens of microns deep and the alloying elements both in solid solution and in precipitates undergo electron fluorescence reactions causing the detected XANES spectra to be a combination of both signals. For instance, in Zircaloy-4, assuming that:
• the ratio of Fe and Cr in the precipitates and in the alloy is the same, which has been found to be true for Fe(wt%) / Cr(wt%) < 4 [153], so that the Fe weight concentration in a Zr(Fe_{0.66}Cr_{0.33})_2 precipitate, W_{Fe}^{SPP}, is equal to 37.1wt%.

• the weight concentration of Fe in solid solution, W_{Fe}^{matrix}, is ranges from 50 to 300 wt·ppm [12, 154-156] and the total amount of Fe in the alloy is equal to 2000 wt·ppm.

• the precipitate volume fraction V_{F}^{SPP} is approximately 0.5%.

thus the amount of Fe in second phase precipitates is given by \( \frac{W_{Fe}^{SPP}}{W_{Fe}^{matrix}} \times V_{F}^{SPP} \) or five to forty times the amount of Fe in solid solution. Although the Fe fluorescence signal is not directly proportional to the amount of Fe, we can conclude that the contribution of alloying elements in solid solution in the XANES signal coming out from the bulk samples cannot be totally neglected.

4.2.2.2. Thin samples preparation

To be able to separate the two contributions, a thin cross-sectional sample was prepared from a pre-transition Zircaloy-4 sheet sample (δ_p~1.7µm). Dimpling or ion milling methods could not be used because they could damage the oxide layer and result in large inhomogeneity in sample thickness, which is known to alter the XANES signal [157].

The preparation of a cross sectional thin sample involved a few extra steps from the thick sample one. Once the final thick sample cross section rounded configuration has been obtained, as described in the previous section (see Figure 4-6 (b)), one side of the brass tube was cut using a low speed diamond saw to expose the sample azimuthal cross section (the azimuthal direction being normal to the azimuthal cross section, see Figure 4-7).
Using focused ion beam (FIB) deposition on the rolling cross section (perpendicular to the cut), tungsten was deposited on the form of a small rectangle (75µm x 20µm x 10µm) covering the metal, the oxide and the epoxy (see Figure 4-8 (a)). This deposition is necessary to homogenize the ion milling rate of the different phases (metal, oxide and epoxy) and to protect the area to be analyzed at the synchrotron from significant ion damage. Then, using FIB, we ion milled the rolling cross section with silicon atoms at a ±7º angle to obtain a sharp wedge using a 20nA current (see Figure 4-8 (b) and (c)). Once enough material has been removed, the wedge is polished with FIB by successively reducing the ion beam current down to 1nA (see Figure 4-8 (d)). A schematic of the polished area is shown in Figure 4-9.

Zirconium metal, zirconium oxide layer and the epoxy are visible on the SEM images of the wedge, shown in Figure 4-8 (d). This sample preparation also allows us to keep the same data acquisition geometry. The synchrotron X-Ray beam is still perpendicular to the sample surface, parallel to the transverse direction. The polished oxide cross section was approximately 30µm long. Using the detected transmitted signal and the characteristic attenuation length of ZrO₂, the FIB’d sample thickness has been determined to be approximately equal to 12µm.
Figure 4-8. Secondary electron micrograph of the rolling cross section of the thin sample: a) tungsten deposition across the interface, b) ion milling around the deposition, c) focused ion beam milling of the wedge to reveal the oxide layer, d) final sample geometry before XANES experiment.
To determine whether this sample thickness is small enough to identify areas in the oxide where no precipitates are present, it is necessary to compute the theoretical probability of hitting a precipitate as a function of the sample thickness. We use for this a derivation previously performed in [12]. A scheme of the geometry used in this derivation is shown in Figure 4-10. Neglecting the secondary fluorescence, the probability to hit a single precipitate is given by:

\[ P = 1 - e^{-N_{SPP} \left( \frac{\pi}{2 \sin(\psi_0)} d(r_B + r_{SPP})^2 \right)} \]  

(4-1)

where \( N_{SPP} \) is the precipitate density in cm\(^{-3} \), \( d \) is the sample thickness in cm, \( r_B \) and \( r_{SPP} \) are respectively the synchrotron X-Ray beam radius and the precipitate radius and \( \psi_0 \) is the synchrotron X-Ray incident beam angle.

TEM examinations of the SPP in Zircaloy-4 have been performed to estimate \( r_{SPP} \) and are shown in Figure 4-11.
Combining TEM results and beamline characteristics, the following parameters are obtained $N_{SPP} = 10^{12} \text{cm}^{-3}$, $r_B = 100\text{nm}$, $r_{SPP} = 100\text{nm}$ and $\psi_0 = 90^\circ$. Using these values, the probability to hit a precipitate and the calculated transmitted intensity ratio as a function of oxide depth in ZrO$_2$ are shown in Figure 4-12. In the case of the thick sample (~200µm), the probability of hitting one precipitate is 100% and thus deconvolution of Fe signals is impossible. The probability of hitting a precipitate with a sample thickness of 10µm to 15µm ranges between 70% and 90%. This is, however, for a “blind” spot. If one obtains a compositional map before acquisition and locates the beam in a low concentration region, the probability to avoid hitting a precipitate is much lower. In the thin sample, it is thus theoretically possible to find volumes in the oxide layer where no precipitates will be hit by the incident beam and where the Fe K-edge XANES signal will only come from Fe in solid solution. In conclusion, the thin sample theoretically fulfills the purpose detailed at the beginning of this section.

Figure 4-10. Schematic drawing of the geometry used to determine the probability to hit a single precipitate.
Figure 4-11. TEM micrographs of a) Zr(Fe,Cr)$_2$ precipitates (indicated by arrows) in the metal of Zircaloy-4 sheet alloy, b) expanded view on a Zr(Fe,Cr)$_2$ precipitate.

Figure 4-12. Probability to hit a single precipitate in a Zircaloy-4 sample with $N_{SPP} = 10^{12}$ cm$^{-3}$, $r_B = 100$nm, $r_{SPP} = 100$nm and $\psi_0 = 90^\circ$ as a function of the sample depth $d$ in micrometers. The theoretical ratio of the transmitted beam intensity over the incident beam intensity in bulk ZrO$_2$ as a function of the sample depth $d$ is also shown on the same scale.
4.2.3. Standards

In order to determine the chemical state of Fe and Nb in the zirconium oxide layer, the Fe and Nb K-edge XANES spectra of reference standards were measured. A total of seven standards were used for Fe in Zircaloy-4 (4 metal standards and 3 oxide standards), six standards for Fe in ZIRLO (3 metal standards and 3 oxide standards) and five standards for Nb in Zr-2.5Nb and ZIRLO (2 metal standards and 3 oxide standards). The list of standards and their origins are shown in Table 4-2.

The XANES spectra are processed using the Athena software (version 0.8.061, Ifeffit 1.2.11c) [158]. After defining a pre-edge line, the edge energy (highest edge inflection point) and a post edge line to determine the edge step, the spectrum is normalized. The normalization constant is evaluated by extrapolating the pre- and post-edge lines to the edge energy and subtracting the edge energy-crossing of the pre-edge line from the edge energy-crossing of the post-edge line. This difference is the value of the edge step parameter used in the normalization algorithm. Then the post edge is flattened using Athena’s flattening algorithm.

4.2.3.1. Fe in Zircaloy-4 sheet and ZIRLO tube

In the case of Fe, we used bcc Fe and FeO, Fe$_3$O$_4$, and Fe$_2$O$_3$ powders obtained from Alfa Aesar as reference spectra. To simulate the various concentrations of Fe in Zircaloy-4, the Fe powders were mixed with a monoclinic ZrO$_2$ powder at weight fraction levels of 100%, 10%, 1%, 0.1% and 0.01% of Fe in ZrO$_2$. However, it is known that metallic Fe in Zircaloy-4 precipitates exhibit a Laves phase crystal structure Zr(Fe,Cr)$_2$ [34, 153]. To serve as metallic standard for Fe in the alloy, we measured a Fe XANES spectrum in the metal part of Zircaloy-4 thick sample (designated type #1).
To acquire the standard spectra of metallic Fe in Laves crystal structure Zr(Fe,Cr)$_2$, we also used the thin sample previously described and located a precipitate in the metal part. A 2D Fe fluorescence map of the metal part is presented in Figure 4-13, in which the location of the precipitate is shown. A XANES spectra at the precipitate location has been acquired (designated type #2) as the closest reference to a pure Zr(Fe,Cr)$_2$ precipitate found in Zircaloy-4.

Finally, another metallic Fe standard has been used. A Fe K-edge XANES spectra of a thick pure zirconium sponge sample with an impurity level of 100 to 600 wt·ppm of Fe has also been acquired (designated type #3) as the closest reference to Fe in solid solution in zirconium.

The XANES spectra of reference standards of metallic Fe in zirconium alloys are presented in Figure 4-14 along with the bcc Fe standard, the Fe$_2$O$_3$ and Fe$_3$O$_4$ spectra. The value of the first inflection point is similar for all the metallic Fe standards (~7.106keV), which confirms that the chemical state of Fe is metallic. However, the pre-edge and edge features of Fe standards in zirconium are different from those seen in the bcc Fe spectra. The spectra from metallic Fe in Zircaloy-4 (standards #1 and #2) and in pure Zr (#3) show no major differences in their pre-edge and edge features. Similar spectra were obtained for Fe in ZIRLO. We measured Fe XANES spectrum in the metal part of a ZIRLO thick sample (similar to #1 in Zircaloy-4) to use as metallic standard. However, even though a thin ZIRLO sample has been prepared, the precipitates in ZIRLO were too small (β-Nb) or too scarce (Zr(Fe,Nb)$_2$) to be detected. From TEM examinations, the Zr(Fe,Nb)$_2$ precipitates found in ZIRLO are large particles, with diameters between 75 and 200 nm but their density is rather low compared to β-Nb precipitates, which are smaller (between 20 and 80 nm in diameter) and more numerous than Zr(Fe,Nb)$_2$ precipitates. Thus a standard of type #2 could not be acquired for ZIRLO.
Figure 4-13. Fe fluorescence 2D map of a metallic region in the thin Zircaloy-4 sample obtained using microbeam SXRF, and which aids in locating precipitates. The SPP location is indicated by an arrow. The grey scale indicates the number of Fe fluorescence in counts per seconds (normalized to the incident beam intensity).

Figure 4-14. Normalized fluorescence (in counts/sec) Fe K-edge XANES spectra of powder standards with different Fe chemical states.
4.2.3.2. Nb in ZIRLO tube and Zr-2.5Nb

A similar approach has been used to acquire XANES spectra of metallic and oxidized Nb standards. In the case of Nb, we used metallic Nb, NbO, NbO$_2$, and Nb$_2$O$_5$ powders as reference spectra. Also, a Nb metallic spectrum has been acquired both in ZIRLO and Zr-2.5Nb metal parts of thick samples to use as metallic standards (similar to #1 for Zircaloy-4). A summary of all the standards used in this study is shown in Table 4-2. The XANES spectra of reference standards of metallic Nb are presented in Figure 4-15 along with the NbO, NbO$_2$ and Nb$_2$O$_5$ spectra. Also, the metallic Nb powder is plotted along with the theoretical metallic XANES spectra recorded in Athena [159] in Figure 4-16.

![Normalized fluorescence (in counts/sec) Fe K-edge XANES spectra of powder standards with different Fe chemical states.](image)

Figure 4-15. Normalized fluorescence (in counts/sec) Fe K-edge XANES spectra of powder standards with different Fe chemical states.
Figure 4-16. Theoretical Nb metallic standard from Athena [159] in blue and experimental data in dots.

A very good agreement is observed between theory and experiment in Figure 4-16.

Table 4-2: List of the different standards used in the fitting process of XANES spectra.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Metal standards</th>
<th>Oxide standards</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>Fe bcc powder</td>
<td>FeO powder</td>
</tr>
<tr>
<td></td>
<td>Fe in Zircaloy-4 metal (#1)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Fe in Zr(Fe,Cr)2 SPP (#2)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Fe in pure Zr (#3)</td>
<td></td>
</tr>
<tr>
<td>ZIRLO</td>
<td>Fe bcc powder</td>
<td>FeO powder</td>
</tr>
<tr>
<td></td>
<td>Fe in ZIRLO metal (#1)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Fe in pure Zr (#3)</td>
<td></td>
</tr>
<tr>
<td>Nb</td>
<td>Nb powder</td>
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</tr>
<tr>
<td></td>
<td>Nb in Zr-2.5Nb metal (#1)</td>
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<td>Zr-2.5Nb</td>
<td>Nb powder</td>
<td>NbO2 powder</td>
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<tr>
<td></td>
<td>Nb in Zr-2.5Nb metal (#1)</td>
<td>Nb2O5 powder</td>
</tr>
</tbody>
</table>
4.3. Microbeam XANES examinations of oxide layers

4.3.1. Thin Zircaloy-4 sample

A 11µm x 11µm Fe fluorescence 2D map of the thin Zircaloy-4 sample was acquired around the oxide/metal interface on the ion polished cross section using a step size of a 100nm. The ratio of the transmitted beam intensity to the incident beam intensity was approximately equal to 35%, which confirmed that the sample thickness was approximately 12µm (see Figure 4-12). Using the Fe fluorescence 2D map, three different “lines” along the oxide depth were selected: one in which no detectable precipitates were present ((1) in Figure 4-17) and two in which precipitates were present in the oxide (the Cr fluorescence signal corroborates the presence of the precipitates) named SPP1 and SPP2 scans ((2) and (3) in Figure 4-17).

In Figure 4-17, the oxide thickness direction is in the Y direction and its position is determined using the Zr fluorescence signal (not shown here). The oxide is located from Y=0 (oxide/metal interface) to approximately Y=1.7µm (oxide/epoxy interface). The Fe fluorescence signals along the oxide depth for these three scans are presented in Figure 4-18.

The FWHM fluorescence peak associated with Fe signal from the precipitates are approximately equal to 0.6µm and thus are 3 times bigger than the average precipitate size. This apparent increase is likely caused by the Gaussian shape of the X-Ray beam. Indeed, when the tails of the Gaussian beam hit a precipitate, the fluorescence signal significantly increases due to much higher Fe concentration in precipitates. The two precipitates have approximately the same sizes (as defined by the FWHM) and are fully embedded in the oxide layer. The small shoulder in Fe fluorescence at the oxide/water interface is due to the Fe pollution from Fe in the autoclave during the corrosion testing as reported previously [28].
Figure 4-17. Fe fluorescence 2D maps of oxide regions in the thin Zircaloy-4 sample showing the lines along which XANES scans (at the Fe K-edge) have been performed. The distance from the oxide/metal interface is represented on the Y axis (the oxide/metal interface being at Y=0 has been determined from Zr fluorescence spectra not shown here). The X axis is parallel to the oxide/metal interface. The grey scale indicates the normalized number of Fe fluorescence counts (in counts/sec).

Figure 4-18. Scans of normalized Fe fluorescence intensity (in counts/sec) of the three different oxide regions in the thin sample.
XANES spectra have been acquired along those three lines. Figure 4-19 shows the XANES spectra for several oxide depths acquired along the scan 1 where no precipitates were present. It is clear that the pre-edge and edge features evolve and that, consequently, the chemical state of Fe varies along the oxide depth. To quantify the Fe chemical state evolution we used the linear combination fitting algorithm of Athena in which an unknown spectrum is fitted by a linear combination of standard spectra, obtained as detailed in the previous section.

![Normalized fluorescence Fe K-edge XANES spectra at different distances from oxide/metal interface in a thin Zircaloy-4 sample, along scan 1 where no precipitate was detected](image)

**Figure 4-19.** Normalized fluorescence Fe K-edge XANES spectra at different distances from oxide/metal interface in a thin Zircaloy-4 sample, along scan 1 where no precipitate was detected (see Figure 4-17).

In all cases the whole spectrum was fitted (pre-edge, edge and post-edge). The standards shown in Table 4-2 were used in the linear combination fitting process. The unknown spectrum is fitted using a linear combination of standards, so that the combinatorial fit has the following mathematical form:

\[
\text{fit} = \sum_i a_i S_i 
\]

(4-2)
where $a_i$ is the weight (or fraction) associated to the $i$th standard $S_i$. The fitting was not sensitive enough to detect the differences between FeO, Fe$_3$O$_4$ and Fe$_2$O$_3$ oxide standards, so the fractions $a_i$ attributed to the oxide reference samples (FeO, Fe$_3$O$_4$ and Fe$_2$O$_3$ powders) were summed as one overall oxide fraction $a_{ox}$. The same has been done with the metallic Fe standards, which was represented by one Fe metallic fraction $a_{met}$. The linear combination fitting results for the three scans are presented in Figure 4-20, where the fraction of oxidized Fe is plotted as a function of oxide depth, when applying the fits to the data shown in Figure 4-19. It is clear that oxidation evolves in the oxide layer.

It was possible to separate out bcc Fe contribution from that of the three metallic Fe in Zr. An example of one of the fits is shown in Figure 4-21 (a) where the Fe oxide fraction and Fe metallic fraction given by the fit are also plotted. The fit reproduces well the measured values. The least-square errors for the fits were smaller than 0.2% for all the fits.

![Graph](image)

**Figure 4-20.** Fraction of oxidized Fe in the thin Zircaloy-4 sample oxide layer as a function of distance from oxide/metal interface in three different regions (defined in Figure 4-17).

As shown in Figure 4-20, the fraction of oxidized Fe gradually increases as the beam approaches the oxide/water interface. The oxidation of Fe in solid solution and in precipitates is
delayed relative to the Zr oxidation, so that a significant fraction of Fe remains metallic in the oxide layer. It is also clear from Figure 4-20 that Fe in the precipitates oxidizes less rapidly than the Fe in solid solution since for a given depth the fraction of oxidized Fe is higher in the solid solution location than in the precipitate locations. The precipitates shown in Figure 4-17 and Figure 4-18 are located respectively 0.8µm (SPP1) away and 1µm away (SPP2) from the oxide/metal interface. Close to the oxide/metal interface, the beam does not hit the precipitates and the fractions of oxidized Fe in the three regions are similar. As the beam goes further away from the oxide/metal interface, the X-Ray beam starts hitting the SPP1 and SPP2 precipitates, the fractions of oxidized Fe of these scans decrease, whereas the fraction of oxidized Fe in solid solution keeps increasing. The lower fractions of oxidized Fe in the scans 2 and 3 are thus due to the presence of metallic precipitates embedded in the zirconium oxide layer. The fraction of oxidized Fe reaches a minimum where the precipitates are located. As the beam goes away from the precipitate locations toward the oxide/epoxy interface, the fraction of oxidized Fe starts increasing again to reach 100% at the oxide/water interface located approximately at 1.7µm from the oxide/metal interface for all the scans.

4.3.2. Thick samples

The same data analysis method used on the thin sample was used to fit the data obtained from the thick samples (a fit in the case of Nb in Zr-2.5Nb oxide is also plotted in Figure 4-21 (b)).

The best fit given by the list of combinatorial fits was systematically used every time and its R-factor plotted as function of incident beam energy to check the precision of the fit and verify if the R-factor was homogeneously distributed across the energy range. In each case the Zr fluorescence signal (straight line without symbols in Figure 4-22) is acquired to detect the
position of the oxide layer and the two interfaces. Figure 4-22 shows an example of a post-transition Zircaloy-4 with a total oxide thickness $\delta \sim 3.6\mu m$ that matches that derived from the weight gain. The fraction of oxidized Fe, and its complementary, the fraction of metallic Fe, is also plotted in Figure 4-22. All other sample’s results are displayed in Appendix C.

Figure 4-21. Linear combination fit of a XANES spectrum in the oxide of a a) Zircaloy-4 sample, b) Zr-2.5Nb sample.
The evolution of the fraction of oxidized Fe in the thick samples was similar to that seen in the thin sample. The fraction of oxidized Fe is close to zero at the oxide/metal interface and gradually increases in the protective oxide ($\delta_p$, the oxide formed since the last transition with its thickness derived from weight gain data), until it reaches 100% in the non-protective oxide (oxide formed up to the previous transition), indicating that all the Fe in the non-protective oxide is oxidized. This is expected since this portion of the oxide is thought to be porous and fully permeable to water [115]. It is observed that the oxidation of Fe in the oxide layer is delayed compared to the zirconium oxidation. ZIRLO and Zr-2.5Nb samples show similar results, Nb and Fe exhibit delayed oxidation in the oxide layer.

The Fe bcc fraction is also plotted in Figure 4-22. While it is almost always equal to zero throughout the scan, a measurable Fe bcc signal is normally detected in Zircaloy-4 near the region...
where the precipitates start to oxidize. This result is present in most of the Zircaloy-4 samples investigated in this study (see Appendix II), and it is in agreement with previous TEM experiments on Zircaloy-4 samples, which show a \textit{segregation of bcc Fe when the precipitates start oxidizing} and the Cr and Zr in the precipitate oxidizing preferentially leaving the Fe to cluster as bcc Fe [67]. The detection of the Fe bcc by this XANES study gives more confidence in the results of the combinatorial fitting as well.

To compare the evolution of alloying element oxidation state between samples of different oxide thickness (i.e. at different exposure time), it is necessary to define a parameter to characterize it and that can be easily evaluated for different samples of the same alloy. The parameter chosen is $\delta_{\text{met}}$, the length of the oxide layer in which the fraction of oxidized Fe or Nb is below 50\% (see Figure 4-22). Thus $\delta_{\text{met}}$ is an indication on the evolution of the oxygen potential in the oxide layer. The ratio $\delta_{\text{met}}/\delta_p$ is an indicator of the fraction of the protective oxide in which alloying elements are mainly metallic. Values of $\delta_{\text{met}}$ for Fe in Zircaloy-4 sheet, ZIRLO tube and Zr-0.4Fe-0.2Cr (H) and for Nb in ZIRLO and Zr-2.5Nb are shown in Figure 4-23. In these plots, $\delta_{\text{met}}$ is plotted as function of $\delta_p$. It is recalled that $\delta_p$ is the portion of the oxide layer formed after the previous transition. The transition thickness $\delta_t$ is represented by a shaded area. Several transition regimes being analysed for Zircaloy-4 and ZIRLO the transition is not represented by a straight line, but by a range of thicknesses, since the transition thickness $\delta_t$ is not exactly the same from a transition to another as observed in Table 2-3. Small $\delta_p$ have only been investigated in the case of Zircaloy-4 sheet, as it is difficult to archive a sample right after its transition. However a general trend of $\delta_{\text{met}}$ as function of $\delta_p$ is observed. At first, $\delta_{\text{met}}$ increases up to a threshold value of approximately 0.75$\mu$m to 0.8$\mu$m for Zircaloy-4, 1$\mu$m for ZIRLO. During this increase the ratio $\delta_{\text{met}}/\delta_p$ is approximately constant. The threshold $\delta_{\text{met}}$ value for Zr-2.5Nb is at least 1.2$\mu$m and for Zr-0.4Fe-0.2Cr (H) it is at least 1.25$\mu$m.
Once $\delta_{\text{met}}$ reaches its threshold value, it remains constant up to when the oxide reaches transition thickness. At the transition, $\delta_{\text{met}}$ drops. In the case of the model alloy Zr-0.4Fe-0.2Cr (H), even though the weight gain curve in Figure 4-5 and the SEM micrographs in Figure 4-23 (b) do not show transition, the fact that $\delta_{\text{met}}$ is already dropping significantly for the sample archived at 463 days, suggests that in the future it may undergo transition. The different transition regimes are indicated for Zircaloy-4 in Figure 4-23 and it appears that $\delta_{\text{met}}$ does not depend on the
transition regime. This was expected since $\delta_{\text{met}}$ is directly dependent on the oxygen potential in the oxide layer and it is known that the corrosion of Zircaloy-4 is periodic [28].

XANES results on several zirconium oxide layers are displayed in Figure 4-24, Figure 4-25 and Figure 4-26 in the same form as Figure 4-22. Figure 4-23 is recalled in these Figures to locate the particular data points corresponding to the spectra. For each points circled in the $\delta_{\text{met}}$ vs $\delta_p$ plot in these Figures, its colour corresponding plot of oxidation state evolution as function of oxide depth is plotted alongside.

Figure 4-24. XANES results on several Zircaloy-4 oxide layers displaying the fraction of oxidized Fe as function of oxide depth. Figure 4-23 (a) is plotted on the upper left to locate the data points corresponding to these analyses. For each point (oxide thickness) circled in the $\delta_{\text{met}}$ vs $\delta_p$ plot (upper left), its colour corresponding plot of oxidation state evolution as function of oxide depth is plotted alongside.
Figure 4-25. XANES results on several Zr-2.5-Nb (left) and Zr-0.4Fe-0.2Cr (right) oxide layers displaying the fraction of oxidized Nb and Fe as function of oxide depth. Figure 4-23 e) and Figure 4-23 (d) are plotted on the lower left for Zr-2.5Nb and lower right for Zr-0.4Fe-0.2Cr alloys. For each point (oxide thickness) circled in the $\delta_{\text{net}}$ vs $\delta_p$ plot (bottom), its colour corresponding plot of oxidation state evolution as function of oxide depth is plotted on top.
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Figure 4-26. XANES results on several ZIRLO oxide layers displaying the fraction of oxidized Fe and Nb as function of oxide depth. Figure 4-23 (b) is plotted on the right. For each oxide thickness (corresponding to two points, one for Fe and one for Nb) circled in the $\delta_{\text{met}}$ vs $\delta_p$ plot (on the right), its colour corresponding plot of oxidation state evolution as function of oxide depth is plotted on left for both Fe and Nb.

The XANES results in Figure 4-24, Figure 4-25 and Figure 4-26 show the large amount of data collected to obtain *one* point on the $\delta_{\text{met}}$ vs $\delta_p$ plot. They also give a more general picture of the evolution of oxidation state of alloying elements as function of oxide depth in zirconium alloy oxide layers. The implication of these results is discussed in the following section.
4.4. Discussion of the results

In Zircaloy-4 sheet, ZIRLO tube, Zr-2.5Nb and Zr-0.4Fe-0.2Cr (H) the oxidation of Fe and Nb in precipitates is delayed relative to Zr oxidation. The results on Nb containing alloys are in agreement with the XANES results from Sakamoto et al. [74] reproduced in Figure 1-13. The results reported in this chapter are also in accordance with previous TEM observations [67, 68], electrochemical measurements [66] and deuterium ingress studies [115]. TEM examinations of oxide layers were done on the samples investigated previously by microbeam XANES mainly to locate and confirm the presence of metallic Fe and Nb in precipitates embedded in the oxide layer and finally confront the results with the XANES experiments. The TEM samples were prepared by lift-out technique (INLO) using FIB with the details of the technique described in length in [160]. This technique produces electron transparent samples with an area of about 10-15µm in length and 5-10µm in width of specific regions in the oxide layer. This sample preparation’s method was used to be able to study specific areas of the oxide layer, such as precipitates embedded in the oxide. The TEM used was a JEOL LaB₆ TEM at 200keV.

Diffraction patterns of precipitates embedded in the oxide layer localized by EFTEM and tilting were taken to determine their crystal structure and thus if they were oxidized or not. Some TEM micrographs taken in bright field configuration of a Zircaloy-4 oxide layer (δₚ ~ 1.8µm) are shown in Figure 4-27. The circled precipitates in Figure 4-27 are metallic Zr(Cr,Fe)₂ precipitates as confirmed by indexing of diffraction pattern. In this specific sample, metallic precipitates have been observed as far as 400 nm away from the oxide/metal interface, while oxidized ones (appearing as a round/oval shape enclosing small equiaxed grains separated by many cracks) where seen further than 800 nm away from the oxide/metal interface. Even though the number of investigated precipitates is rather small compared to the statistics of the XANES experiments,
these qualitative results are in general agreement with the XANES results as shown in in Figure 4-24.

Precipitates in ZIRLO oxide scales were also investigated by TEM. However, in that case, rather than the small grain oxides found in Zircaloy-4, the oxidized precipitates would exhibit amorphous contrast as it is shown in Figure 4-28 (b). Amorphous precipitates show as high oxygen content as the surrounding matrix (as measured by EDS), which might indicate they are oxidized but the signal could also come from the matrix surrounding the investigated precipitates. Thus there is no clear evidence from TEM that amorphous precipitates are actually oxidized in ZIRLO.

Figure 4-27. TEM BF images of Zircaloy-4 oxide layer ($\delta_p \sim 1.8 \mu$m). Metallic precipitates are circled and the oxide/metal interface is also delimited.
Figure 4-28. a) β-Nb crystalline precipitate (250 nm away from the oxide/metal interface), b) amorphous β-Nb precipitate (600 nm away from the oxide/metal interface) observed in the oxide layer of a ZIRLO sample oxidized for 120 days (δ~ 3.6 μm - δ_p~ 0.6 μm).

Zr(Fe,Nb)_2 precipitates – that are larger than β-Nb precipitates – remain metallic longer in the oxide: amorphous β-Nb precipitates have been observed as close as 350 nm from the oxide/metal interface, while the closest amorphous Zr(Fe,Nb)_2 precipitate was 700 nm away from it for and oxide layer of δ~ 3.6 μm (δ_p~0.6 μm). Once again these results are in general agreement with the XANES results in Figure 4-26. The TEM results are shown in Figure 4-30 in terms of oxide region in which precipitates are observed to be metallic (see red transparent rectangles in Figure 4-30), along with the XANES results previously shown in Figure 4-23. It is observed that the distance from the oxide/metal interface of metallic precipitates localized by TEM is smaller than δ_{met}. This was expected since δ_{met} is the length of the oxide layer in which the fraction of oxidized Fe or Nb is below 50%, whereas the elements in precipitates investigated by TEM are 100% metallic in the oxide region (red rectangle) shown in Figure 4-30. Thus the results of the two techniques are in good agreement, TEM qualitative results correlating with the quantitative XANES results.
The oxidation of Fe in solid solution in Zircaloy-4 also appears to be delayed compared to Zr oxidation according to the results of the thin sample. Thus, Fe in solid solution also remains metallic for a while after incorporation in the oxide. One possible mechanism for this to occur is that the Fe “in solid solution” in the oxide are actually Fe atoms segregated at oxide grain boundaries or dislocations due to local compressive strains induced by the differences in volume density between the metal and the oxide. Atom probe measurements [146, 161] have shown that this was to some extent the case for Fe in solid solution in the oxide part. However we cannot rule out that the observation of Fe in solid solution might be altered by small hidden precipitates undetected in the 2D fluorescence map shown in Figure 4-17. Since alloying element oxidation appears to be controlled by thermodynamics rather than kinetics [65], we can conclude that alloying elements in precipitates are protected by the preferential oxidation of zirconium up to a certain distance from the oxide/metal interface where the oxygen potential is high enough to oxidize Fe and/or Nb in precipitates. No bcc Fe signal was detected in the metal (it actually represents 0% of the fit at the oxide/metal interface), and it is only detected when the precipitates embedded in the oxide start oxidizing. It is believed that bcc Fe starts to form when Zr and Cr in the precipitates become oxidized. Indeed Cr has a lower oxidation potential compared to Fe [30]. Once the Cr is oxidized, metallic Fe starts to segregate and forms bcc Fe as observed in [67]. Eventually, once the oxidation potential of Fe in precipitates is reached, Fe starts to oxidize to form $\text{Fe}_3\text{O}_4$, and $\text{Fe}_2\text{O}_3$ oxides. A similar evolution from Nb metal to Nb oxides also occurs in Nb-based alloys.

An oxidation model based on the $\mu$XANES results is proposed:

1. When a new protective oxide is formed (right after transition), a continuous gradient in oxidation potential in the protective oxide layer is established. The boundary conditions at the oxide/metal and oxide/water (or porous oxide) interfaces fix the oxygen potentials at these locations. As the protective oxide
thickens, the oxygen potential gradient decreases but the ratio $\delta_{\text{met}}/\delta_p$ remains constant (even though $\delta_{\text{met}}$ increases). This situation is schematically described in Figure 4-29 (a) (the oxygen potential is represented as the dotted line).

2. Then $\delta_{\text{met}}$ reaches a threshold value and remains constant, even though $\delta_p$ increases. Thus, the ratio $\delta_{\text{met}}/\delta_p$ decreases and the oxygen potential in the oxide layer cannot remain continuous since the boundary conditions do not change. The oxygen potential in the outer part of the protective oxide increases. This situation is schematically described in Figure 4-29 (b).

3. Finally, the oxide transition occurs, and $\delta_{\text{met}}$ drops to zero (Fe and Nb are fully oxidized). This is because the oxide is no longer protective and is permeable to water. The oxygen potential in the oxide is everywhere higher than the oxidation potential of the alloying elements either in precipitates or in solid solution.

This oxidation model is valid for Zircaloy-4 sheet, ZIRLO tube and Zr-2.5Nb alloys as well as for the model alloy Zr-0.4Fe-0.2Cr (H). According to the results, a layer in which most of the alloying elements are metallic, develops as the oxide grows and remains at a constant thickness once the protective oxide reaches a thickness of approximately 1.2$\mu$m to 1.5$\mu$m. This threshold thickness is alloy dependent and is displayed in Table 4-3 for the different zirconium alloys.

Table 4-3: Threshold $\delta_{\text{met}}$ value for different alloys.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Threshold $\delta_{\text{met}}$ (maximum distance from the O/M interface where the fraction of oxidized Fe or Nb is less than 50%)</th>
<th>Oxygen partial pressure at a given oxide depth</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zircaloy-4 sheet</td>
<td>0.75 $\mu$m</td>
<td>increase from Zr-0.4Fe-0.2Cr (H) to Zircaloy-4</td>
</tr>
<tr>
<td>ZIRLO tube</td>
<td>1.0 $\mu$m</td>
<td></td>
</tr>
<tr>
<td>Zr-2.5Nb</td>
<td>$&gt; 1.2$ $\mu$m</td>
<td></td>
</tr>
<tr>
<td>Zr-0.4Fe-0.2Cr (H)</td>
<td>$&gt; 1.25$ $\mu$m</td>
<td></td>
</tr>
</tbody>
</table>
Figure 4-29. Schematic evolution of the oxidation of precipitates in zirconium oxide layer as function of the oxygen partial pressure across the oxide: a) before $\delta_{\text{met}}$ reached its threshold value, b) after $\delta_{\text{met}}$ reached its threshold value (see Table 4-3).
There is no apparent reason to consider different boundary conditions between the alloys and from free energy calculations the oxidation potential of $\text{Zr(Fe,Cr)}_2$ precipitates is higher than the oxidation potential of $\beta\text{Nb}$ and on the same order of magnitude than $\text{Zr(Nb,Fe)}_2$ precipitates [65]. Thus, at a given oxide depth, the oxygen partial pressure would increase from Zr-0.4Fe-0.2Cr (H) alloy to Zircaloy-4 sheet alloy (see Table 4-3).

The development of porosity in these oxide layers could explain why $\delta_{\text{met}}$ reaches a threshold and why this threshold would be different from alloy to alloy. Many studies have shown a development of porosity in the protective oxide of zirconium alloys [44, 87, 162, 163]. However, few of them have reported a quantitative analysis of porosity as function of oxide thickness. The evolution of the micro-porosity in zirconium oxide layers as function of oxide depth has been qualitatively studied by Ni et al., using TEM Fresnel contrast to localize small pores (1-3 nm) in the oxide layer [92]. The distance from the oxide/metal interface up to where the pores start to be vertically connected in the oxide has been measured for different alloys. For a Zircaloy-4 sample with a 1.5$\mu$m oxide thickness (pre-transition), this distance was approximately equal to 0.6$\mu$m. For a second Zircaloy-4 sample with a 1.9$\mu$m oxide thickness (still pre-transition) this distance increased to approximately 1$\mu$m. For a post-transition ZIRLO sample (~1 $\mu$m oxide thickness since the previous transition), a distance of 0.7$\mu$m was measured. These qualitative results are shown in Figure 4-30 (blue transparent rectangle) along with the XANES and TEM results (red transparent rectangle). These values of an oxide thickness free of interconnected pores are in very good agreement with our reported values of $\delta_{\text{met}}$ as a function of $\delta_p$ (see Figure 4-23 (a) and (b)) from the XANES experiments and also with the reported distances from the oxide/metal interface where metallic precipitates are found with TEM.
The formation of a connected network of pores would thus be related to the oxidation of precipitates, suggesting that the inter-connection of pores would increase the mobility of the oxidizing species (such as oxygen anions) and would increase the partial pressure of oxygen in this part of the oxide layer (see Figure 4-29 (b)). This effect of pores on the mobility of oxidizing species was actually proposed by Cox [45]. However it is unclear if the pores are filled with water or not and if so, how does the soaking evolve as the micro-porosity develops. EIS measurements tend to show that liquid soaking of cracks and pores in the protective layer occurs progressively during corrosion [164]. Also, water filled cracks and pores are in accordance with boron and lithium concentrations variations as function of oxide depths measured by secondary ion mass spectroscopy [165]. In any case, **XANES measurements would agree with an increase in oxygen partial pressure in the outer protective oxide layer due to interconnected porosity development, resulting in a threshold distance from the oxide/metal interface where second phase precipitates remain metallic.**
For the ZIRLO alloy, one can notice that δ_{meq} at a given δ_{p} (and so at a given level of porosity) for Fe and for Nb are close to each other. These results would suggest that the oxidation of Fe and Nb in Zr(Nb,Fe)$_2$ is occurring simultaneously. But closer to transition, the Nb is preferentially oxidized compared to the Fe suggesting at least that βNb precipitates oxidize preferentially. The oxidation free energy of different compounds found in zirconium alloys are reproduced in Table 4-4 from Proff et al. [65]. The preferential oxidation of βNb precipitates over Zr(Nb,Fe)$_2$ precipitates is confirmed from thermodynamics. However since the βNb precipitates are also smaller than Zr(Nb,Fe)$_2$ precipitates this preferential oxidation of βNb precipitates could also be a kinetic effect.

Table 4-4: Free energy of oxide formation for the different phases encountered in precipitates of zirconium alloys normalized to the number of mols of oxygen in the oxidized precipitate from Proff et al [65].

According to these results it appears that a layer, in which alloying elements are mostly unoxidized, thickens until it reaches a constant thickness due to the formation of interconnected porosity at the outer part of the oxide. The correlation between alloying element oxidation and hydrogen pickup fraction evolution will be discussed in Chapter 7.
4.5. Conclusion on the XANES experiments

The results of the microbeam XANES experiment show that:

- Oxidation of Fe and Nb in second phase precipitates are delayed compared to zirconium oxidation. Thus metallic precipitates are embedded into the growing oxide.
- Thanks to a new type of sample preparation, the oxidation of Fe in solid solution in oxides grown on Zircaloy-4 was characterized. The results show that, to a lesser extent, oxidation of Fe in solid solution is also delayed compared to zirconium oxidation. This suggests a possible segregation of Fe at oxide grain boundaries.
- An inner layer (of thickness $\delta_{met}$) in which most of the alloying elements in precipitates are still metallic develops as the oxide grows. At first $\delta_{met}$ increases as the oxide layer thickens. Then, after the oxide layer thickness reaches approximately a thickness of
1.2µm to 1.5µm, $\delta_{\text{met}}$ reaches a threshold until the oxide reaches transition (see Table 4-3). At transition $\delta_{\text{met}}$ drops to zero. These microbeam XANES results are supported by TEM investigations of oxide layers of the same samples.

- This threshold $\delta_{\text{met}}$ value is alloy dependent and has been connected to the development of micro-porosity in the oxide.

Following these conclusions, the concentration of metallic alloying elements in the protective oxide layer evolves according to the scheme in Figure 4-31. As the oxide grows, the fraction of metallic alloying elements remains constant in the layer. Then, once the oxide layer thickness reaches approximately half of its transition thickness, the fraction of metallic alloying elements starts decreasing. Eventually, at transition (or even before depending on the considered alloys), all the alloying elements are oxidized.
Chapter 5

In-situ Electrochemical Impedance Spectroscopy

The purpose of this experiment is to measure the zirconium oxide electronic conductivity in-situ for a variety of zirconium alloys as function of exposure time in order to verify the hydrogen pickup mechanism hypothesis previously proposed in Chapter 3.

This chapter reviews some fundamental aspects of electrochemical impedance spectroscopy and briefly details the key findings relative to zirconium corrosion available in the literature. Then, the experimental procedure is detailed and the results obtained from the examination of Zircaloy-4, Zr-2.5Nb and Zr-2.5Nb-0.5Cu samples are presented and discussed.

5.1. Fundamentals of Electrochemical Impedance Spectroscopy

The purpose of the in-situ EIS experiment is to electrically stimulate the various fundamental microscopic processes that take place throughout the Zr|ZrO$_2$|water cell and lead to the overall electrical response. The study of this response gives insights on the transport of different charged species across the oxide, such as electrons and vacancies, but also on the charge transfer at the anodic and cathodic sites and the transport of ions in the electrolyte. In direct current (d.c.) systems, resistance can be derived by Ohm’s law $R = V/I$, where $R$ is resistance in $\Omega$, $V$ is the voltage applied across the resistor and $I$ is the resulting current that flows through the resistor. However, no information on the carrier types and transport processes can be obtained from these experiments. In the zirconium corrosion studied by EIS, an alternating current (a.c.) signal is applied to the Zr|ZrO$_2$|water cell and the response current signal is recorded. The equipment measures the voltage-current relationship corresponding to each frequency, in order to obtain the impedance spectrum. Although electrochemical systems are often non-linear, it is
assumed that they can be treated as linear system (i.e., the relationship between current and voltage is independent of signal amplitude), providing the amplitude of signal fluctuations is small. Thus, EIS experiment is the study of the transfer function \( Z(\omega) \) called impedance, which is defined as \( Z(\omega) = V(\omega)/I(\omega) \) [166].

On the time scale of interest of EIS studies (> 1µs), the ac electric field can interact with the bulk oxide in two principal ways: the reorientation of defects having electric dipole moments (complex defects, space charged defects – the electron reorientation around the nuclei and ionic vibrations are out of the EIS time scale range) leading to dielectric relaxation and the motion of charged carriers leading to conductivity. It is recalled that both effects present real and imaginary impedance (for instance, the real part of the impedance in defect reorientation arises from dielectric losses, which are associated dissipative process resulting in energy absorbed by the system). The electric field also interacts with interfaces where both polarization and charge transfer occur. These electrochemical responses can be modeled by more or less well defined circuit elements. Indeed, although it is predicted that electrochemical properties such as conductivity and interface capacitance are independent of frequency, EIS studies have indicated that they actually show a significant amount of frequency dispersion. Thus the electrochemical response cannot be properly modeled by the single use of pure circuit elements [167]. Although many EIS studies have been performed on zirconium oxide scales, few of these have been conducted at operating conditions (in-situ at high temperatures) and for long exposure times because of obvious experimental difficulties [56, 136, 147, 168, 169]. Impedance spectra (Bode plots) acquired in these studies are shown in Figure 5-1. The spectra analyses are done in the following sections. A brief review of the main conclusions from these studies is presented in the following.
EIS experiments at high temperatures on oxides grown thermally conducted to date show that it is a suitable technique to follow the oxidation kinetics in situ. Indeed, by extrapolating the capacitance at infinite frequency it was generally possible to monitor in-situ the oxidation kinetics. Impedance results prove satisfactory when compared to thickness determined by SEM and/or weight gain [136, 169]. All studies also concluded that the oxide shows a significant dispersion such that the oxide dielectric permittivity appears to depend on frequency. Because of this observation, the oxide capacitance is usually modelled by a constant phase elements (CPE) rather than a pure capacitance, the physical meaning of which is still a matter of debate [170].

It is known from microscope observations that the oxide is a combination of a thin region close to the oxide/metal interface in which the tetragonal phase fraction is rather high compared to further away from the interface where the monoclinic phase predominates [28]. EIS spectra analyses support the theory of a bi-layered oxide with different oxide layer properties: a very thin (a few nm) protective inner layer and an outer porous non protective layer. This system has been proposed as the only system to successfully reproduce the impedance measurements [56, 169]. However no general agreements on the layers oxidation kinetics has been reach in the literature questioning the nature of that model. Also, this very thin (~10nm) inner protective layer does not
correlate with microscopy observations of zirconium alloy oxides. However, there have been no correlations found between the tetragonal phase observed in TEM and this inner protective layer deduced from EIS spectra analysis. Finally, it has generally been observed that oxide impedance at low frequency increases with exposure time. By assuming that the low frequency impedance is related to the inverse of the oxidation rate [169], it is concluded that the resistance to charged species transport across the oxide layer increases with the oxide thickness [147]. This was expected since the flux of charged species across the oxide decreases as the oxide thickness increases. Thus the resistance of the oxide is directly proportional to the oxide thickness.

The electronic conductivity of yttria stabilized ZrO$_2$ at 400ºC has been calculated in [171] as being approximately equal to $10^5 \, \Omega \cdot \text{cm}$. Gohr et al [56] have also shown that the quality (or conductivity) of the oxide layer degrades as the oxide thickens in the protective regime confirming the hypothesis presented in Chapter 3 of an increase in oxide resistivity as the oxide thickness increases. However, the modeling of the electrochemical circuit using EIS measurements is rather difficult and no consensus has been reached as to how the electrochemical response can be interpreted in terms of oxide layer properties [147].

5.2. Equivalent circuits

Equivalent circuits are very useful as an idealized way to represent electrochemical processes. The electrochemical response of the system is modeled using electrical circuit elements (i.e., passive circuit elements). Passive circuit elements are components such as resistor and capacitor that do not generate a current or a potential in an electrical circuit. An electrical circuit consisting of an electrolyte and a blocking electrode is modeled by a solution resistance $R_s$ in series with a double layer capacitor $C_{dl}$ as shown in Figure 5-2 (a). On the other hand, a non-blocking electrode is ideally modeled by a charge transfer resistance $R_{ct}$ (representing the current
crossing the interface) in parallel with a double layer capacitor $C_{dl}$ (representing the charge accumulation on both sides of the interfaces) in Figure 5-2 (b) [172].

![Figure 5-2. Example of blocking electrode (a) and non-blocking electrode (b) equivalent circuits.](image)

The system under study in this experiment can be well represented by pure circuit elements as shown in Figure 5-3 (the electrolyte – here water – capacitance does not appear in the frequency range investigated in this study because $1/C_e R_e \gg 10^6$ Hz $\rightarrow R_e/(1+j\omega C_e R_e) \sim R_e$).

![Figure 5-3. Electrochemical system corresponding to zirconium corrosion.](image)

The total impedance of this system is equal to:

$$Z = R_m + R_e + \sum_{i=\text{ox}, \text{M}}^{\text{O/M}} \frac{R_i}{1+j\omega C_i R_i}$$

(5-1)
where $R_m$ is the resistance of the zirconium metal, $R_e$ the electrolyte resistance and $R_i$ and $C_i$ the resistance and capacitance of the bulk oxide and interfaces as shown in Figure 5-3.

Thus, from eq.5-1, $Z(\omega \to \infty) \sim R_m + R_e$ and:

$$Z(\omega \to 0) = R_m + R_e + \sum_{i=\text{ox,} \atop o/M} R_i \tag{5-2}$$

In this ideal system, the metal resistivity can be neglected: $R_m \sim 0$ and $Z(\omega \to \infty) \sim R_e$.

The double layer at the interface is only a few nanometers thick [173] and can be expressed via the plane capacitor formula:

$$C_{dl} = \frac{\varepsilon_{dl}\varepsilon_0 S}{d_{dl}} \tag{5-3}$$

where $C_{dl}$ is the double layer capacitance at the oxide/electrolyte interface, $\varepsilon_{dl}$ the relative permittivity of the double layer, $\varepsilon_0$ the vacuum permittivity, $S$ the surface of the interface and $d_{dl}$ the thickness of the double layer.

The oxide capacitance can be derived similarly:

$$C_{ox} = \frac{\varepsilon_{ox}\varepsilon_0 S}{d_{ox}} \tag{5-4}$$

where the terms are defined as in the double layer case in eq.5-3 but for the oxide.

The double layer being extremely thin compared to the oxide thickness $d_{dl} \ll d_{ox}$, then, since the relative permittivity $\varepsilon_{ox}$ and $\varepsilon_{dl}$ are of the same order of magnitude and the surface is the same in both systems, comparing eqs.5-3 and 5-4, it is verified that $C_{dl} \gg C_{ox}$. The double layer capacitance at the interfaces can be neglected compared to the oxide capacitance at high frequency.

$$Z(\omega \gg 1) \sim R_e + \sum_{i=\text{ox,} \atop o/M} \frac{1}{j\omega C_i} = R_e - \frac{j}{\omega C_{ox}} \tag{5-5}$$
The resistivity of the charge transfer the oxide/metal interface is also supposed to be negligible at low frequency since the Fermi level of zirconium metal is inside the conduction band of zirconium oxide.

\[
Z(\omega \to 0) \sim R_e + \sum_{i=O/\omega_{ox}} R_i
\]  

(5-6)

Using eqs.5-1 to 5-6, the expected ideal Bode diagram (modulus and argument of \(Z\) as function of frequency) is displayed in Figure 5-4 in the case of zirconium oxidation. As expected from eqs.5-6 and the limit of eq.5-1 at infinite frequency, the modulus reaches two plateaus at zero and infinite frequency and the phase is zero at these extremes indicating that the impedance is a pure resistance. At intermediate frequencies, the system behaves as a pure capacitor so that the modulus depends on the frequency (with a slope of -1 in the Bode representation) and the phase is 90° indicating a pure imaginary number. From this light development of electrochemical oxide response, it appears possible to determine oxide resistivity and oxide capacitance from EIS impedance spectra. The experimental setup used to record these spectra is the subject of the next section.

Figure 5-4. Expected Bode diagram of EIS experiment on zirconium (modulus and phase)
5.3. Experimental procedures

Figure 5-5 presents a schematic diagram of the in-situ EIS experimental setup [147]. The measurements were taken at 633K and 18MPa, mainly in pure water (use of different electrolytes will be specified). Electrical feedthroughs were provided by Pt wires in cooled Teflon seal elements at the top of the autoclave. Tube-shaped zirconium samples served as the working electrodes. A perforated Pt cylinder served as coaxial reference electrode for an approximate distance of 0.5mm between the electrodes (preventing significant ohmic drop in the electrolyte) leading to a symmetrical two-electrode configuration. A two-electrode cell was used since electrochemical reactions at the Pt electrode are much faster than at the Zr electrode making the Pt electrode a very good quasi-reference electrode. Tube ends were isolated with spring-loaded Al₂O₃ ceramics exposing an outer surface area of about 8 cm². A Pt/Pt dummy cell of identical geometry was used for electrolyte conductivity monitoring. Autoclave EIS measurements were taken at the open-circuit potential at frequencies about 10⁻⁴ to 10⁶ Hz in a floating configuration. Indeed, the autoclave is not isolated from the ground so to avoid the interference of an unknown and possibly varying impedance between the elements and the ground, it is safer to work in a floating configuration with a PAR4000 potentiostat. A schematic of the potential profile corresponding to this Zr|ZrO₂|water|Pt cell is displayed in Figure 5-6.
The overall potential drop $\Delta V$ is equal to $V_M - V_{Pt}$ and thus is the sum of the potential drops across the oxide bulk and electrolyte and the active overpotential $\Pi_{O/M}$ and $\Pi_{O/W}$ at the oxide interfaces at equilibrium in corrosion conditions.
In order to perform EIS measurements on pre-corroded tube samples (see Chapter 2), it is necessary to connect the pre-corroded zirconium alloy tube to the potentiostat. Originally, on bare tubes, the connectivity was assured by a welding on the inside of the tube of a Zr-Sn wire [147]. The weld zone did not perturb EIS measurements (the EIS spectra were identical when the weld zone at the end of the tube was immersed or not in the electrolyte) and the electrical contact was not lost during autoclave corrosion. However, this technique is difficult to reproduce on pre-corroded samples for several technological and experimental reasons:

- It is necessary to remove the oxide on a local spot. This removal will induce sample-to-sample variability.
- The “strength” of the welding is not assured because of the presence of oxide around it.
- Even though the weld zone did not perturb EIS measurements, visual observation showed that it did perturb corrosion locally [147].

Thus there was a need to develop a new experimental design and the possibility to connect the tubes by screwing an end plug in Zircaloy-4 on which a Zircaloy-4 wire is connected (see Figure 1) was investigated (see Figure 5-7).

![Diagram](image)

Figure 5-7. Different parts of the working electrode mounting design.

The electrical conductivity of the contact between the cap and the tube needs to be measured after autoclave corrosion since oxide could form in the screw thread and impact the overall electrical response of the cell. An impedance scan under dry conditions has been performed before corrosion and a second one after 10 days of corrosion in primary water in
autoclave at 360°C. The two measurements were superimposed on each other, which confirmed that no perturbation of local oxidation of the tube/cap contact is to be expected in the measurements.

The amplitude of the applied alternative potential $U_{ac}$ is an important parameter: if it is too high, the linearity of the electrochemical response is not ensured and if it is too low, the signal-to-noise ratio will be poor. So long as $U_{ac} < k_B T / e \sim 55$ mV at 633K ($k_B T / e$ is the thermal voltage, where $k_B$ is the Boltzmann constant and $e$ is the electron charge), it can be shown that the basic differential equations governing the response of the system become linear to an excellent approximation [172]. EIS spectra on a pre-oxidized Zircaloy-4 sample have been recorded for different $U_{ac}$ (the Bode plots are displayed in Appendix D) and it is observed that $U_{ac} = 50$mV is a reasonable choice.

5.4. Results

5.4.1. General experimental observations

An example of Bode plots acquired on a Zircaloy-4 sample is shown in Figure 5-8 before and after corrections for the series electrolyte impedance $R_e$, plotted along with previously performed measurements.
The shapes of the plots are in very good agreement with previous experiments [147]. The only significant difference is that a phase relaxation peak is observed at low frequency in [147], and which is absent in the Zr4 spectra. This was expected, since this peak has been ascribed to a phenomenon occurring closer to transition, and the Zr4 sample used here is far from transition (22 days) compared to the ZrSn sample studied in [147] (75 days). Spectra are highly dispersive and, as seen after correction for the series electrolyte term (filled symbols in Figure 5-8), at higher frequencies they are dominated by the capacitive contribution of the oxide (real part of the

Figure 5-8. Real impedance and phase plotted as function of frequency of a pre-corroded Zircaloy-4 sample and compared to ZrSn [147]. The unfilled symbols are raw data, and the filled symbols are corrected for the electrolyte impedance.
impedance equals to zero and the phase to 90°). The spectra measured experimentally in Figure 5-8 before corrections shows a shape similar to the theoretical shape shown in Figure 5-1 and Figure 5-4.

As detailed in the previous section, at high frequencies the oxide layer can be considered as a pure capacitor. It is also observed in Figure 5-8 that the real impedance at low frequency tends towards a plateau as the phase goes to zero indicating a pure resistive behavior of the system. This trend was expected from the theory and the low frequency impedance of the system is a combination of the interfacial oxide/water resistance and the bulk oxide resistance. Thus, in order to determine the bulk oxide resistance, one needs to evaluate the significance of the oxide/water interfacial resistance.

In order to evaluate the influence of the oxide/water interfacial impedance on the total impedance recorded at low frequency, EIS spectra of a pre-corroded Zircaloy-4 sample (δ~1μm) were acquired in electrolytes with different Li concentrations (2.2ppm, 4.4ppm and 8.8ppm). It is indeed believed that Li should at least have an impact on the oxide/water interfacial reaction (probably by reducing the impedance) [174]. It has also been shown that even though Li has an effect on the interface, it does not affect the oxidation and hydriding kinetics at low concentrations [175]. If no measurable influence of Li concentrations is observed on the low frequency impedance of the EIS spectra then one can be confident that the measured impedance is indeed solely due to the bulk oxide impedance and that the interfacial impedance is negligible.

5.4.2. Effect of lithium concentration on EIS measurements

A two-cell geometry was used. The first cell consisted of a Pt tube surrounded by a coaxial Pt quasi-reference electrode (dummy cell), whereas the second cell consisted of a Zircaloy-4 pre-oxidized tube surrounded by a similar Pt quasi-reference electrode. The cells were
immersed in an electrolyte in the autoclave at 360°C. The starting electrolyte is pure water into which Li injections were performed to reach Li concentrations of 2.2ppm, 4.4ppm and 8.8ppm. Electrolyte samples were tested for Li concentrations before any further injection in the autoclave. Two different EIS spectra were acquired for every Li concentrations between:

- Pt tube/ Pt ref electrode (to determine the evolution of electrolyte resistivity as function of Li concentration).
- Zr4 tube/ Pt ref electrode.

5.4.2.1. Electrolyte conductivity measurements (Pt/Pt electrochemical cell)

The geometry of the Pt tube/ Pt ref electrode cell is similar to a cylindrical capacitor of length \( L > r_2 \) as seen in Figure 5-9. If \( r_1 < r < r_2 \) the current intensity \( I \) is defined in terms of current density \( \vec{j} \) and the surface \( S \) as:

\[
I = \iint \vec{j} \cdot d\vec{S} = \iint j_r \, dS \, \vec{e}_r = \iint j_r \, dS = 2\pi r L j_r
\]  

where \( L \) is the tube length and \( j_r \) the current density in the radial direction.

Ohm’s law gives: \( \vec{j} = \sigma \vec{E} \rightarrow j_r = \sigma E_r = -\sigma \frac{\partial V}{\partial r} \)

Thus:

\[
\int dV = - \int \frac{j_r}{\sigma} dr = - \frac{I}{2\pi \sigma L} \int \frac{dr}{r} = \frac{I}{2\pi \sigma L} \ln \left( \frac{r_1}{r_2} \right)
\]

Figure 5-9. Top view of the cell geometry.
Thus the electrolyte impedance is equal to:

\[ R = \frac{1}{2\pi \sigma L} \ln \left( \frac{r_1}{r_2} \right) \]  

(5-9)

The limiting ionic conductances \( \lambda \) for both Li\(^+\) and OH\(^-\) (in S.cm\(^2\)) have been found in the literature at different temperatures up to 300°C [176]. An interpolation was performed to estimate the limiting ionic conductance at 360°C (see Figure 5-10).

![Figure 5-10. Interpolation of the limiting ionic conductance at 360°C.](image)

The specific ionic conductivity of the electrolyte can be determined using the following formula:

\[ \sigma = \frac{d_{water}}{1000} \times 10^{-3} \sum m_i \lambda_i \]  

(5-10)

where \( m_i \) is the mass of the different ions in wt.ppm. The density of water, \( d_{water} \), at 360°C and 180 bars is equal to 0.53 g/cm\(^3\). Thus the theoretical impedance of the electrolyte in the cell geometry described in Figure 5-9 can be calculated and is displayed in Table 5-1 for various concentrations of LiOH (since LiOH is a strong base, it is totally dissociated in water).
The Bode plots of the impedance spectra acquired at different LiOH concentrations between the Pt tube and the Pt ref electrode are presented in Figure 5-11. The modulus of the impedance decreases as the Li concentration increases (see Figure 5-11 (a)). Consequently, the impedance of the system decreases as the LiOH concentration increases. This was expected, since the electrolyte should be more conductive when more ions are available to conduct the current. The change in slopes of the modulus of the impedance is directly related to phase relaxation peaks (see Figure 5-10.b). The significance of the electrochemical phenomena related to the relaxation peaks is also concentration dependent. The impedance of the electrolyte is measured at high frequency (between $10^3$Hz and $10^4$Hz) and is reported in Table 5-2.

An effect of the Li concentration is clearly observed on the two different time constants around 200 Hz and 0.1Hz, suggesting that the interfacial reaction Pt/electrolyte is indeed affected by Li.

The results in Table 5-1 and Table 5-2 are plotted in Figure 5-13. It is observed that the theoretical impedance matches the results of the actual measured impedance. These experiments tend to validate the experimental setup since the measurements are in agreement with the theory.

Table 5-1: Theoretical electrolyte impedance at different LiOH concentrations

<table>
<thead>
<tr>
<th>LiOH concentration (g/L)</th>
<th>Li$^+$ concentration (wt-ppm)</th>
<th>Electrolyte impedance (Ω) (theory)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1.3 \times 10^{-2}$</td>
<td>2.2</td>
<td>30</td>
</tr>
<tr>
<td>$2.7 \times 10^{-2}$</td>
<td>4.4</td>
<td>14</td>
</tr>
<tr>
<td>$5.4 \times 10^{-2}$</td>
<td>8.8</td>
<td>7</td>
</tr>
</tbody>
</table>
Figure 5-11. Bode plots (modulus and phase) of the Pt tube/Pt ref system for different electrolytes

Table 5-2: Measured electrolyte impedance

<table>
<thead>
<tr>
<th>LiOH concentration (g/L)</th>
<th>Electrolyte impedance (Ω) (measured)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1.3 \times 10^{-2}$</td>
<td>29</td>
</tr>
<tr>
<td>$2.7 \times 10^{-2}$</td>
<td>16</td>
</tr>
<tr>
<td>$5.4 \times 10^{-2}$</td>
<td>7</td>
</tr>
</tbody>
</table>
5.4.2.2. Effect of LiOH on the zirconium oxide impedance measurements (Zr/Pt electrochemical cell)

As detailed before, four different electrolytes have been used: pure water, 2.2ppm of Li, 4.4ppm of Li and 8.8ppm of Li and the sample oxide thickness was approximately 1µm. Before acquiring Zircaloy-4 EIS spectra, the system was left at high temperature for 2 days so that it was at equilibrium when the EIS spectra were acquired. The autoclave remains at temperature for approximately 4 days before cooling for further Li injection. Thus at the end of the experiments, the Zircaloy-4 sample is supposed to be still far from transition and, since not much oxide is supposed to have formed during the 16 days of oxidation required by the experiment, the EIS spectra can be readily compared to each other. The averaged impedance (between $10^{-4}$ and $10^{-3}$ Hz) is plotted as function of the electrolyte Li concentrations in Figure 5-13.
No significant influence of Li concentrations on the low frequency system impedance is observed, up to a concentration of 8.8ppm of Li. Thus the oxide/water interfacial impedance is supposed to be negligible and the measurement of the low frequency impedance is directly related to the bulk resistance of the oxide (see eq.5-2):

\[
Z(\omega \to 0) \sim R_e + \sum_{i=0/\text{ox}} R_i \sim R_e + R_{\text{ox}}
\]  

(5-11)

### 5.4.3. EIS experiments on pre-oxidized Zircaloy-4 tube samples in pure water

The corrected modulus and phase of a selected number of archived Zircaloy-4 tube samples are plotted in Figure 5-14 along with the weight gain kinetics of this alloy reproduced from Chapter 2. It is observed that both the modulus and the phase of the electrochemical response evolve with exposure time and oxide thickness. Analyzing the modulus evolution of the oxide layer impedance, it is concluded that it increases as the protective oxide thickness increases with a general aspect close to the expected trends in Figure 5-1 and Figure 5-4. The phase also
evolves as function of oxide thickness. Two phase relaxation peaks are observed with largely different time dependences (around 1kHz and 1Hz, arrowed) and their relative significance changes as function of exposure time. These two relaxation peaks have also been observed in [147] but at slightly larger frequencies. The significance phase relaxation peak at 10kHz appears to be related to the transition since at 150 days (closer to 1st transition) and 240 days (closer to 2nd transition) the relaxation peak is more marked. The precise analysis of these spectra in terms of oxide thickness and resistivity is the subject of the next section.

5.4.3.1. Oxidation kinetics

The measurements have been performed in pure water since it was observed that the potential drop across the working and reference electrodes is small in pure water and it was reasonable to use the original corrosion medium. The same general observations as in Figure 5-8 on the EIS spectra can be drawn. The evolution of the oxide thickness deduced from the plane capacitor formula (see eq.) is plotted in Figure 5-15 (filled dots).

To determine the oxide thickness from EIS measurements, it is supposed that the oxide layer acts as a pure capacitor at high frequencies. The capacitance is then equal to $1/(2\pi jZ'' f)$ with $Z''$ the imaginary part of the complex impedance and $f$ the imposed voltage frequency. The plane capacitor formula (see eq.5-4) is used to deduce oxide thickness with $\varepsilon = 24$ and $f = 0.6\text{kHz}$ Values of zirconia dielectric constant $\varepsilon$ ranges from 18 to 25 [147]. Reasons for $\varepsilon$ variability stems from experimental design, materials heterogeneity, various means of analysis… It was decided to take $\varepsilon$ as a fitting parameter whose value was to be adjusted in the range of previous results. The experimental oxide thickness and its power law fit are also plotted for comparison. The oxide transitions are also indicated at 130 days and 263 days of exposure.
Cole-Cole representations were not used to extrapolate the capacitance at high frequencies as their use at high temperatures is not straightforward [177].

Figure 5-14. Bode plots of selected Zircaloy-4 samples and weight kinetics of Zircaloy-4 tube alloy.
Although one can observe significant scatter in the data (especially right after transition), the evolution of the capacitance in series is similar to that of the oxide thickness. The difference observed in the weight gain deduced from EIS spectra might come from the use of sister samples instead of a single sample in the EIS experiment or from the low value of the frequency. Indeed, a phase relaxation peak is observed around $f = 1\text{kHz}$ (see Figure 5-13) so that the derived capacitance might be affected by the evolution of the phenomena related to this high frequency relaxation peak. It has indeed been suggested in the literature that at this frequency, only the dense oxide layer is probed by EIS measurements \cite{56, 147}. Using a capacitance determined at a higher frequency (further away from this peak) would have also been questionable because of the removal of the series electrolyte term affecting the results in this frequency range. Consequently, the results shown in Figure 5-15 show that using the plane capacitor formula on sister samples is not an accurate method to determine oxidation kinetics because high frequency measurements are subjected to variations due to the use of sister samples.

Figure 5-15. Oxide thickness deduced from EIS spectra and from weight measurements in Zircaloy-4. The fit of the oxide thickness measurements and the transitions are also plotted.
5.4.3.2. Oxide resistivity

The averaged value of the impedance over the last frequency decade (from $10^3$Hz to $10^4$ Hz) on the Bode plots has been measured to determine the oxide resistivity (as discussed in previous sections). This method has been chosen instead of extrapolating the Nyquist plots to $f=0$ (where the plot crosses the real axes) to avoid any further errors in the measurements. Also the exact absolute value of the oxide resistivity was not the main purpose of this study but rather its evolution from sample to sample is investigated here.

Since not all the samples have the same surface and oxide thickness, a geometric factor has to be applied to properly compare their oxide resistivity. The non-integral Ohm’s law is given by:

$$\vec{j} = \sigma \cdot \vec{E} \tag{5-12}$$

where $j$ is the current density in A.cm$^2$, $\sigma$ the oxide conductivity in (Ω.cm)$^{-1}$ and $E$ the electric field in V.cm$^{-1}$. Considering cylindrical coordinates and the symmetry of the system $j = j_r \cdot \vec{e}_r$ ($j_r$ being the current density modulus in the radial direction, and $\vec{e}_r$ the basis vector in the radial direction), and we can rewrite eq.5-12 in a scalar form:

$$j_r = \sigma E_r = -\sigma \frac{\partial V}{\partial r} = -\sigma \frac{\Delta V}{\Delta r} \tag{5-13}$$

where $E_r$ is the electric field vector component in the radial direction.

Using $I = j_r \cdot S$, where $I$ is the current intensity in A and $S$ the sample surface and considering that $\Delta r = \delta$, the oxide thickness (the voltage drop should occur mostly across the oxide):

$$\frac{I}{S} = -\sigma \frac{\Delta V}{\delta} \rightarrow \Delta V = -\frac{\delta}{\sigma S} \cdot I = -\frac{\rho \delta}{S} \cdot I \tag{5-14}$$

where $\rho = 1/\sigma$ is the oxide resistivity.

The impedance of the system $Z$, is measured by the potentiostat using the integral Ohm’s law:

$$\Delta V = Z \cdot I \tag{5-15}$$
Finally, since eq.5-14 and 5-15 are equivalent:

\[ \rho = \frac{ZS}{\delta} \]  

(5-16)

In conclusion, a geometrical factor \( S/\delta \) must be applied on all measurements to compare the oxide resistivity of different samples. The measured oxide resistivity (in \( 10^6 \, \Omega \cdot \text{cm} \)) is plotted in Figure 5-16 as function of exposure time on selected Zircaloy-4 archived samples.

![Figure 5-16. Oxide resistivity as function of exposure time in Zircaloy-4 tube](image)

The measured oxide resistivity varies between 20 to 140 M\( \Omega \cdot \text{cm} \) and is in very good agreement with the expected values of yttria stabilized zirconia at 360\( ^\circ \)C [171]. If the oxide microstructure does not change, the oxide resistivity is a material property, and should be independent of oxide thickness. However, as observed in Figure 5-16 that the resistivity varies as function of exposure time, indicating a change in oxide properties and in the resistance to charge transport in the oxide as the oxide grows. Basically, Figure 5-16 shows that as the oxide grows, there is a cyclic behavior to the resistance to charge transport across the oxide, increasing up to transition and decreasing at transition. These results confirm the hypothesis made in [56] about the degradation of the quality (in terms of charge transport) of the oxide layer as the oxide grows.
These results on archived samples are compared with the instantaneous hydrogen pickup fraction of these particular archived samples in Chapter 7 to assess the hypothesis made in Chapter 3 about the possible correlation between the oxide resistivity and the hydrogen pickup mechanism. The motivation behind using sister samples in this experiment is that the exact experimental $f_H^i$ are available for these particular samples, so that a direct correlation between oxide resistivity and $f_H^i$ can be made. However, it is of interest to follow the evolution of the oxide resistivity in-situ on a single sample even though $f_H^i$ on this sample has not been measured experimentally (indeed the continuous instantaneous hydrogen pickup fraction as function of exposure time is available from weight gain and hydrogen content fits – see Chapter 2). Also, comparing different alloys together would certainly indicate some alloying element effects on the oxide electric properties. This is the subject of the next section.

5.4.4. **Ageing of zirconium alloys followed by in-situ EIS**

Following the encouraging results on archived Zircaloy-4 samples, the ageing of three different alloys - Zircaloy-4, Zr-2.5Nb and Zr-2.5Nb-0.5Cu - has been investigated by in-situ EIS.

5.4.4.1. **Bode plots and potential measurements**

EIS spectra have been recorded at different time intervals from approximately $10^3$Hz to $10^4$Hz for the three different alloys. The results are displayed in Figure 5-17.
Figure 5-17 Bode and Nyquist plots of (a) Zircaloy-4, of (b) Zr-2.5Nb and of (c) Zr-2.5Nb-0.5Cu at different exposure times (CONTINUED NEXT PAGE).
Figure 5-17. Bode and Nyquist plots of (a) Zircaloy-4 and of (b) Zr-2.5Nb and (c) Zr-2.5Nb-0.5Cu at different exposure times (CONTINUED NEXT PAGE).
Figure 5.17. Bode and Nyquist plots of (a) Zircaloy-4 and of (b) Zr-2.5Nb and (c) Zr-2.5Nb-0.5Cu at different exposure times.
The results show marked changes of the impedance as function of exposure time and significant differences among the three alloys. Both Zr-2.5Nb and Zircaloy-4 alloys show phase relaxation peaks at $10^2$Hz and 0.5Hz which increase as the oxide grows. Both Zr-2.5Nb-0.5Cu and Zircaloy-4 show another phase relaxation peak at lower frequency, around $10^2$Hz, and which is absent from Zr-2.5Nb. The Nyquist plots show multiple depressed semi-circles. These semi-circles are associated to the phase relaxation peaks and each of them represents a particular physical process. However it is not the purpose of this study to investigate the nature of these phenomena. The semi-circles being depressed, it is concluded that the oxide show a significant amount of dispersion, probably related to its inhomogeneity (cracks, precipitates,…) [166].

The potential between the Zr tube sample and the coaxial Pt ref electrode as defined in the schematic of Figure 5-5 has been measured as function of exposure time and is plotted in Figure 5-18 for the different alloys. The potential decreases as a function of exposure time as observed in [147]. It is believed that the dissolved hydrogen in solution gets trapped in the cold region of the autoclave so that the amount of hydrogen dissolved decreases as function of exposure time. The potentials at the Pt half-cell electrode is given by the Nernst equation:

$$E_{(H^+/H_2)}^{Pt} = E_{(H^+/H_2)}^{0 Pt} + \frac{2RT}{F} \log \left( \frac{[H^+]}{P_{H_2}} \right)$$  \hspace{1cm} (5-17)

As a result of the decrease in the hydrogen pressure, the potential at the Pt reference electrode increases (see eq.5-17) and the potential difference between the two electrodes increases as well. It is actually observed that after $H_2$ injection into the autoclave, the potential difference goes back to its initial value.
5.4.4.2. Oxidation kinetics

Following the same analysis performed previously on archived samples (see section 5.4.3), the sample oxide thickness can be calculated from the extrapolation of the capacitance at infinite frequency. The results are plotted in Figure 5-19 along with the weight gain measurements and the weight gain fit functions for the different alloys.

The oxidation kinetics determined from weight gain measurements and EIS data analysis at high frequencies (eq.5-4 with $f=13-50$ kHz and $\varepsilon=24$) in Figure 5-19 agree very well. However, after 30 days of exposure, Zircaloy-4 oxidation kinetics deduced from EIS spectra analysis diverges (not reproduce here). It is indeed observed that in the Bode plots in Figure 5-17 (a) of Zircaloy-4, the impedance slope at high frequency unexpectedly increases as function of exposure time. The reason for this behavior has not be found for the moment.
Compared to Figure 5-15 showing oxidation kinetics determined from archived sister samples, the use of a single sample appears to significantly improve the accuracy of the oxide thickness measurements as function of exposure time.

Figure 5-19. Oxidation kinetics of Zircaloy-4, Zr-2.5Nb and Zr-2.5Nb-0.5Cu followed by weight gain measurements and EIS.
5.4.4.3. Oxide resistivity

The oxide resistivity of the alloys at different exposure times has been determined as detailed previously. However, in this case, since the oxide thickness is not known from weight gain measurements, it is assumed that the oxidation kinetics of the sample follows the oxidation kinetics fit determined from sister samples (see Chapter 2). The results along with the results on archived samples are shown in Figure 5-20.

Firstly, the oxide resistivity trend determined from results acquired on a single sample at different exposure times is in good agreement with previous results on archived samples as it is observed in Figure 5-20 (a). This gives more confidence on the overall quality and accuracy of the oxide resistivity measurements made on archived samples. This trend seems to confirm that the oxide resistivity increases as the oxide grows.

Unfortunately, only a few data points are available at that moment because the experiment had to be stopped due to unexpected experimental difficulties. Indeed, after approximately 40 days of oxidation, the electric contact between the cap and the tube (see Figure 5-7) has been lost because of oxidation of the screw path. Before performing the in-situ experiment on a single sample, this connection was only tested for 10 days of corrosion and the results were satisfactory (there was still an electrical contact), but it appears that after further exposure the screw path eventually gets oxidized. Thus only a few data points are available for Zircaloy-4 and only one data point is available for Zr-2.5Nb-0.5Cu and Zr-2.5Nb alloys and no conclusive observations can be drawn at that moment from the in-situ experiments. A solution is being put in place at the moment to melt a Zr wire to the tube and remove the cap from the design. The experiment should restart in the near future. In any case, a certain number of conclusions can be made from the observed experimental results.
Figure 5-20. Oxide resistivity in MΩ.cm of archived and single samples as function of exposure time for Zircaloy-4, Zr-2.5Nb and Zr-2.5Nb-0.5Cu alloys. The weight gain fits are also plotted in a different axis.
5.5. Conclusions

To measure oxide resistivity in-situ, an autoclave designed for electrochemical impedance spectroscopy studies has been set up. After proper validation of the experimental setup, measurements of oxide resistivity of oxides grown on zirconium alloys have been performed. Several key conclusions are deduced from these EIS experimental results:

- **A new EIS cell setup** has been designed on archived samples for studies of short exposure times and the results agree very well with the literature (in terms of Bode spectra and oxide resistivity values).

- The EIS experiment presented in that study is going further than previous reported experiments in relating EIS results to oxidation kinetics. Indeed the samples used were well characterized (oxide thickness, hydrogen pickup, microstructure) so that EIS measurements could be related to these characterizations.

- Zirconium oxide shows a significant amount of dispersion as shown by the depressed semi circles in the Nyquist plots. This dispersion could be related to inhomogeneity in the oxide such as cracks or precipitates (see Chapter 4), which would result in space charges. Further work is needed to relate the amount of dispersion to oxide microstructure.

- Assuming that [Li] in the electrolyte affects the oxide/electrolyte interfacial impedance, it has been verified that this impedance is indeed negligible compared to the bulk oxide impedance. Thus, the oxide resistivity is directly measurable from EIS measurements.

- The measured Zircaloy-4 oxide resistivity ranges from 10 to 140 MΩ.cm in accordance with literature values.
• **The oxide resistivity is not constant** but varies as function of oxide thickness. It is clearly observed from the measurements that oxide resistivity follows a cyclic behavior (as oxidation kinetics), *increasing up to transition and decreasing before or at transition*.

• Consequently the resistance to electron transport varies as function of protective oxide thickness $\delta_p$, being smaller for small $\delta_p$ and greater as $\delta_p$ increases. This suggest that *microstructural or chemical variations of the oxide take place as the oxide grows that would alter the electron transport from the oxide /metal interface to the oxide/water interface*. These results directly demonstrate hypotheses made in the literature about a possible *degradation of the quality of the zirconium oxide layer in terms of electron transport*.

• The oxide resistivity as function of exposure time trend of the in-situ experiment on a single sample appears to follow the one determined from archived samples. Conclusions on the variations of oxide resistivity between alloys could not be made because of the scarcity of data points but it *would appear that oxide resistivity of Zr-2.5Nb and Zr-2.5Nb-0.5Cu is smaller compared to Zircaloy-4* at similar oxide thickness.
Chapter 6

Corrosion models of zirconium alloys

This chapter presents various successively complex models from the well-known Wagner oxidation theory [35] to the more complex effect of space charge on oxidation kinetics [81]. The general purpose of the modeling effort is to provide a rationale for the sub-parabolic oxidation kinetics and demonstrate the correlation with hydrogen pickup kinetics developed in Chapter 3.

6.1. General motivation of the models

The objective of the models is to provide a rationale for the observed oxidation kinetics. These models arrive at the kinetics by solving the diffusion equation in the oxide layer:

\[
J_s = -D_s \frac{dC_s(x)}{dx} + \mu_s E(x)C_s(x)
\]  

with \(J_s\) the flux of particles (in particles.cm\(^{-2}\).s\(^{-1}\)), \(D_s\) the diffusion coefficient (in cm\(^2\).s\(^{-1}\)), \(C_s(x)\) the concentration of the particles at the distance \(x\) from the oxide/metal interface (in particles.cm\(^{-3}\)), \(\mu_s\) the mobility (in cm\(^2\).V\(^{-1}\).s\(^{-1}\)) and \(E(x)\) the oxide electric field (in V.cm\(^{-1}\)) to determine the anionic current responsible for oxide growth to a given oxide thickness. The potential across the oxide is divided into 3 parts: the two potential drops at the oxide interfaces, which control the interfacial reactions and the potential drop in the oxide layer, which controls the transport of species across the oxide as shown in Figure 6-1.

The model is constructed based on the following hypotheses:

1. **Only the diffusion of doubly charged oxygen vacancies and electrons is considered.** As detailed in Chapter 1, zirconium oxide is a n-type semiconductor [38, 178, 179] and it is well established that the cation transport number is close to zero at normal operating conditions, which means Zr atoms do not diffuse in the oxide layer and the oxygen anion...
is the only diffusing ion in the oxide (proton diffusion is not considered) [31, 32]. The vacancy diffusion mechanism hypothesis is also well established [169] for corrosion of zirconium alloys at normal operating conditions.

![Diagram](image.png)

Figure 6-1. Scheme of the potential drop in the metal/oxide/solution system [180]

2. The **one-dimensional charge conservation law** can be written as follows:

   $$\frac{\partial J_s(x, t)}{\partial x} + \frac{\partial \rho(x, t)}{\partial t} = 0$$

   (6-2)

   We assume a quasi-steady state, so that $J_s$ is independent of $x$. The quasi-steady state limit is the nonzero particle current case obtained in the theoretical limit in which the boundaries of the oxide film are not moving relative to each other, and following a time lapse sufficient for all transient effects to disappear from the system. In this limit the particle currents are uniform throughout the lattice, having sources and sinks only at the interfaces and the interfacial potentials are at equilibrium before the formation of a new oxide monolayer.

3. The concentrations of species at the interfaces are fixed during the exposure time. This implies that the vacancy formation and the hydrogen evolution interface reactions are at equilibrium, their kinetics being much faster than the transport of species across the
oxide. The concentration values are imposed by the structure of the oxide/metal interface and the Nernst equilibrium, respectively. The diffusion of species across the oxide as the rate-limiting step has indeed been confirmed experimentally [181]. Also, the fact that oxidation kinetics depend on oxide thickness is an additional evidence of the diffusion of species being rate-limiting.

4. A direct consequence of the last assumption is that the interfacial potential drops are independent of oxide thickness so that only the potential drop across the oxide is allowed to vary as function of oxide thickness. Thus, the interfacial reactions are under steady-state conditions.

5. The composition of the metallic substrate, especially the oxygen concentration gradient in the metal ahead of the oxide, does not to affect the oxide growth.

6. The interfaces are planar. The waviness of the oxide/metal interface often observed in SEM is not considered.

7. **Hydrogen pickup is not considered.** Indeed the model has been developed to determine what would be the driving force for hydrogen pickup and how it would evolve as function of exposure time and parameters. **The evolution of this driving force for hydrogen pickup is not measurable experimentally because at equilibrium, it is screened by its counter balancing effect: the hydrogen pickup itself.** However, determining the presence and the evolution of the driving force is essentially equivalent to determining hydrogen pickup, so in order to simplify the model, hydrogen is not considered. Certainly there is a physical relationship between the driving force and hydrogen pickup but it is beyond the scope of this model to develop it explicitly.

8. **The coupled-current condition of a net zero charge transport through the film at all times:**
This assumption is less restrictive than the Wagner hypothesis of zero volume charge density 
\[ \sum_{i}^{all\ species} Z_i e J_s = 0 \] (6-3)
used in the Point Defect Model [182], the Mixed Conduction Model [183] or the Generalized Oxidation Model [180]. Electroneutrality hypothesis is indeed too strict especially in an oxide in which the dielectric constant is not negligible thus allowing it to sustain a certain amount of space charge so that locally, electroneutrality may not be verified.

Under the above assumptions **the formulation of the general corrosion model to solve** is as follows:

- The one dimensional diffusion equation linking the fluxes to the electric field and charged species concentrations (similar to eq.6-1).
- The Maxwell Gauss equation expresses the electric charge density as a source of electric field linking the charged species concentration to the local electric field, reducing the diffusion equation to a relationship between fluxes and concentrations.
- The coupled current equation is the assumption necessary to solve the one dimensional diffusion equation (eq.6-3).
- The boundary conditions are the concentrations of charged species at the interfaces.
- The relationship between the vacancy flux and the oxide thickness.

\[
\begin{align*}
  & \text{I – E law: } J_s = f(E, C_s) \\
  & \text{Maxwell – Gauss equation: } \frac{\partial E(x, t)}{\partial x} - \frac{\rho}{\varepsilon \varepsilon_0} = 0 \\
  & \text{Coupled current equation: } 2J_{V_0} - J_{e^-} = 0 \\
  & \text{\( \Delta \delta / \Delta t = f(J_{V_0}) \)} \\
  & \text{Boundary conditions: } C_{V_0}(\delta), C_{e^-}(\delta), C_{V_0}(0), C_{e^-}(0)
\end{align*}
\]
6.2. Homogeneous Field Parabolic Growth Law using Linear Diffusion Equation

6.2.1. Theory

Let us consider the diffusion of anion vacancies and electrons through the oxide film under conditions in which there are concentration gradients and a built-in electric field in the oxide (see section 1.2.1 for the interpretation of the built-in electric field).

The Gauss-Maxwell law rewritten locally (Poisson’s equation) is:

\[ \frac{d^2V(x)}{dx^2} = -\frac{4\pi}{\varepsilon\varepsilon_0}\rho(x) \]  

(6-4)

where \( V(x) \) is the electric potential at a position \( x \) in the oxide, \( \varepsilon \) the relative permittivity of \( \text{ZrO}_2 \), \( \varepsilon_0 \) the vacuum permittivity and \( \rho(x) \) the volumic charge density (coulomb.cm\(^{-3}\)).

By single integration of eq.6-4 along \( x \), the oxide depth, we obtain:

\[ \frac{dV(x)}{dx} = A - \int_0^x \frac{4\pi e}{\varepsilon\varepsilon_0}\rho(x) \]  

(6-5)

Where the constant \( A \) is equal to the surface charge electric field \( E_0 \) by evaluating eq.6-5 at \( x=0 \):

\[ A = \left. \frac{dV(x)}{dx} \right|_0 = -E_0 \]  

(6-6)

Thus we have the following equation for the electric field:

\[ E(x) = -\frac{dV(x)}{dx} = E_0 + \int_0^x \frac{4\pi e}{\varepsilon\varepsilon_0}\rho(x) = E_0 + E_{sp}(x) \]  

(6-7)

where \( E_{sp} \) is defined as the electric field due to space charge.

Two additional assumptions are made for the homogeneous field limit model:

9. In this section the space charge contribution to the built-in electric field \( E_{sp}(x) \) is neglected with respect to the surface charge field \( E_0 \). This means either that the space charge resulting from the differences in electron and vacancy local concentrations are
negligible or that the space charge is compensated by external factor such as aliovalent ions in the oxide. In either conditions: \( E_0 \gg E_{sp}(x) \) and the electric field \( E(x) \) in eq 6-7 can thus be replaced by the homogeneous electric field \( E_0 \) which is the same as the surface charge field and is independent of \( x \).

10. For a value of \( E_0 \) low enough that \( \frac{Z_s e E_0 a}{k_B T} \ll 1 \), then:

\[
\sinh \left( \frac{Z_s e E_0 a}{k_B T} \right) \sim \frac{Z_s e E_0 a}{k_B T} \rightarrow E_0 \ll 10^5 \text{V/cm} \tag{6-8}
\]

(eq.6-8 is going to be verified for oxide thickness greater than 20nm as detailed later in Figure 6-15), the linear diffusion equation can be used, which provides sufficient good approximation to deduce the various particle currents responsible for oxide growth under concentration and potential gradients in thick oxide films.

Under these assumptions, the current-potential relationship \( J_s = f(E) \) called linear diffusion equation is verified:

\[
J_s = -D_s \frac{dC_s(x)}{dx} + \mu_s E_0 C_s(x), s = e^-, V_0 \tag{6-9}
\]

where \( E_0 \) is the homogeneous electric field (in V.cm\(^{-1}\)). This equation simply relates the flux to the concentrations and electric driving forces. Thus the general problem can be rewritten in the homogeneous field approximation:

\[
\begin{cases}
1 - E \text{ law (linear diffusion equation):} & J_s = -D_s \frac{dC_s(x)}{dx} + \mu_s E_0 C_s(x) \\
\text{Maxwell – Gauss equation (electroneutrality):} & \frac{\partial E(x, t)}{\partial x} = 0 \rightarrow E(x) = E_0 \\
\text{Coupled current equation:} & 2J_{V_o} - J_{e^-} = 0 \\
J_{V_o} - \Delta \delta \text{ relationship:} & \Delta \delta = R_{V_o} J_{V_o} \Delta t \\
\text{Boundary conditions:} & C_{V_o}(\delta), C_{e^-}(\delta), C_{V_o}(0), C_{e^-}(0)
\end{cases}
\]

Where \( R_{V_o} \) is the volume of oxide formed for each anion vacancy which traverses the oxide film.

In this section \( \mu_s \) and \( D_s \) are assumed to be constant and independent of the defect concentrations and independent of the oxide thickness.
The particularity of this first development is that it accepts an analytical solution [184]. Thus, any error in the coding is easily traceable and the reliability of the code is easier to demonstrate. It is also easier to optimize the parameter’s values to match the experimental observations in that case. Thus, even if its applicability is limited (because of assumptions 9 and 10), it seems reasonable to start with this model before delving into more general and involved cases.

The mobility of a particle (electron or oxygen vacancy) is given by:

$$\mu_s = \frac{4Z_s e a^2}{k_B T} \nu e^{-\frac{E_m^s}{k_B T}} \times s = e^- V_0$$

(6-10)

where $2a$ is the jump distance, $k_B$ the Boltzmann constant, $T$ the temperature, $\nu$ the jump frequency, $E_m^s$ the migration energy and $e$ is the electron charge. The diffusion coefficient $D_s$ and the mobility $\mu_s$ are related through the well-known Einstein equation:

$$\mu_s = \frac{e Z_s D_s}{k_B T}$$

(6-11)

$Z_s$ being the electric charge of the particle.

Under these conditions, one can integrate the linear diffusion equation (eq.6-9) between the oxide/metal interface and the position $x$ in the oxide:

$$\int_0^x \frac{d}{dx} \left( C_s(x) e^{-\frac{\mu_s E_0 x}{D_s}} \right) = \int_0^x \frac{J_s}{D_s} e^{-\frac{\mu_s E_0 x}{D_s}}$$

(6-12)

$$C_s(x) = C_s(0) e^{-\frac{\mu_s E_0 x}{D_s}} + \frac{J_s}{\mu_s E_0} \left( 1 - e^{-\frac{\mu_s E_0 x}{D_s}} \right)$$

(6-13)

$C_s(0)$ being the concentration of particles at the oxide/metal interface.

Considering that the oxidation of zirconium alloys in normal operation is limited by the diffusion of charged species, $C_s(0)$ and $C_s(\delta)$ can be considered to be independent of the currents and therefore independent on film thickness $\delta = \delta(t)$. Solving eq.6-13 for the current between $x = 0$ and $x = \delta$ gives:
This equation is basically a current-potential relationship. In this homogeneous model, *even though space charges are allowed, their effects on diffusion are neglected*. The coupled current equation gives:

\[ 2j_{\nu_0} - j_e^- = 0 \]  \hspace{1cm} (6-15)

Let us define the non-dimensional parameter \( \eta \) as:

\[ \eta = e^{\frac{eE_0\delta}{k_BT}} \]  \hspace{1cm} (6-16)

Using eq.6-16, we can rewrite the particle current from eq.6-14 as:

\[ J_s = \mu_s E_0 \left( \frac{C_s(\delta) - C_s(0)e^{\frac{\mu_s E_0 \delta}{D_s}}}{1 - e^{\frac{\mu_s E_0 \delta}{D_s}}} \right) \]  \hspace{1cm} (6-17)

By inserting this equation in the coupled-current equation (eq.6-3) we get:

\[ 2\mu_{\nu_0} \left( \frac{C_{\nu_0}(\delta) - C_{\nu_0}(0)\eta}{1 - \eta^2} \right) - \mu_e^- \left( \frac{C_{e^-}(\delta) - C_{e^-}(0)\eta^{-1}}{1 - \eta^{-1}} \right) = 0 \]  \hspace{1cm} (6-18)

Once the two roots of this equation are found only one called \( \eta \) will be real and positive (see Appendix E-I for the derivation and the uniqueness of a physical root). The homogeneous electric field is thus defined as:

\[ E_0 = \frac{k_BT}{e\delta(t)} \ln \eta \]  \hspace{1cm} (6-19)

The electrostatic potential across the oxide due to the homogeneous field will be:

\[ V(x) = -E_0 x = -\left(\frac{k_BT}{e} \frac{x}{\delta(t)}\right) \ln \eta \]  \hspace{1cm} (6-20)

So that the total potential developed across the oxide film is constant and equal to:

\[ V(\delta) = -\frac{k_BT}{e} \ln \eta \]  \hspace{1cm} (6-21)

Also the anion vacancy current is given by rewriting eq.6-17:
\[ J_{V_o} = \mu_{V_o} E_0 \left( \frac{C_{V_o}(\delta) - C_{V_o}(0) \eta^2}{1 - \eta^2} \right) = \frac{\gamma_{V_o}}{\delta(t)} \]  \hspace{1cm} (6-22)

where \( \gamma_{V_o} \) is a constant given by:

\[ \gamma_{V_o} = \frac{k_B T}{e} \ln \eta \left( \frac{C_{V_o}(\delta) - C_{V_o}(0) \eta^2}{1 - \eta^2} \right) \]  \hspace{1cm} (6-23)

Thus the total growth rate is given by:

\[ \frac{d\delta(t)}{dt} = \frac{R_{V_o} \gamma_{V_o}}{\delta(t)} \]  \hspace{1cm} (6-24)

This gives us the homogeneous field parabolic growth law for zirconium corrosion:

\[ \delta(t) = \sqrt{2R_{V_o} \gamma_{V_o} t} \]  \hspace{1cm} (6-25)

No matter the rate limiting species (either electrons or oxygen vacancies) the oxidation kinetics are always parabolic!

6.2.2. Choice of parameters and code optimization

The Matlab code is detailed in Appendix E-II. This model needs eight different inputs to run: the concentrations of vacancies and electrons at the two interfaces, the migration energies for electrons and vacancies in the oxide, the jump distance for particles to migrate and the temperature. The temperature is set at 633K and the jump distance for particle migration is set at 0.5nm. The lattice parameter for electron untrapping is on the same order of magnitude [185]. Thus, for the sake of simplicity, the same lattice parameter is used for electron untrapping and vacancy migration.

It is supposed that the concentration of defects at the oxide/water interface is negligible so that \( C_{V_o}(\delta) \sim C_e(\delta) = 10^{17} \) particles/cm\(^2\) (the number of oxygen particles in
stoechiometric ZrO₂ being equal to \(5.55 \times 10^{22}\) molecules/cm\(^3\). The number of ZrO₂ particles per cm\(^3\) is given by:

\[
\frac{\rho_{\text{ZrO}_2}}{M_{\text{ZrO}_2}} \times N_A = \frac{5.68}{128.218} \times N_A = 2.67 \times 10^{22} \text{ molecules/cm}^3 = \frac{1}{R_{\text{V}_0}} \quad (6-26)
\]

The sub-stoichiometry at the oxide/metal interface is rather small and even though thermodynamic data predicts a sub-stoichiometry of 0.76% (ZrO\(_{1.985}\)) \([7]\), the oxygen deficiency has never been observed experimentally although we know ZrO₂ is sub-stoichiometric because of its black color (see Chapter 3). If we assume a sub-stoichiometry of 0.2% at the oxide/metal interface (ZrO\(_{1.996}\)), then \(C_{\text{V}_0}(0) \sim 5 \times 10^{19}\) vacancies/cm\(^3\). The electron concentration at the oxide/metal interface is chosen to compensate the charge so that \(C_e(0) \sim 10^{20}\) electrons/cm\(^3\).

The electron untrapping energy \(E_{m}^{e^-}\) and vacancy migration energy \(E_{m}^{V_0}\) are not well known. In order to determine the range of possible values for these two parameters, an optimization code has been written. The oxide thickness after 75 days of exposure has been chosen for optimization: \(1.5\mu m < \delta_{\text{opt}} < 3.5\mu m\). This range covers most of the oxidation kinetics observed in a protective regime (see Chapter 2). Both energies \(E_{m}^{s}\) are set to vary between 0.1eV and 2eV. The results are plotted in Figure 6-2, as a contour plot in which \(E_{m}^{s}\) are along the x and y axis whereas the oxide thickness \(\delta\) is along the z axis. The contour lines correspond to different values of \(\delta\) that are indicated. One can draw the conclusion that in order to grow oxide layers of the same order of magnitude as observed experimentally \(E_{m}^{s}\) have to verify:

\[
E_{m}^{e^-} < 1.45\text{eV and } E_{m}^{V_0} < 1.52\text{eV} \quad (6-27)
\]
Figure 6-2. Contour plots of $\delta$ as function of (a) $E_{m}^{V_{0}}$ and $E_{m}^{m-}$, (b) $C_{V_{0}}(0)$ and $C_{m-}(0)$. The lines show different values of oxide thickness.
If \( E_m^{e^-} \) exceeds these limits, the anodic current resulting from oxygen ion migration would be too small. This model taking into account both cathodic and anodic currents, it is interesting to notice that if the electron mobility is low (\( E_m^{e^-} > 1.45 \text{eV} \)), the oxide growth (and thus the anodic current) is equally limited (no matter how small \( E_m^{V_O} \) is assumed) because of the coupled current equation. Thus the modeling of oxide growth without taking into account the electronic properties of the oxide is not correct. Because of this, both the Point Defect Model and the Generalized Model contain hypotheses for oxide growth, which are too restrictive to quantitatively model zirconium oxidation.

In many electrochemical measurements available in the literature, electron transport mechanism theories have been fitted to I-V curves to estimate \( E_m^{e^-} \) (see Table 6-1), but no general agreement on the value of \( E_m^{e^-} \) has been reached on the subject. It is well known that the energy band gap of monoclinic \( \text{ZrO}_2 \) is rather large and greater than 4.5eV [186]. Since, in order to grow micrometer oxide scales, \( E_m^{e^-} \) has to be smaller than 1.45 eV, it is believed that the electron conduction arises from thermal ionization of shallow donor states or centers into the conduction band followed by relaxation into empty energy states in the band gap [51, 187] rather than by a valence to conduction band mechanism. The chemical nature of these centers cannot be straightforwardly determined by (photo-)electrochemical measurements but has been assigned in the literature to oxygen defects in the band gap [43, 169, 187-190]. Of particular interest is the oxygen vacancy energy defect level located approximately at 0.8eV for \( V_O \) and 1.2eV for \( V_O \) from the zirconia conduction band [186, 190]. Since it is supposed in the model that oxygen vacancies are present in the oxide layer, it appears reasonable to consider that electrons are trapped at anion vacancies [191, 192]. However, since most studies (including the present one) show a significant dispersion of the oxide properties as function of applied voltage frequency (see Chapter 5), it is probable that
there is an energy distribution of donor states rather than a single localized state below the conduction band. However, as a first attempt $E_{m}^{\text{e}^-}$ is set at a fixed value of 1eV.

Table 6-1: Electron untrapping energy in the literature

<table>
<thead>
<tr>
<th>$E_{m}^{\text{e}^-}$ (eV)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$0.2 &lt; E_{m}^{\text{e}^-} &lt; 0.4$</td>
<td>[168, 185]</td>
</tr>
<tr>
<td>$0.2 &lt; E_{m}^{\text{e}^-} &lt; 2$</td>
<td>[43]</td>
</tr>
<tr>
<td>0.5</td>
<td>[193]</td>
</tr>
<tr>
<td>0.65</td>
<td>[190]</td>
</tr>
<tr>
<td>$0.2 &lt; E_{m}^{\text{e}^-} &lt; 1$</td>
<td>[188]</td>
</tr>
<tr>
<td>$0.3 &lt; E_{m}^{\text{e}^-} &lt; 1.1$</td>
<td>[187]</td>
</tr>
</tbody>
</table>

As a sanity check, it is interesting to compare the $E_{m}^{\text{V}_0}$ upper limit from this model based on diffusion of charged species, to the $E_{m}^{\text{V}_0}$ in the case of oxide growth due to diffusion of neutral oxygen atoms solely under a concentration gradient. Since the oxygen atom is uncharged, there is no built-in electric field in that case and the linear diffusion equation is equivalent to the Fick’s law. Using the same parameters, an upper value of 1.36eV for $E_{m}^{\text{V}_0}$ is calculated. Thus, if the electric field and the cathodic current are included in the model, the available spectrum of $E_{m}^{\text{V}_0}$ is larger. This was expected because, if $\mu_{\text{V}_0} \ll \mu_{\text{e}^-}$, the electric field lowers the height of the actual energy barrier height $E_{m}^{\text{V}_0}$ by the amount $\alpha = 2eE_0x$, which allows larger $E_{m}^{\text{V}_0}$ for a similar anodic current. *This phenomenon similar to the Frenkel-Poole effect [51], models the thermal excitation of a charged species over a field lowered Coulombic barrier surrounded by a charge.*

In conclusion, the sanity check validates the value of $E_{m}^{\text{V}_0} < 1.52eV$.

A similar study has been done to investigate the sensitivity of the model to the electron and vacancy concentrations at the oxide/metal interface. The results are plotted in Figure 6-2 (b) as a contour plot in which $C_s(0)$ are along the x and y axis whereas the oxide thickness $\delta$ is along...
the z axis. The contour lines correspond to different values of δ (indicated aside of the contour line). It is observed that the model is much less sensitive to concentrations at the oxide/metal interface compared to the migration energies. Thus it seems rather reasonable to use the migration energies as fitting parameters rather that the concentrations.

This limit of $E_m^{\text{VO}}$ is smaller than the activation energy of oxygen vacancy $E_a^{\text{VO}} = 2.3 \text{eV}$ in ZrO$_2$ determined with tracer experiments [33] and is in agreement with the experimental and modeling results in [191, 194]. In order to estimate $E_m^{\text{VO}}$, the oxidation model has been fitted to the oxidation kinetics of Zr-0.4Nb model alloy which are the closest to parabolic $n \sim 0.49$ [39]. The experimental curve fit using a power law (dotted line) and the oxidation model (full line) are plotted in Figure 6-3. The fit gives $E_m^{\text{VO}} = 1.45 \text{eV}$, which is smaller than the predicted value of the vacancy activation energy in ZrO$_2$ bulk $E_a^{\text{VO}}$. Thus it is not surprising that the experimental value of $E_m^{\text{VO}}$ is smaller than the theoretical $E_a^{\text{VO}}$ based on bulk diffusion.

The voltage drop across the oxide depends only on the mobility difference between electrons and vacancies rather than on the migration and untrapping energies as seen in Figure 6-4.
Figure 6-3. Oxidation kinetics of Zr-0.4Nb model alloy along with its power law fit (dotted black curve) and the oxidation model (full line) developed in this section.

Figure 6-4. Electrical potential across the oxide as function of $E_{m}^{V0} - E_{m}^{e^-}$. The case under study in this section is indicated by a black dot on the curve.
Some conclusions can be drawn from the result shown in Figure 6-4:

i. **The potential drop across the oxide layer is constant.** Thus the homogeneous electric field $E_0$ decreases as function of exposure time (or oxide thickness).

ii. If $E^{V_0}_m - E^{-}_m < 0$ (the transport of vacancy being easier than the transport of electrons) then the potential across the oxide is positive and the homogeneous electric field is negative. **Thus the homogeneous electric field increases the flux of electrons and reduces the flux of vacancies to verify the coupled current equation.** The opposite case is also verified.

iii. The fact that the curve is not symmetric on 0 is due to the difference of charge between the electrons and the doubly charged oxygen vacancies.

iv. Above a certain magnitude in the difference of migration and untrapping energy (approximately 0.5eV), the electric potential reaches a threshold value (see eq.6-20). This is a state of virtual current equilibrium [195] in which the potential is constant and equal to:

$$ V = \frac{k_BT}{Z_se} \ln \left( \frac{C_s(0)}{C_s(L)} \right) $$

With the chosen parameters the potential limits are indeed -376mV and 169mV. The lower limit of the potential corresponds to the case where the oxide is a relatively good electronic conductor whereas the upper limit corresponds to the case where the oxide is a relatively good ionic conductor. These limiting cases are called virtual current equilibrium of that species which conductivity greatly exceeds its counterpart conductivity at any point in the oxide. A current nearly equal to zero for the most mobile species is due to the fact that forward and backward current nearly compensate each other. It also means that the flux due to the concentration gradient is almost equal but opposite to the flux due to the electric field. The oxide growth will be limited of course not by the species in virtual current equilibrium but by the other one defined as the rate
limiting step under the potential created by the most mobile species. \textit{As a consequence of these considerations only in these extreme cases can the term rate limiting species be correctly employed.}

### 6.2.3. Results

The results obtained running the Matlab code of the homogeneous field model discussed in the previous section are shown here (the code is displayed in Appendix \textbf{E-III}). The set of chosen parameters used for the calculation is summarized in Table \textbf{6-2}.

Table \textbf{6-2}: Set of parameters for the homogeneous electric field oxidation model

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electron untrapping energy ($E_{m}^{e^-}$)</td>
<td>1eV</td>
</tr>
<tr>
<td>Vacancy migration energy ($E_{m}^{V_o}$)</td>
<td>1.45eV</td>
</tr>
<tr>
<td>Migration distance ($a$)</td>
<td>5Å</td>
</tr>
<tr>
<td>Temperature ($T$)</td>
<td>633K</td>
</tr>
<tr>
<td>Concentration of vacancies at the O/M interface ($c_{V_o}(0)$)</td>
<td>$5 \times 10^{19}$ atoms/cm$^3$</td>
</tr>
<tr>
<td>Concentration of electrons at the O/M interface ($c_{e^-}(0)$)</td>
<td>$10^{20}$ atoms/cm$^3$</td>
</tr>
<tr>
<td>Concentration of vacancies at the O/W interface ($c_{V_o}(\delta)$)</td>
<td>$10^{17}$ atoms/cm$^3$</td>
</tr>
<tr>
<td>Concentration of electrons at the O/W interface ($c_{e^-}(\delta)$)</td>
<td>$10^{17}$ atoms/cm$^3$</td>
</tr>
</tbody>
</table>

Note that $E_{m}^{V_o} - E_{m}^{e^-} = 0.45$ eV, putting as at the black dot position in Figure \textbf{6-4}. This means that this case is close to a vacancy migration rate-limiting step. The electron and vacancy fluxes obtained from this model (see eq.6-22) are shown in Figure \textbf{6-5}. These fluxes are constant throughout the oxide depth because of the \textit{steady state assumption}. As expected, the fluxes decrease as function of exposure time and their decreases are exactly balanced since the \textit{coupled current equation (eq.6-3) is verified}. 
The homogeneous electric field (see eq.6-19) is plotted as function of exposure time in Figure 6-6. In the case studied its value is positive. Thus, in this case the rate-limiting step is the diffusion of vacancies (as it was expected from the differences in migration energies between the electrons and the vacancies). Note that the homogeneous electric field (or surface charge field) has the same sign as the rate limiting species.

Figure 6-5. Flux particle (vacancy and electron) as function of exposure time.

Figure 6-6. Homogeneous electric field as function of exposure time.
The effect of the homogeneous electric field can be evaluated using the electric field modification factor defined as:

\[ \xi = \frac{J_{V_{\text{Homogeneous Field Limit}}}}{J_{V_{\text{Zero field}}}} \]  

where \( J_{V_{\text{Zero field}}} \) is simply defined as the flux due to the concentration gradient (Fick’s law):

\[ J_{V_{\text{Zero field}}} = D_{V_{\text{o}}} \frac{(C_{0}^{V_{\text{o}}}) - (C_{L}^{V_{\text{o}}})}{\delta} \]  

The electric field modification factor is independent of time and is equal to 13. In our case, it shows that the electric field significantly impacts the oxidation kinetics by increasing the vacancy flux by a factor of 13.

The concentrations of vacancies and electrons as functions of normalized oxide position are plotted in Figure 6-7. The concentrations on a normalized oxide depth scale do not depend on exposure time (or oxide thickness), as expected since the parameters are independent of time. Thus the oxide properties are independent of time and the concentration profiles as function of normalized oxide depth are constant.

Figure 6-7. Electron and vacancy concentrations as function of normalized oxide depth
Because of the widely different mobilities between the two species \( (\mu_m^{V_0} \ll \mu_m^{e^-}) \), the electron concentration profile (the most mobile species) is noted to deviate somewhat from a nearly straight line behavior on the semi logarithmic plot, while the vacancy concentration profile (the rate limiting species) is somewhat horizontal until it takes a sudden plunge downward near the oxide/water interface. Qualitatively, there tends to be less curvature of the profiles for the most mobile species than for the species that is rate limiting. The electron mobility \( \mu_m^{e^-} \) calculated from the model is equal to \( 2 \times 10^{-8} \text{ cm}^2\text{ V}^{-1}\text{ s}^{-1} \). Even if it is rather low compared to other semi-conductor areas, it is in total agreement with the literature on zirconium corrosion \cite{43,188}.

One important aspect of the concentration profiles is the determination of the space charge in the oxide due to significant differences in species concentrations. Because in this model, the space charge contribution to the electric field is neglected, it is of interest to verify if this assumption is valid in this fundamental case. The space charge monolayer density is equal to \( 2a(2C^{V_0}(x) - C^{e^-}(x)) \) and, from Figure 6-7, goes through a maximum approximately at 75% of the oxide depth. This space charge arises from the simple fact that the coupled current equation is verified instead of the electroneutrality. The coupled current equation hypothesis is less strict and allows for a certain amount of space charge. However in this model the electric field emerging from space charge does not affect the kinetics itself.

6.2.4. Conclusions and limits of the homogeneous electric field limit oxidation model

The homogeneous electric field oxidation model, even though relatively simple, leads to interesting results and reproduces quite well the parabolic oxidation of Zr-0.4Nb alloy using meaningful parameters. However, its use is limited to parabolic oxidation kinetics whereas a majority of zirconium alloys present sub-parabolic oxidation kinetics (see Chapter 2 and 3). Also,
because the electric potential across the oxide (identified as the driving force for hydrogen pickup) is constant, the model cannot explain the observed variations in $f_H^d$ as function of exposure time. Another limitation is that space charges in the oxide are neglected. From Figure 6-7, the space charge is positive and thus, of the same sign as the homogeneous electric field (and of the rate limiting species). These observations lead us to predict that the space charging being the same sign as the rate limiting species, its effect would be to retard the homogeneous field limit kinetics [196]. The electric field due to space charge is proportional to the area between the two concentration profiles (see Figure 6-7) and thus its magnitude is dependent on oxide thickness. Basically, the thicker the oxide the greater the electric field due to space charge. The variations of electric field due to space charge as function of normalized oxide depth for various oxide thicknesses are plotted in Figure 6-8.

![Electric field due to space charge as function of normalized oxide depth.](image)

As expected, the electric field due to space charge increases with oxide thickness. It is much greater than the homogeneous electric field previously determined and thus should not be
neglected. In theory, the implementation of space charge is necessary and is discussed in the next section. However, it appears that in the particular case of Zr-0.4Nb oxidation, the homogeneous field model correctly fits the experimental data. This implies that that space charge effects might be compensated by other effects, such as niobium in substitution in the oxide layer with a lower valence than Zr$^{4+}$. The amount of niobium in substitution needed to compensate the space charge would be equal to:

$$\omega_{Nb^{m+}}(x) = \frac{M_{Nb} \times (2C^V_0(x) - C^e_0(x))}{(4 - m) \times N_a \times \rho_{ZrO_2}}$$  \hspace{1cm} (6-31)

where $\omega_{Nb^{m+}}$ is the amount of Nb$^{m+}$ (wt%) in solution in the oxide, $M_{Nb}$ is the molar mass of niobium and $\rho_{ZrO_2}$ is the density of ZrO$_2$. The results of eq.6-31 for $m = 2$ and $m = 3$ (corresponding to NbO and Nb$_2$O$_3$ oxides, respectively) are plotted in Figure 6-9. It is clear that there is more than enough niobium in solid solution in Zr-0.4Nb to compensate the space charge. Thus it is reasonable to consider that the homogeneous field limit model correctly predicts the oxidation of Zr-0.4Nb. XANES experiments tend to confirm that the Nb oxidation state is lower than 4+ in the oxide with the exception of the oxide/water interface where $m = 5$ [74, 140, 149]. In Figure 6-9, it is indeed observed that there is no significant space charge at the oxide/water interface so that $m = 5$ at the oxide/water interface is compatible with the homogeneous field model.
6.3. Non-homogeneous field limit with space charge oxidation model

The previous section showed that the development of a homogeneous field model, which does not account for space charge and, thus, produces results at variance with experiment. To address this, a more complete model is proposed with the full consideration of space charge.
6.3.1. Space charge theory

The purpose of this model is to explicitly solve the general equations without further assumptions (without hypotheses #9 and #10). To achieve this purpose, the oxide layer is decomposed into a lattice consisting of $N$ potential barriers of height $E^*_m$ for the $s$th diffusing species located at $x_k = (2k - 1)a, k = 1 \ldots N$, with $2a$ representing the jump distance between two potential minima. The scheme is depicted in Figure 6-10.

![Figure 6-10. Scheme of the discrete lattice and the effect of the built-in electric field on the potential energy diagram.](image)

The non-linearity between the electric field and the current arises from the electric field difference from potential maximum to potential maximum, because the areal densities ($n_K^c$) of the charged species in the intervening potential minima do not necessarily compensate (it is possible to have local space charge). Thus the electric field if high enough has a significant influence on the total barrier height.

The change in electrostatic potential between two successive potential minima is given by:

$$\Delta V_{k-1} = V_k - V_{k-1} = -2aE_k$$

(6-32)
Each particle current $J^s_k$ is the difference between the forward current $J^{s+}_k$ due to particles with areal density $n_{k-1}^s$ jumping from $x_{k-1}$ to $x_k$ through the $k$th potential maxima with frequency $v^s$ and the reverse current $J^{s-}_k$ due to the particles with areal density $n_k^s$ attempting the same barrier jump with the same frequency:

$$J^s_k = J^{s+}_k - J^{s-}_k$$  \hspace{1cm} (6-33)

The barrier height depends on the location of the particles because of the presence of the local electric field $E_k$ such that the barrier height in the forward direction is equal to $E_{m,k}^s - Z_s e E_k a$ and to $E_{m,k}^s + Z_s e E_k a$ in the reverse direction. Assuming Boltzmann statistics we have:

$$J^{s+}_k = n_{k-1}^s v^s e^{- \frac{(E_{m,k}^s - Z_s e E_k a)}{k_B T}}$$  \hspace{1cm} (6-34)

$$J^{s-}_k = n_k^s v^s e^{- \frac{(E_{m,k}^s + Z_s e E_k a)}{k_B T}}$$  \hspace{1cm} (6-35)

Using eq.6-33, eq.6-34 and eq.6-35, the particle current $J^s_k$ is equal to:

$$J^s_k = v^s e^{- \frac{(E_{m,k})}{k_B T}} \left( n_{k-1}^s e^{- \frac{Z_s e E_k a}{k_B T}} - n_k^s e^{- \frac{Z_s e E_k a}{k_B T}} \right)$$  \hspace{1cm} (6-36)

$$= 2a v^s e^{- \frac{(E_{m,k})}{k_B T}} \left( C_{k-1}^s e^{- \frac{Z_s e E_k a}{k_B T}} - C_k^s e^{- \frac{Z_s e E_k a}{k_B T}} \right)$$

And, the steady state assumption leads to (see eq.6-2):

$$J^s_k = J^s_{k+1}$$  \hspace{1cm} (6-37)

Thus the flux in eq.6-36 is independently of $k$:

$$J^s(t) = 2a v^s e^{- \frac{(E_{m,k})}{k_B T}} \left( C_{k-1}^s(t) e^{- \frac{Z_s e E_k(t) a}{k_B T}} - C_k^s(t) e^{- \frac{Z_s e E_k(t) a}{k_B T}} \right)$$  \hspace{1cm} (6-38)

The continuous electric field with space charge included is equal to:

$$E(x) = - \frac{dV(x)}{dx} = E_0 + \frac{4\pi e}{\varepsilon \varepsilon_0} \int_0^x \sum_s Z_s C_k^s \, dx$$  \hspace{1cm} (6-39)
By decomposition on the discrete \( x_k \) lattice:

\[
E_{k+1} = E_k + \frac{8\pi a e}{\varepsilon \varepsilon_0} \sum_s Z_s C^s_k
\]  

(6-40)

Thus the general formulation is as follows:

\[
\begin{align*}
\left. \begin{array}{l}
I - E \text{ law: } J^s(t) &= 2av^s e \left( \frac{E^s_{m,k}}{k_B T} \right) \left( C^s_{k-1}(t)e \frac{Z_s e E(x_k,t) a}{k_B T} - C^s_k(t)e \frac{Z_s e E(x_k,t) a}{k_B T} \right) \\
\text{Maxwell – Gauss equation: } E_{k+1} &= E_k + \frac{8\pi a e}{\varepsilon \varepsilon_0} \sum_s Z_s C^s_k \\
\text{Coupled current equation: } 2J_{V_0}(t) - J_e^-(t) &= 0 \\
 J_{V_0} - \Delta \delta \text{ relationship: } &\Delta \delta = R_{V_0} J_{V_0} \Delta t \\
\text{Boundary conditions: } C_{V_0}(-\delta), C_e^-(\delta), C_{V_0}(0), C_e^-(0)
\end{array} \right. 
\]

In the homogeneous field electric model \( E_k \sim E_0 \) because space charges were neglected, there were no dependences of \( E_k \) on \( C^s_k \). However if space charges are included one can easily perceive the following difficulty: \( E_k \) is needed to determine the fluxes allowing the calculations of the local concentrations which in turn modify the electric field... **This difficulty can be circumvented by means of an iterative procedure involving the coupled current equation and local steady state assumptions as detailed next.**

### 6.3.2. Growth of the 1\textsuperscript{st} monolayer

\( E_1 \) is defined as the electric field at the first monolayer surface, so that in the particular case of the 1\textsuperscript{st} monolayer growth, \( E_1 = E_\delta \). From Poisson’s equation (see eq.6-39):

\[
E_\delta = E_0 + \frac{8\pi a e}{\varepsilon \varepsilon_0} \left( 2C^0_{\delta} - C^e_{\delta} \right)
\]

(6-41)

And, using eq.6-38, the fluxes can be written as:
If \( \varepsilon_\delta \) is defined as:

\[
\varepsilon_\delta = \frac{8\pi ae}{\varepsilon \varepsilon_0} \left( 2C_0^V - C_\delta^- \right)
\]

Then, using eq.6-42 and 6-43:
There is only one unknown in the system of equations 6-45 and 6-46: \( E_0 \). To solve the problem and determine \( E_0 \) the coupled current equation 2\( J_v^0 = J_e^- \) (see eq.6-3) is used:

\[
j_v^0 = 2\alpha_0 v^0 \left( \frac{e_{m,\delta}}{k_B T} \right)
\left( C_0^V e^{2\alpha \left( E_0 + \epsilon_\delta \right)/k_B T} - C_0^V e^{-2\alpha \left( E_0 + \epsilon_\delta \right)/k_B T} \right) + \frac{\epsilon_\delta}{k_B T}
\]

\[
j_e^- = 2\alpha_e e^{-\frac{e_{m,\delta}}{k_B T}} \left( C_0^- e^{-\alpha \left( E_0 + \epsilon_\delta \right)/k_B T} - C_0^- e^{\alpha \left( E_0 + \epsilon_\delta \right)/k_B T} \right)
\]

To find \( E_\delta \) one can use eq.6-41 and: \( E_\delta = E_0 + \epsilon_\delta \)

### 6.3.3. General case: growth of the \( N^{th} \) monolayer

To describe oxide growth it is necessary to generalize the derivation above to the \( N^{th} \) monolayer. At the \( N^{th} \) monolayer, there will be 2\( N - 1 \) unknowns:

- 2\((N - 1)\) concentrations – the concentrations of electron and vacancy at the outer oxide interfaces are known.
- The homogeneous field (or surface charge field) \( E_0 \).

Correspondingly there are 2\( N - 1 \) equations:

- 2\((N - 1)\) flux equations due to the steady state assumption
- The coupled current equation

Thus we can solve this system of non-linear equations. The system of equations to be solved is:
For $k = 2$ to $N$

\[
\begin{cases}
\zeta_{k-1}^{V_0} \left( C_{k-2}^{V_0} \Phi_{k-1}^{-2} - C_{k-1}^{V_0} \Phi_{k-1}^{-2} \right) - \zeta_k^{V_0} \left( C_{k-1}^{V_0} \Phi_k^{-2} - C_k^{V_0} \Phi_k^{-2} \right) = 0 \\
\zeta_k^{e} \left( C_{k-2}^{e} \Phi_{k-1}^{-1} - C_{k-1}^{e} \Phi_{k-1}^{-1} \right) - \zeta_k^{e} \left( C_{k-1}^{e} \Phi_k^{-1} - C_k^{e} \Phi_k^{-1} \right) = 0 \\
2V_0 q_0 \left( C_0^{V_0} \Phi_1^{-2} - C_{-1}^{V_0} \Phi_1^{-2} \right) - \nu e \zeta_0 \left( C_{-2}^{e} \Phi_1^{-1} - C_{-1}^{e} \Phi_1^{-1} \right) = 0
\end{cases}
\]

Where:

\[
\zeta_k^{e} = e^{-\frac{E_{m,k}}{kB_T}}
\]

\[
\Phi_k = e^{\frac{ea(E_0 + \sum_{j=1}^{k} \epsilon_j)}{kB_T}}
\]

Here $\epsilon_j$ is defined in each monolayer of thickness $2a$.

**This system can be rewritten in a vector-like fashion** defining:

\[
\lambda = \begin{bmatrix} C_1^{-}, & C_1^{V_0}, & C_2^{-}, & C_2^{V_0}, & \ldots, & C_{N-1}^{-}, & C_{N-1}^{V_0}, & E_0 \end{bmatrix}
\]

\[
F(\lambda) = \begin{bmatrix}
\begin{cases}
V_0 \left( C_1^{-}, C_1^{V_0}, C_2^{-}, C_2^{V_0}, \ldots, C_{N-1}^{-}, C_{N-1}^{V_0}, E_0 \right) = 0
\end{cases}
\end{bmatrix}
\]

where “cc” stands for coupled current.

Thus, $F(\lambda)$ is a $(2N - 1)^2$ matrix and the problem is equivalent to solving $F(\lambda) = 0$. We can thus define its Jacobian $F'(\lambda)$:

\[
\text{...}
\]
Newton’s approximation method [128] is used and $F(\lambda) = 0$ in Taylor series takes the form of:

$$F(\lambda + \Delta \lambda) = F(\lambda) + \Delta \lambda F'(\lambda) + \theta(\Delta \lambda^2)$$

(6-52)

Thus by setting $F(\lambda + \Delta \lambda) = 0$:

$$\Delta \lambda = -\frac{F(\lambda)}{F'(\lambda)} = \lambda^{(m+1)} - \lambda^{(m)}$$

(6-53)

$$\lambda^{(m+1)} = \lambda^{(m)} - F(\lambda^{(m)})/F'(\lambda^{(m)})$$

(6-54)

Eq.6-54 is equivalent to solving:

$$F'(\lambda^{(m)}) \times (\Delta \lambda)^{(m)} = -F(\lambda^{(m)})$$

(6-55)

And then solve $\lambda^{(m+1)} = (\Delta \lambda)^{(m)} + \lambda^{(m)}$. After $M$ iterations, once the system has satisfied the stopping criteria defined as $\Delta \lambda_{\text{lim}}$, the vector $\lambda^{(M)}$ is taken as an approximate solution of $\lambda$. Then both $J_{V_0}$ and the time necessary to grow the extra monolayer can be easily determined. Since:

$$\Delta t = \frac{R_{V_0}J_{V_0}}{2a}$$

(6-56)

the time necessary to grow that $N^{th}$ extra monolayer is known and determination of the oxidation kinetics is straightforward.

The Matlab code is detailed in Appendix E-IV.
6.3.4. Results of the space charge model

In contrast with the homogeneous field oxidation model, Poisson’s equation (eq.6-4) is verified at every location in the oxide and the space charge modifications on the kinetics are taken into account in the space charge model. The main assumption remains the coupled current equation, but the assumption of local electroneutrality is not necessary to solve the problem. To perform the calculation, the same set of parameters as in Table 6-2 is used. However because of computation time limitations, the calculation of oxide growth could only be extended up to 200 monolayers (equals to 200nm since $a = 5\text{Å}$).

The oxidation kinetics is presented in Figure 6-11 along with the homogeneous field limit parabolic oxidation case (see Figure 6-3). One can notice that as expected the space charge reduces the kinetics compared to the homogeneous field limit case. Furthermore, fitting the oxidation kinetics with a power law, the presence of space charges leads to sub-parabolic oxidation kinetics with $n \sim 0.4$ in that case. The net current is equal to zero everywhere in the oxide so that the coupled current equation is verified.
The evolutions of vacancy and electron concentrations as function of normalized oxide depth for different oxide thickness are plotted in Figure 6-12. Now that space charge effects are included, the concentration of the different charged species is dependent on the total oxide thickness (the concentration profiles plotted as function of normalized oxide depth do not superimpose on each other for different total oxide thickness as was observed in Figure 6-7). In this case concentration profiles evolve to reduce the local space charge imbalance as much as possible. This evolution is confirmed by plotting the space charge monolayer density defined as $2a \left(2C_k^{V_o} - C_k^{e^-}\right)$ as function of oxide depth for different oxide thickness in Figure 6-13 on a log scale.

Figure 6-11. Oxidation kinetics with space charge included (in red) and its comparison to the homogeneous field limit (in black). The oxidation kinetics is fitted using a power law (red line).
As the oxide grows, the space charge in the oxide layer at a given normalized oxide depth decreases. After the oxide thickness reaches approximately 100nm, the space charge is essentially negligible in a region located in the center of the oxide (approximately between 10% and 70% of the total oxide thickness) and is of significance only in the regions near the interfaces. This was anticipated by Fromhold [197].

Figure 6-12. Concentrations of vacancies and electrons as function of normalized oxide depth for different total oxide thickness. The homogeneous field (HFL) limit case is also shown in black.
The total electric field defined from Poisson’s equation in eq.6-39 as:

\[ E(x) = E_0 + E_{sp}(x) = E_0 + \frac{4\pi e}{\varepsilon_0} \int_0^x \rho(x)dx - \frac{8\pi ae}{e_0} \sum_{k=1}^K \left(2C_k^{V\delta} - C_k^{e}\right) \]  

(6-57)

as a function of normalized oxide depth at different oxide thickness is plotted in Figure 6-14. The total electric field increases as function of oxide depth since the space charge monolayer density is positive \( (2C_k^{V\delta} > C_k^{e}) \) as observed in Figure 6-13. After \( \delta \) reaches approximately 100nm, the space charge effects between 10% and 70% of \( \delta \) are negligible and the total electric field is **indeed approximately constant in this range**. Thus the conclusion from Figure 6-13 that the effect of space charges on the electric field is negligible between 10% and 70% of the total oxide thickness is verified. This is going to be of central importance in the development of subsequent models.

Figure 6-13. Space charge density on each monolayer as function of normalized oxide depth for different oxide thickness. The homogeneous field limit case is also plotted in black.
The absolute value of the surface charge field defined in eq. 6-6 as:

\[ |(6-58)| \]

is plotted as function of total oxide thickness in Figure 6-15. It is interesting to note that \( E_0 \) changes sign after \( \delta \) reaches approximately 20nm. For \( \delta < 20nm \), \( E_0 \) is positive, indicating that the vacancy diffusion is rate limiting whereas for \( \delta > 20nm \) \( E_0 \) is negative. This change of sign in \( E_0 \) is due to the high electric field value at small oxide thicknesses so that the linearity hypothesis (#10 of the homogeneous field limit model) assuming eq.6-8 is not verified for small oxide thickness. This effect was not taken into account in the homogeneous field model.
It is also observed that for \( \delta > 20 \text{nm} \) \( E_0 \) is negative indicating a change in the rate-limiting species, electron diffusion being now rate limiting compared to the homogeneous field model. *Thus the consideration of space charge significantly affects and indeed changes the rate-limiting species in the corrosion reaction.*

The potential defined as:

\[
V(x) = \int_{0}^{x} E(x) \, dx \sim 2a \sum_{k=1}^{K} \left( E_0 + E_{sp}(x_k) \right)
\]  

(6-59)

is plotted as function of oxide depth for different total oxide thickness in Figure 6-16.

The potential increases as function of oxide depth. As expected, the potential exhibits a linear dependence on \( x \) from 10\% to 70\% of \( \delta_p \) for oxide thicknesses greater than 100nm because electroneutrality is mostly verified in this region.
The oxide resistivity $\rho_{e}^{ox}$ is obtained from the calculated electric potential across the oxide layer, the flux of electrons and the oxide thickness using non integral Ohm’s law by:

$$\rho_{e}^{ox} = \frac{1}{6.242 \times 10^{-18} \frac{\Delta V}{\delta J_{e}^{-}}}$$  \hspace{1cm} (6-60)

where $\rho_{e}^{ox}$ is in Ω.cm, $\Delta V$ is the electric potential across the oxide in V determined by the model, $J_{e}^{-}$ is the electron flux in electrons.cm$^{-2}$.s$^{-1}$ determined by the model and $\delta$ is the oxide thickness in cm determined by the model. The factor $6.242 \times 10^{-18}$ is the number of electrons per coulomb (or number of electrons per ampere second). $\rho_{e}^{ox}$ is plotted as function of the oxide thickness and the exposure time in Figure 6-17. Of course $\rho_{e}^{ox}$ is constant in the case of the homogeneous field model studied in the previous section since according to eq.6-21 and eq.6-22 $\delta J_{e}^{-} = \text{constant}$ and $\Delta V$ is also time independent. Figure 6-17 shows that the oxide resistivity increases when space charges are included compared to the homogeneous field model and that it increases with exposure time following a power law with $n \sim 0.33$. Thus an increase of $\rho_{e}^{ox}$ at the start of corrosion (first 200nm) is a natural consequence of space charge build-up in the oxide.
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6.3.5. Verification of the model using the space charge factor

In order to verify that the code and theory are correct and that the effect of space charge on oxidation kinetics is correctly accounted for, the space charge factor $z$ in the total electric field defined as $E(x) = E_0 + zE_{sc}(x)$, $z = [0; 1]$ is used. Of course if $z = 1$, the results should be identical to the one found with the space charge model. On the other hand, $z = 0$ results in parabolic growth law after a sufficient oxide thickness ($\sim 20$ nm) has grown to cause linear approximation (hypothesis #10) to be verified (see eq.6-8). The oxidation kinetics for different

Figure 6-17. Oxide resistivity (in $\text{M}\Omega\text{.cm}$) as function of oxide thickness and exposure time for the space charge model and homogeneous field limit model.
space charge factor have been plotted and fitted between 20 and 70 nm of oxide growth to a power law. The results of the power law fit are displayed in Figure 6-18.

![Graph showing scaling factor and oxidation kinetics exponent as functions of space charge factor](image)

Figure 6-18. Scaling factor and oxidation kinetics exponent of a power law fit ($\delta = At^n$) as function of the space charge factor $z$.

It is observed that as $z \to 0$ the oxidation exponent $n$ tends towards 0.5 and the scaling factor also increases towards its value for parabolic oxidation. Basically, the space charge reducing the corrosion rate in the studied case, the corrosion rate indeed increased as $z \to 0$. More importantly, it is concluded that even though the exponent $n$ has no physical derivation (it is an empirical fit), it is related to the amount of space charge in the oxide. The lower the space charge, the closer the $n$ is to parabolic and the higher the space charge, the lower the value of $n$! The following trends are verified:
i. If the space charge can be compensated (by aliovalent alloying elements for instance), then the oxidation kinetics are parabolic, $n = 0.5$.

ii. If the space charge cannot be compensated, then the oxidation kinetics are sub-parabolic and the higher the space charge, the lower the value of $n$.

The experimental results shown in Chapter 3 indicate, that the value of $n$ is related to hydrogen pickup fraction. *Thus, it seems reasonable to conclude that the space charge compensation during oxidation has a direct relationship with hydrogen pickup fraction.* However, in order to investigate this correlation, it is necessary to model the effect of space charge on thicker oxides (on the order of 1 to 2 micrometers). The space charge model is unfortunately too time-consuming to model oxides thicker than hundreds of nanometers (it actually took three weeks to compute a 200nm oxide growth). Thus a new model has to be written to reduce the number of equations by simplifying the problem but without removing the significant effect of space charge on the oxidation kinetics. This has been attempted but has not been achieved because of a lack of time.

### 6.4. Conclusions of the oxidation models

Three oxidation models of increased complexity have been developed in this study. Even though the different models state various hypotheses on the corrosion mechanism, the obtained results shed more light into the hydrogen pickup mechanism and the relationship between oxidation kinetics and hydrogen pickup:

- The models do not assume a strict hypothesis of local electroneutrality as often observed in the literature but *use a more general (and more valid) assumption* of a zero net current (no charge accumulation) everywhere in the oxide.
• First of all, in order to correctly describe zirconium oxidation kinetics it is shown that it is absolutely necessary to model not only the oxygen anion diffusion but also the electron transport. The modeling of oxide growth without taking into account the electronic properties of the oxide is not correct because of the coupling of electron and anion diffusion.

• The electric field across the oxide has a significant impact on diffusion of charged species when compared to the single concentration gradient effect.

• The electric potential across the oxide has been identified as a significant driving force for hydrogen pickup.

• An analytical model, which neglects space charge effects on oxidation kinetics, has been developed (called homogeneous field limit model – HFL):
  o HFL model only predicts parabolic kinetics and thus its use is limited to the study of alloy with kinetics close to parabolic.
  o HFL model fits very well experimental data of Zr-0.4Nb alloy (alloy with the closest kinetics to parabolic) assuming meaningful physical parameters obtained by code optimization. The optimized value of the electron energy untrapping energy suggests that the electron transport occurs via thermal ionization of shallow donor states or centers into the conduction band followed by relaxation into empty energy states in the band gap.
  o Although modelling results show that the effect of space charges should not be neglected, experimental data on Zr-0.4Nb agree well with the HFL model. Thus, Nb additions compensate the effect of space charge and make the effect of space charge on kinetics negligible. The effect of Nb above the solubility limit on the space charge is still unknown.
o Nb is *likely oxidized as 2+ or 3+* (but *not* 5+) to compensate the positive space charge in the bulk oxide.

- *To account for space charge in the oxide and to model sub-parabolic kinetics*, a model based on an iterative procedure has been developed, *which fully describe the effect of space charges on the kinetics* (called non-homogeneous field space charge model – NHFSC). The model could only describe the oxidation kinetics up to a 200nm oxide thickness because of computational time limitation but the following key results have been obtained:
  
  o As expected, *the electric field resulting from space charges in the oxide tend reduce the magnitude of space charges* in the oxide.
  
  o The modelling of *space charge effects directly induces sub-parabolic kinetics* without assumptions regarding change in oxide microstructure or microchemistry of the oxide with exposure time.
  
  o The effect of *space charge is directly related to the oxidation kinetics exponent* (value of $n$). The lower the space charges in the oxide, the closer the kinetics is to parabolic. As the space charges in the oxide increase, the kinetics tends towards cubic and even lower (depending on input parameters and exposure time).
  
  o Thus, *Nb additions lower the space charge in the oxide and the alloy oxidation kinetics is close to parabolic*. Fe and Cr have a lower solubility limit than Nb in zirconium so that *the space charges in Fe/Cr containing alloys are not as compensated compared to Nb containing alloys and the alloy oxidation kinetics is then closer to cubic*.

- Comparing the oxide resistivity of HFL and NHFSC models shows that:
  
  o The oxide resistivity is constant in the HFL formulation but *varies with exposure time* when the effects of space charges are modelled.
Compared to the HFL model, the oxide resistivity is higher when space charges are modelled.

As the oxide thickness (or the exposure time) increases, the oxide resistivity also increases. It is believed that oxide resistivity will eventually saturate with exposure time (from data up to a 200nm oxide thickness it appears that oxide resistivity follows a cubic law with exposure time – see Figure 6-17).

- The oxide resistivity directly impacts the electric potential across the oxide (identified as the driving force for hydrogen pickup) and its variations result in variations of the electric potential across the oxide and consequently in variations of hydrogen pickup fraction.
- The results of the NHFSC model show that after a sufficient oxide growth (~100nm), the space charge is negligible in the middle part of the oxide when compared to interfacial regions.
Chapter 7

Discussions of the modelling and experimental results and conclusions

This chapter presents an overall discussion and evaluation of this study, including the correlations between the different experiments (XANES – Chapter 4, EIS – Chapter 5), models (Chapter 6) and the hydrogen pickup mechanism hypothesis (Chapter 3) based on the hydrogen pickup fraction measurements (Chapter 2). From these discussions, some conclusions on the hydrogen pickup mechanism are derived and some suggestions for future work are proposed.

7.1. Discussions and comparisons of the experimental and modelling results

7.1.1. Oxide resistivity and hydrogen pickup fraction

The oxide resistivity of different alloys with significantly different hydrogen pickup fraction has been measured by in-situ EIS as function of exposure time, as presented in Chapter 5. In Figure 7-1, the oxide resistivity of Zircaloy-4 alloy measured at different exposure times for archived samples (see section 5.4.3) and continuously on a single sample (see section 5.4.4) is plotted as function of the instantaneous hydrogen pickup fraction of these samples (see also Figure 5-20 (a)). The hydrogen pickup fraction depends on the alloy (see Chapter 2), but unfortunately not enough EIS data on the other alloys (Zr-2.5Nb and Zr-2.5Nb-2.5Cu) is available at the moment to generate useful discussions and significant conclusions.

A clear relationship is observed between the oxide resistivity and the instantaneous hydrogen pickup fraction in Zircaloy-4 suggesting that the resistance to electron transport in the oxide has a causal connection to hydrogen absorption. It is observed that the higher the oxide resistivity, the higher the instantaneous hydrogen pickup fraction. This result confirms the key
role of oxide electronic resistivity on the hydrogen pickup mechanism, which was proposed in Chapter 3. Basically, the increased resistance to electron transport in the oxide (as measured as the oxide resistivity), increases the driving force for proton absorption (the electric potential across the oxide), resulting in a higher instantaneous hydrogen pickup fraction. Thus, it seems reasonable to consider that the electrical potential across the oxide represents a significant driving force for hydrogen absorption into the underlying metal. The reasons for the alteration of electron transport in the oxide (or increase in oxide resistivity) with exposure time, which are observed in Figure 7-1, are not explicitly known at the moment but some hypotheses are discussed later in this chapter.

![Figure 7-1](image.png)

Figure 7-1. Oxide resistivity (in MΩ.cm) as function of instantaneous hydrogen pickup fraction for Zircaloy-4 alloy

In the case of Zircaloy-4, a linear relationship between the oxide resistivity and the instantaneous hydrogen pickup fraction is clearly observed in Figure 7-1, suggesting that the hydrogen pickup mechanism does not change during corrosion. Thus an oxide resistivity increase results immediately in an equivalent increase of hydrogen pickup fraction.
For hydrogen to be absorbed into the oxide both a driving force and a getter are needed. In this picture, the getters would be preferential sites for hydrogen absorption (the sites with the smallest absorption energy for hydrogen) and the driving force for hydrogen absorption in zirconium alloys would be the electric potential across the oxide (lowering the energy barrier for hydrogen absorption at the getters). Preliminary results (see Figure 5.20 (b)) suggest that the oxide resistivity is higher for Zircaloy-4 compared to Zr-2.5Nb at a given oxide thickness suggesting that Nb additions help maintaining a high oxide electronic conductivity throughout the corrosion and thus a low driving force for hydrogen absorption.

One possibility already evoked in Chapter 3 is that Nb additions in solid solution act as donors, increasing oxide electronic conductivity. However, to act as a donor, Nb in solid solution would have to be oxidized to 5+, which contradicts the XANES results from Sakamoto et al who found that Nb was mainly oxidized as 2+ and 3+ in the bulk oxide [74]. A 5+ oxidation state for Nb also contradicts the results from the space charge model in Chapter 6. Indeed, it was shown in Chapter 6 that to model the parabolic oxidation of Nb alloys \((n \to 0.5)\) observed experimentally, oxidized Nb would have to compensate the positive space charge in the oxide and thus Nb would have a lower oxidation state than 4+ (see Figure 6.9). Thus, the doping effect of Nb would not be responsible for the higher oxide electronic conductivity of ZrNb alloys compared to other zirconium alloys but rather the positive space charge compensation in the oxide by Nb in solid solution would be the reason for higher oxide electronic conductivity in ZrNb alloys.

For an oxide layer that is 200nm thick, the oxide conductivity from the space charge model is equal to \(\sigma_{\text{NHFS}} = 4.04 \times 10^{-4} (\text{M} \Omega \text{ cm})^{-1}\) and in the homogeneous field limit model, \(\sigma_{\text{HFL}} = 9.1 \times 10^{-3} (\text{M} \Omega \cdot \text{ cm})^{-1}\) and thus \(\sigma_{\text{HFL}} > \sigma_{\text{NHFS}}\) (see Figure 6.17 and eq.6-60). Thus the oxide electronic conductivity is smaller when space charges are present in the oxide, increasing the electric potential across the oxide, driving for hydrogen pickup. The parabolic case (HFL model) corresponding to Zr-Nb alloys, the space charge compensation by Nb would indeed
increase the oxide electronic conductivity (decrease resistivity) compared to alloys showing cubic oxidation kinetics (NHFSC model).

The electronic resistivity determined by the model is in the same range but slightly higher by one order of magnitude compared to EIS experimental results (compare Figure 6-17 and Figure 7-1). This small difference between the experiment and modeling is actually reasonable, considering the multiple assumptions of the model and of the experimental data analysis.

7.1.2. Space charge and hydrogen pickup fraction

However, it is necessary to determine whether the amount of oxidized Nb in the oxide is high enough to compensate the calculated space charge determined by the NHFSC model (see eq.6-57 and 6-60). The results of microbeam XANES of Nb absorption edge performed on Zr-0.4Nb alloy (see Chapter 4) are plotted in Figure 7-2 as the total amount of oxidized Nb in wt% as function of oxide depth along with the results shown in Figure 6-9.

As discussed in detail in Chapter 4, the XANES measurements give the % of Nb atoms oxidized but it is not possible to differentiate between 2+, 3+ and 5+. The solid and dotted curved lines in Figure 7-2 represent the amount of Nb in wt% necessary to fully compensate the space charge in the oxide and thus achieve exact parabolic kinetics (the 5+ case is not represented since it would induce more positive space charge in the bulk oxide). If the measured percent oxidized is assumed to be 3+, it is seen that a good fit of the experimental data is achieved. These results show that there is enough oxidized Nb in the oxide (either 2+ or 3+) at the different oxide locations probed by XANES to compensate for the space charge calculated by the model at these locations. It is likely that Nb oxidizes mainly to 3+.
Thus the measured weight gains and hydrogen contents, the EIS and the XANES experimental results and the models confirm the hypothesis made on Chapter 3 regarding the variations of hydrogen pickup in different Zr alloys that:

- The oxide electronic conductivity is a key parameter in hydrogen pickup and oxidation mechanism.
- The variations of electronic conductivity between different Zr alloys are due to the availability of aliovalent ions in the oxide to compensate the positive space charge.
- The possibility to compensate space charges leads to a high oxide electronic conductivity and thus in parabolic oxidation kinetics \( n \to 0.5 \). If no aliovalent ions are available to...
compensate space charges, it results in low oxide electronic conductivity and in \( n \to 0.3 \) and even below.

- Electric potential across the oxide is a significant driving force for hydrogen absorption.
- Oxide electronic conductivity variations between alloys induce variations of the electric potential across the oxide. \( n \to 0.5 \) (high oxide electronic conductivity) is observed for low electric potential across the oxide and thus is related to a low driving force for hydrogen pickup. The opposite is also verified. This explains the trends observed in Figure 3-2 and why Zr alloys with kinetics close to parabolic show smaller pickup fraction compared to Zr alloys with cubic kinetics.
- Space charge compensation by \( \text{Nb}^{2+} \) and/or \( \text{Nb}^{3+} \) in solid solution in the oxide is the reason Nb alloys show close to parabolic oxidation and lower hydrogen pickup fraction.
- In contrast the concentrations of Fe and Cr in solid solution being at maximum around 0.03wt\% in the metal, the Fe or Cr in solid solution in Zircaloy-4 is at too low a concentration to allow space charge compensation. This causes corrosion to slow down and builds up a high electric potential which results in high hydrogen pickup.
- Thus Zircaloy-type alloys show cubic kinetics and higher hydrogen pickup fraction compared to Nb alloys.

It is recalled here that the variations of electric potential between alloys stated above are not observable experimentally because there are automatically compensated by their effects, the hydrogen absorption. Thus the effect of the driving force rather than the driving force itself is observable experimentally.

The relationship between the oxidation kinetics (the value of \( n \)) and space charge has been well demonstrated in section 6.3.5. Thus, Figure 3-2 can be replaced by Figure 7-3 replacing the value of \( n \) in the abscissa axis by space charge compensation:
The scheme in Figure 3-3 can also be completed as follows in Figure 7-4.

Figure 7-3. Hydrogen pickup fraction as function of space charge compensation for different Zr alloys

Figure 7-4. Relationship between different parameters and their effect on Zircaloy and ZrNb type alloys

However a few questions remain. Among them, it is still not clear what the specific effects are of:

- \( \text{Zr(Fe,Cr)}_2 \) and \( \text{ZrNb precipitates in the oxide} \): do they promote electron transport and lower the oxide electronic conductivity or are they just a stress stabilizer delaying the transition and do not affect the oxidation kinetics or hydrogen pickup.
- **Sn in solid solution.** Sn should also act as a positive space charge compensator if it is oxidized to 2+ in the oxide. Because of its large ionic radius, it is expected that Sn (like Nb) would be in substitutional rather than interstitial position in the oxide. The amount of Sn (in wt%) needed to compensate space charge would be higher than Nb because of its higher atomic weight, but 1%Sn (or even 0.8% as it appears that Sn is rejected from the oxide [161]) as it is present in solid solution in Zircalloys is more than enough to compensate the calculated space charge. Thus, Sn would be present not only in solid solution in the oxide but also as precipitates. Sn precipitates in the oxide have indeed recently been observed and Sn segregation in the oxide region has been suggested by APT results [75, 161]. It is also possible that solid solution Sn is oxidized but its oxidation state is 4+ and not 2+. The oxidation state of Sn in the oxide has been investigated by Mossbauer spectroscopy and a mixture of 2+ (25%-50%) and 4+ (50%-75%) has been observed [71, 198]. A more detailed microbeam XANES investigation of Sn in the oxide should be conducted to assess this particular point.

Additionally to the effect of the driving force on hydrogen pickup, the favored absorption of hydrogen at specific sites (getters) should also be investigated. Preliminary results on Zr-2.5Nb-0.5Cu (see Figure 5-19 (c)) tend to suggest that even though this alloy presents a much higher hydrogen pickup fraction compared to Zircaloy-4, its oxide conductivity is higher by one order of magnitude at similar oxide thickness. *Thus it is believed that there is an additional effect that promotes hydrogen pickup in Cu containing alloys besides the effect of conductivity on the driving force for hydrogen pickup*. EIS measurements as well as hydrogen and oxidation kinetics correlate with this assessment but dedicated chemical experiments should be conducted to validate it and examine further the specific properties of Zr-(Nb)-Cu alloys.
7.1.3. Oxidation of alloying elements and hydrogen pickup fraction

In the previous sections, only the differences between alloys were discussed. However, for a given alloy, significant variations of the hydrogen pickup fraction and oxide electronic conductivity with exposure time are observed (see Figure 7-1 and Figure 2-22). Difficulties arise when postulating that change in space charge compensation is the reason for the increase in $f_H^t$ and $\rho_e^{0x}$ after the oxide thickness has reached approximately 70% of $\delta_t$ (see Figure 2-25), since there are no apparent reasons for space charge compensation to be suddenly modified at large oxide thicknesses (Figure 6-17 actually suggests that $\rho_e^{0x}$ saturates at large oxide thickness). Even though the space charge model results are available only for a maximum oxide thickness of 200nm, it is believed that no significant changes in space charge would occur around 70% of $\delta_t$. Thus, it is likely that the increase in oxide resistivity $\rho_e^{0x}$ with oxide thickness observed by EIS (see Figure 5-20) stems from another reason.

In this study, the evolution of the oxidation of alloying elements mainly present in second phase precipitates has been investigated by microbeam XANES. The evolution of the fraction of the protective oxide in which more than half of alloying elements are metallic was followed by the means of the parameter $\delta_{\text{met}}/\delta_p$ (see Chapter 4). This parameter and the instantaneous hydrogen pickup fraction (the fit, if available, is plotted rather than the experimental data) are plotted as function of the protective oxide thickness $\delta_p$ in Figure 7-5. It appears that variations in $\delta_{\text{met}}/\delta_p$ and $f_H^t$ are correlated, that is as $\delta_{\text{met}}/\delta_p$ decreases $f_H^t$ increases. That is if the oxidation of metallic precipitates causes an alteration to electron transport (for instance if metallic precipitates act as shortcuts for electron conduction), at first the concentration of metallic precipitates in the protective oxide layer, represented by the ratio $\delta_{\text{met}}/\delta_p$, is constant (see Figure 7-5 (e) and Figure 4-31), so that $\rho_e^{0x}$ is constant. This is the case until $\delta_{\text{met}}$ reaches its threshold value, as detailed in Chapter 4. According to the hypothesis that hydrogen absorption results from
the need to balance charge, a constant $\rho^\infty$ would result in constant $f_H^i$. This trend is somewhat observed in Figure 7-5 (b) and (e).

Figure 7-5. Instantaneous (or total for (e)) hydrogen pickup fraction fit (or experimental data for (c) and (f)) and evolution of the parameter $\delta_{\text{met}}/\delta_p$ as function of protective oxide thickness $\delta_p$ for various zirconium alloys.
As explained in Chapter 4, likely because of the development of micro-porosity in the outer part of the protective oxide layer, the ratio \( \delta_{\text{met}}/\delta_p \) decreases as the oxide grows and consequently the concentration of metallic precipitates in the protective layer decreases. As a result, both \( \rho_e^{\text{ox}} \) and \( f_H^1 \) would also increase. This correlation is observed in all the plots of Figure 7-5. The same mechanism takes place in the following transition period. Thus the increased metallic precipitate oxidation is correlated with a marked increase in \( f_H^1 \).

The fact that Zr-0.4Fe-0.2Cr alloys with two different precipitate sizes show different values of \( f_H^1 \) would also indicate that precipitates play a role in the hydrogen pickup mechanism. But it is still unclear at the moment if the increased oxidation of precipitates as the oxide layer grows is at the origin of the observed increase in hydrogen pickup fraction or if both observations result from yet another event, such as increased oxide porosity. It would thus be necessary to verify if metallic precipitates promote electronic conduction in the oxide.

Thus the measured weight gains and hydrogen contents, the EIS and the XANES experiments confirm the hypothesis made on Chapter 3 regarding the variations of hydrogen pickup with exposure time and that the increased oxidation of metallic precipitates is correlated to the marked increase in \( f_H^1 \) and \( \rho_e^{\text{ox}} \) observed after the oxide reached 70% of \( \delta_t \) (see Figure 3-1). However, to conclude on the causality of the above point, a study on the effect of metallic precipitates embedded in an oxide on the averaged oxide electronic properties should be conducted.

### 7.2. Conclusions

Detailed measurements were performed for hydrogen pickup and oxide growth as a function of exposure time for a set of chosen zirconium alloys with specific chemistries and microstructures using Vacuum Hot Extraction and Cold Neutron Prompt Gamma Activation
Analysis. The observations of the oxidation and hydriding kinetics as function of exposure time and alloying additions resulted in the formulation of a general corrosion mechanism hypothesis of zirconium alloys. Dedicated experiments and modelling were designed and developed to verify this hypothesis. The overall “construction” of the study is schematically represented in Figure 7-6.

Figure 7-6. General construction of the hydrogen pickup study.
This study of the hydrogen pickup mechanism has shown that:

- The **hydrogen pickup fraction is not a constant** and varies significantly as function of exposure time and between alloys. It presents a common trend to every zirconium alloys (see Figure 2-25).

- The **hydrogen pickup fraction is directly related to the oxidation mechanism** and more precisely to the oxide electronic conductivity monitoring the electric potential across the oxide, driving force for hydrogen absorption.

- Consequently, **the oxide electronic conductivity is a key parameter to control hydrogen pickup**. It has been shown by both experiments and modelling that if oxide electronic conductivity is high, then the oxidation kinetics is closer to parabolic and the hydrogen pickup fraction is low. On the other hand, if oxide electronic conductivity is low, then the oxidation kinetics tends towards cubic (and even lower) and the hydrogen pickup fraction is high. Thus **there is a balance between oxidation kinetics and hydrogen pickup fraction driven by oxide electronic conductivity effects on electric potential across the oxide**.

- Modelling and experimental results have shown that space charge effects alter the oxide electronic conductivity by (in our case) impeding electron transport and lowering the oxide electronic conductivity. **Thus Zr alloys with high oxide space charges have a lower oxide electronic conductivity compared to Zr alloys with lower oxide space charges.** Consequently, **even relatively low alloying additions, can affect oxide electronic conductivity** by compensating or not the space charges in the oxide resulting in variations of oxidation and hydriding kinetics among Zr alloys.

- Since the space charge effects increase as the oxide thickens (especially at small oxide thicknesses), **the oxide conductivity decreases with oxide thickness resulting in sub-parabolic kinetics and increase in hydrogen pickup fraction**.
• Nb in solid solution is likely oxidized to 3+ in the oxide. Thus **Nb additions compensate the positive space charges in the oxide making their effects on the kinetics negligible**. On the other hand, oxidized Fe and Cr in solid solution are not present at high enough concentrations to compensate space charges. That is why Nb alloys tend to have oxidation kinetics closer to parabolic, higher oxide electronic conductivity and lower hydrogen pickup fraction compared to Zircaloys.

• Indeed, preliminary results tend to show that **oxide resistivity of Zr-2.5Nb and Zr-2.5Nb-0.5Cu is smaller compared to Zircaloy-4** at similar oxide thickness.

• **The oxide resistivity is not constant** but varies as function of oxide thickness. It is clearly observed from the measurements that oxide resistivity follows a cyclic behavior (as oxidation kinetics – see Figure 5-20), **increasing up to transition and decreasing before or at transition**, following the instantaneous hydrogen pickup fraction variations.

• The reasons for these oxide electronic conductivity variations are not explicitly known at the moment but **the possible effect of delayed oxidation of alloying elements affecting electron transport has been studied**.

• The concentration of metallic alloying elements in the protective oxide layer evolves according to the scheme in Figure 4-31. It is observed that **the oxidation of Fe and Nb in second phase precipitates are delayed compared to zirconium oxidation**. Thus metallic precipitates are embedded into the growing oxide.

• There is **a correlation between the increase in hydrogen pickup fraction and an increase in the concentration of oxidized alloying elements in the oxide layer**. If it is assumed that metallic precipitates embedded in the oxide layer promote electron transport, then their oxidation would decrease the oxide electronic conductivity and increase hydrogen pickup fraction following the mechanism developed above. However,
this point needs further confirmation as the effect of metallic precipitates on the conductivity has not been developed in this study.

Finally, in order to design better alloys that would pick up less hydrogen it is absolutely necessary to study the effect of alloying additions on the oxide electronic conductivity and more precisely on their ability to compensate space charges in the oxide. The chosen alloying element should have a high solubility limit in zirconium oxide, be located in substitution in the oxide, present an oxidation state lower than 4+ to compensate positive space charge in the oxide. It is also probably better if its oxidation is delayed compared to the zirconium oxidation. Of course niobium validates all the above points and that is why ZrNb alloys pick up less hydrogen compared to other type of alloys. But other candidates should be investigated as well such as scandium, bismuth, antimony and vanadium.

**7.3. Future work**

In order to fully understand the hydrogen pickup mechanism in zirconium alloys and to design better alloys for future cladding in nuclear reactors, some experiments and modelling should be performed:

- It is planned to keep on developing the GCM model code in the near future to decrease the computation time and be able to model the sub-parabolic oxide growth of thick zirconium oxide layers. Then, it will be possible to investigate the effects of the alteration of electron transport at approximately 70% of the transition oxide thickness.

- It is also planned to continue the EIS experiments to investigate the relationship between oxide resistivity and hydrogen pickup fraction at larger exposure times as well as for other zirconium alloys such as Zr-(Nb)-Cu alloys.
It is proposed to perform EIS experiments on alloys with different precipitate sizes (for instance on Zr-0.4Fe-0.2Cr (H) and Zr-0.4Fe-0.2Cr (L) alloys) to investigate the effect of precipitate sizes on oxide electronic conductivity. Some modelling work should also be done to develop a relationship between precipitate sizes and distributions and oxide conductivity. Once this is done, the GCM model can be easily transcribed in 2D with different electron untrapping energies at the different nodes representing the heterogeneity of the oxide.

It would also be interesting to implement interfacial reactions in the GCM model to avoid electron and vacancy concentrations parameter inputs in the model since these parameters are not well known at the moment.

To better describe electron transport in the GCM model, a realistic energy distribution of untrapping energies below the conduction band should be implemented. It is proposed to use the random walk theory, which is well known in the semiconductor area.

The evolution of the oxidation state of Sn as function of exposure time and oxide depth should be investigated by microbeam XANES. A study is currently being done on the subject at Manchester University in the context of a partnership with the present study.

The reasons for the increase of hydrogen pickup fraction from a transition regime to the next have not been investigated in this study. It was proposed that the non-protective oxide layer has an effect of the pressure of hydrogen at the cathodic site but chemical experiments should be performed to assess this hypothesis.

The peculiar effect of Cu or Ni on the hydrogen pickup fraction has not been precisely investigated either. It was proposed that these elements act as preferential sites for hydrogen absorption (getters) but once again dedicated chemical experiments should be performed.
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### Appendix A-I

**Weight gain tables in mg/dm²**

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Appendix A-II

Weight gain fit of production alloys

ZIRLO sheet:

\[
\text{Fit: } y = 6.08x^{0.41}
\]

Zircaloy-4 sheet:

\[
\text{Fit: } y = 8.45x^{0.29}
\]
ZIRLO tube:

Zircaloy-4 tube:

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Zr-2.5Nb-0.5Cu tube:
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<th>456</th>
<th>463</th>
<th>493</th>
</tr>
</thead>
<tbody>
<tr>
<td>VHE results</td>
<td>47</td>
<td>63</td>
<td>71</td>
<td>56</td>
<td>78</td>
<td>74</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Exposure time (days)</th>
<th>399</th>
<th>409</th>
<th>435</th>
<th>456</th>
<th>463</th>
<th>493</th>
</tr>
</thead>
<tbody>
<tr>
<td>VHE results</td>
<td>47</td>
<td>63</td>
<td>71</td>
<td>56</td>
<td>78</td>
<td>74</td>
</tr>
</tbody>
</table>
Appendix A-IV

Hydrogen content fit of production alloys

ZIRLO sheet:

--- Graph showing experimental data and fit.

Zircaloy-4 sheet:

--- Graph showing experimental data and fit.
ZIRLO tube:

![Graph showing hydrogen content (wt. ppm) vs exposure time (days) for ZIRLO tube.]

Zircaloy-4 tube:

![Graph showing hydrogen content (wt. ppm) vs exposure time (days) for Zircaloy-4 tube.]

Zr-2.5Nb tube:

![Graph showing hydrogen content (wt. ppm) vs exposure time (days) for Zr-2.5Nb tube.]
Zr-2.5Nb-0.5Cu tube:
Appendix A-V

\[ \frac{df_H^t}{dt} \text{ vs } f_H^t \]

The instantaneous pickup fraction is defined as:

\[ f_H^t = \alpha \frac{d[H]}{d\delta} \]

With \( \alpha \) a constant.

Thus:

\[ f_H^i = \alpha \frac{d[H]}{d\delta} \rightarrow \frac{d[H]}{dt} = f_H^i \frac{1}{\alpha} \frac{d\delta}{dt} \]

The total pickup fraction is defined as:

\[ f_H^t = \alpha \frac{[H]}{\delta} \]

Thus:

\[ \frac{df_H^t}{dt} = \alpha \delta \frac{d[H]}{dt} - [H] \frac{d\delta}{dt} = \alpha \frac{\delta f_H^i \frac{1}{\alpha} \frac{d\delta}{dt} - [H] \frac{d\delta}{dt}}{\delta^2} = \frac{1}{\delta} \frac{d\delta}{dt} \left( f_H^i \frac{1}{\alpha} - \left[ \frac{d\delta}{dt} \right] \right) \]

Finally:

\[ \frac{df_H^t}{dt} = \frac{(f_H^t - f_H^i) d(\ln \delta)}{\alpha} \]
Appendix B

Quantification of the effect of stress on diffusion in Zr oxides

The elasticity limit $\sigma_y$ of ZrO$_2$ is equal to $2 \times 10^9$Pa and the Young modulus $E$ to $2 \times 10^{11}$Pa.

Thus the maximum elastic energy stored is equal to:

$$E_{el} = \frac{\sigma_y^2}{2E} = 10^7 \text{J.m}^{-3}$$

The number of atoms $N_{\text{ZrO}_2}$ in a 3µm oxide layer is equal to:

$$N_{\text{ZrO}_2} = 3 \frac{\rho_{\text{ZrO}_2}}{M_{\text{ZrO}_2}} N_a V_{\text{ZrO}_2} = 2.4 \times 10^{23} \text{atoms.m}^{-2}$$

If we assume that $E_{el}$ is evenly distributed in a 3µm oxide layer:

$$E_{\text{layer}} = 10^7 \times 3 \times 10^{-6} = 30 \text{J.m}^{-2}$$

And thus the maximum elastic energy per atom $E_{\text{atom}}$ is equal to:

$$E_{\text{atom}} = \frac{30}{2.4 \times 10^{23}} = 1.5 \times 10^{-22} \text{J.atoms}^{-1} = 9.4 \times 10^{-4} \text{eV.atoms}^{-1}$$

Thus, $E_{\text{atom}}$ is negligible compared to the migration energy of vacancy or untrapping energy of electrons in zirconium oxides (see Chapter 6). Consequently it is verified that the chemical energy is much greater than the elastic energy per atom. In order to definitely eliminate the possibility of an effect of stress on diffusion of charged species, the local effect of a spatial stress gradient on the migration energy should be investigated.
Appendix C

Results of XANES spectra

Zircaloy-4 sheet thick samples:

<table>
<thead>
<tr>
<th>Z4S20</th>
<th>Exposure time (days)</th>
<th>45</th>
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<tbody>
<tr>
<td></td>
<td>Weight gain (mg/dm²)</td>
<td>25,1</td>
</tr>
<tr>
<td></td>
<td>Oxide thickness (microns)</td>
<td>1,7</td>
</tr>
</tbody>
</table>

![Graph showing weight gain and oxide thickness over exposure time]
<table>
<thead>
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<th>Exposure time (days)</th>
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</thead>
<tbody>
<tr>
<td>Weight gain (mg/dm²)</td>
<td>29.9</td>
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<tr>
<td>Oxide thickness (microns)</td>
<td>2.0</td>
</tr>
<tr>
<td>Parameter</td>
<td>Value</td>
</tr>
<tr>
<td>---------------------------------------</td>
<td>---------</td>
</tr>
<tr>
<td>Exposure time (days)</td>
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<tr>
<td>Weight gain (mg/dm²)</td>
<td>41.6</td>
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<td>Protective oxide thickness</td>
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<td>Property</td>
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<tr>
<td>--------------------------------</td>
<td>--------</td>
</tr>
<tr>
<td>Exposure time (days)</td>
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<tr>
<td>Weight gain (mg/dm²)</td>
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</tr>
<tr>
<td>Oxide thickness (microns)</td>
<td>3.4</td>
</tr>
<tr>
<td>Weight gain at transition</td>
<td>30.9</td>
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<tr>
<td>Porous layer thickness</td>
<td>2.1</td>
</tr>
<tr>
<td>Protective oxide thickness</td>
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![Graph showing experimental data and fit to model.](image-url)
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<td><strong>Weight gain (mg/dm²)</strong></td>
<td>53,5</td>
</tr>
<tr>
<td><strong>Oxide thickness (microns)</strong></td>
<td>3,6</td>
</tr>
<tr>
<td><strong>Weight gain at transition</strong></td>
<td>30,9</td>
</tr>
<tr>
<td><strong>Porous layer thickness</strong></td>
<td>2,1</td>
</tr>
<tr>
<td><strong>Protective oxide thickness</strong></td>
<td>1,5</td>
</tr>
</tbody>
</table>

![Graph showing weight gain over exposure time](image)

![Graph showing normalized Zr fluorescence counts](image)

- Zr fluorescence
- Fraction of bcc Fe
- Fraction of metallic Fe
- Fraction of oxidized Fe
Z4517

<table>
<thead>
<tr>
<th>Property</th>
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<tbody>
<tr>
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<td>Weight gain (mg/dm²)</td>
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<tr>
<td>Porous layer thickness</td>
<td>2.1</td>
</tr>
<tr>
<td>Protective oxide thickness</td>
<td>1.8</td>
</tr>
</tbody>
</table>

Graph showing:
- Normalized Zr fluorescence counts vs. distance from oxide/metal interface (microns)
- Fractions of oxidized and metallic Fe

Graph legend:
- Zr fluorescence
- Fraction of bcc Fe
- Fraction of metallic Fe
- Fraction of oxidized Fe
**Z4S6**

<table>
<thead>
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<tbody>
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<tr>
<td>Weight gain (mg/dm²)</td>
<td>59.9</td>
</tr>
<tr>
<td>Oxide thickness (microns)</td>
<td>4.1</td>
</tr>
<tr>
<td>Weight gain at transition</td>
<td>30.9</td>
</tr>
<tr>
<td>Porous layer thickness</td>
<td>2.1</td>
</tr>
<tr>
<td>Protective oxide thickness</td>
<td>2.1</td>
</tr>
<tr>
<td>Parameter</td>
<td>Value</td>
</tr>
<tr>
<td>---------------------------------</td>
<td>---------</td>
</tr>
<tr>
<td>Exposure time (days)</td>
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</tr>
<tr>
<td>Weight gain (mg/dm²)</td>
<td>62.7</td>
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<tr>
<td>Oxide thickness (microns)</td>
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<tr>
<td>Weight gain at transition</td>
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</tr>
<tr>
<td>Porous layer thickness</td>
<td>2.1</td>
</tr>
<tr>
<td>Protective oxide thickness</td>
<td>2.2</td>
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</table>

![Graph showing normalized Zr fluorescence counts and fractions of oxidized and metallic Fe as a function of distance from oxide/metal interface (microns).](image-url)
**Z451S**

<table>
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<tbody>
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<tr>
<td>Weight gain at transition</td>
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</tr>
<tr>
<td>Porous layer thickness</td>
<td>4,5</td>
</tr>
<tr>
<td>Protective oxide thickness</td>
<td>1,4</td>
</tr>
</tbody>
</table>

---

**Graph**

- **Normalized Zr fluorescence counts**
- **Distance from oxide/metal interface (microns)**
- **Fractions of oxidized and metallic Fe**
- **Experimental data**
- **Fit**

**Legend**

- Zr fluorescence
- Fraction of bcc Fe
- Fraction of metallic Fe
- Fraction of oxidized Fe

**Axes**

- Y-axis: 0 to 2.5
- X-axis: Distance from oxide/metal interface (microns)
- Experimental data
- Fit

**Graph Notes**

- The graph illustrates the normalized Zr fluorescence counts against the distance from the oxide/metal interface.
- The fractions of oxidized and metallic Fe are indicated by different markers.
- The experimental data is shown with a distinctive marker and the fit is represented by a line.

---

**Additional Observations**

- The analysis indicates a significant change in Zr fluorescence and Fe fractions as the distance from the oxide/metal interface increases.
- The protective oxide thickness is critical in preventing further oxidation.
- The weight gain at transition suggests a change in material properties at this stage.

---

**Conclusion**

- The study highlights the importance of oxide thickness and protective layers in preventing material degradation under exposure conditions.
- Further research is recommended to understand the transition phase in detail.
<table>
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<td>Porous layer thickness</td>
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</tr>
<tr>
<td>Protective oxide thickness</td>
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</tbody>
</table>

![Graph showing weight gain vs. exposure time](image)

![Graph showing normalized Zr fluorescence vs. distance from oxide/metal interface](image)
ZIRLO tube thick samples (Fe and Nb investigation – except for ET8):

<table>
<thead>
<tr>
<th>ET2</th>
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<tr>
<td></td>
<td>Weight gain (mg/dm2)</td>
<td>25.3</td>
</tr>
<tr>
<td></td>
<td>Oxide thickness (microns)</td>
<td>1.7</td>
</tr>
<tr>
<td>ET3</td>
<td>Exposure time (days)</td>
<td>60</td>
</tr>
<tr>
<td>-----</td>
<td>----------------------</td>
<td>----</td>
</tr>
<tr>
<td></td>
<td>Weight gain (mg/dm²)</td>
<td>33.9</td>
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<td></td>
<td>Oxide thickness (microns)</td>
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ET4

<table>
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</thead>
<tbody>
<tr>
<td>Exposure time (days)</td>
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<tr>
<td>Weight gain (mg/dm²)</td>
<td>40.0</td>
</tr>
<tr>
<td>Oxide thickness (microns)</td>
<td>2.7</td>
</tr>
</tbody>
</table>

**Graph**: Weight gain (mg/dm²) vs. Exposure time (days)

**Graph**: Fraction of oxidized Fe and Nb vs. Distance from oxide/metal interface (microns)

- Zr fluorescence
- Fraction of Fe bcc
- Fraction of oxidized Nb
- Fraction of oxidized Fe
<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>ET8</strong></td>
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</tr>
<tr>
<td>Exposure time (days)</td>
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<tr>
<td>Weight gain (mg/dm²)</td>
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</tr>
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<td>Oxide thickness (microns)</td>
<td>5.5</td>
</tr>
<tr>
<td>Weight gain at transition</td>
<td>46</td>
</tr>
<tr>
<td>Porous layer thickness</td>
<td>3.1</td>
</tr>
<tr>
<td>Protective oxide thickness</td>
<td>2.4</td>
</tr>
</tbody>
</table>

![Graph showing weight gain over exposure time](image)

![Graph showing normalized Zr fluorescence and fractions of oxidized Fe and Nb](image)
Zr-2.5Nb tube thick samples:

<table>
<thead>
<tr>
<th>CT3</th>
<th></th>
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</thead>
<tbody>
<tr>
<td>Exposure time (days)</td>
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</tr>
<tr>
<td>Weight gain (mg/dm²)</td>
<td>33,0</td>
</tr>
<tr>
<td>Oxide thickness (microns)</td>
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</table>

![Graph showing weight gain (mg/dm²) over exposure time (days) and normalized Zr fluorescence counts along the distance from oxide/metal interface (microns).]
CT5

<table>
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<th>Exposure time (days)</th>
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CT6

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<tbody>
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<td>Weight gain (mg/dm²)</td>
<td>47.7</td>
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<tr>
<td>Oxide thickness (microns)</td>
<td>3.2</td>
</tr>
</tbody>
</table>
Zr-0.4Nb sheet thick samples:

<p>| | |</p>
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</thead>
<tbody>
<tr>
<td><strong>Zr-0.4Nb</strong></td>
<td></td>
</tr>
<tr>
<td>Exposure time (days)</td>
<td>326.4</td>
</tr>
<tr>
<td>Weight gain (mg/dm²)</td>
<td>68.6</td>
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<tr>
<td>Oxide thickness (microns)</td>
<td>4.6</td>
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![Graph showing exposure time, weight gain, and oxide thickness](image)

![Graph showing normalized Zr fluorescence, fractions of metallic Nb, and oxidized Nb](image)
Zr-0.4Fe-Cr (H) sheet thick samples:

<table>
<thead>
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<th>Value</th>
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</thead>
<tbody>
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<td>Exposure time (days)</td>
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<tr>
<td>Weight gain (mg/dm2)</td>
<td>35.2</td>
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<tr>
<td>Oxide thickness (microns)</td>
<td>2.4</td>
</tr>
</tbody>
</table>

![Graph showing weight gain and oxide thickness over exposure time](image)

![Graph showing fractions of Zr fluorescence and metallic Fe](image)
<table>
<thead>
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<th>Exposure time (days)</th>
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</tr>
</thead>
<tbody>
<tr>
<td>Weight gain (mg/dm²)</td>
<td>47.7</td>
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<tr>
<td>Oxide thickness (microns)</td>
<td>3.2</td>
</tr>
</tbody>
</table>
Appendix D

EIS spectra at different $U_{ac}$
Appendix E-I

Derivation of the roots of the coupled current equation with anion vacancies and electrons in homogeneous field limit (HFL model):

\begin{align*}
2\mu V_0 \left( \frac{C_{V_0}^-(\delta) - C_{V_0}^-(0)\eta^2}{1 - \eta^2} \right) - \mu e^- \left( \frac{C_{e^-}(\delta) - C_{e^-}(0)\eta^{-1}}{1 - \eta^{-1}} \right) &= 0 \\
2\mu V_0 \left( \frac{C_{V_0}^-(\delta) - C_{V_0}^-(0)\eta^2}{1 - \eta^2} \right) - \mu e^- \left( \frac{C_{e^-}(\delta) - C_{e^-}(0)\eta^{-1}}{1 - \eta^{-1}} \right) \left( \frac{\eta}{\eta} \right) &= 0 \\
2\mu V_0 \left( \frac{C_{V_0}^-(\delta) - C_{V_0}^-(0)\eta^2}{1 - \eta^2} \right) - \mu e^- \left( \frac{C_{e^-}(\delta)\eta - C_{e^-}(0)}{\eta - 1} \right) &= 0 \\
2\mu V_0 \left( \frac{C_{V_0}^-(\delta) - C_{V_0}^-(0)\eta^2}{1 - \eta^2} \right) + \mu e^- \left( \frac{C_{e^-}(\delta)\eta - C_{e^-}(0)}{1 - \eta} \right) \left( \frac{1 + \eta}{1 + \eta} \right) &= 0 \\
2\mu V_0 \left( \frac{C_{V_0}^-(\delta) - C_{V_0}^-(0)\eta^2}{1 - \eta^2} \right) + \mu e^- \left( \frac{C_{e^-}(\delta)\eta - C_{e^-}(0)}{1 - \eta^2} \right) (1 + \eta) &= 0
\end{align*}

\begin{align*}
2\mu V_0 \left( C_{V_0}^-(\delta) - C_{V_0}^-(0)\eta^2 \right) + \mu e^- \left( C_{e^-}(\delta)\eta - C_{e^-}(0) \right) + \mu e^- \left( C_{e^-}(\delta)\eta^2 - C_{e^-}(0) \right) &= 0 \\
\eta^2 \left( \mu e^- C_{e^-}(\delta) - 2\mu V_0 C_{V_0}(0) \right) + \eta \left( \mu e^- C_{e^-}(\delta) - \mu e^- C_{e^-}(0) \right) + \left( 2\mu V_0 C_{V_0}(\delta) - \mu e^- C_{e^-}(0) \right) &= 0
\end{align*}

\[
\eta_z = \frac{\mu e^- (C_{e^-}(0) - C_{e^-}(\delta)) \pm \sqrt{\mu e^- \left( C_{e^-}(0) - C_{e^-}(\delta) \right)^2 - 4 \times \left( \mu e^- C_{e^-}(\delta) - 2\mu V_0 C_{V_0}(0) \right) \left( 2\mu V_0 C_{V_0}(\delta) - \mu e^- C_{e^-}(0) \right)}}{2 \left( \mu e^- C_{e^-}(\delta) - 2\mu V_0 C_{V_0}(0) \right)}
\]
Appendix E-II
Matlab optimization code for the homogeneous field limit (HFL) model:

```matlab
function y=HFLPARAOPTE(Ceom,Cvom,Ceow,Cvow,T,Tr)
%Definition of the different parameters
Emvv=0.1:0.025:2; %Input vector of vacancy migration energies
Emee=0.1:0.025:2; %Input vector of electron untrapping energies
b=zeros; %Vector of oxide thickness at 75 days of exposure
Rv=123.218/(6.02*10^23*5.68); %Volume occupied by one molecule (/cm^3)
nu=10^13; %Jump frequency (Hz)
kb=1.3806488*10^(-23); %Boltzmann constant (J/K)
e=1.60217646*10^(-19); %Electron charge (C)
a=5*10^(-8); %Jump distance (cm)
K=273; %Kelvin point (K)
eps=22; %Dielectric constant of zirconia
epso=8.854187817*10^(-12); %Dielectric constant of vacuum
for o=1:numel(Emvv)
    Emv=Emvv(o); %Choice of vacancy migration energy
    for p=1:numel(Emee)
        Eme=Emee(p); %Choice of electron untrapping energies
        L=0; %Initial thickness increment
        Lt=0; %Initial total oxide thickness
        for m = 1:Tr %From 0.1 days to transition
            t(m)=m/10;
            mue=4*(-1)*e*a^2*nu/(kb*(T+K))*exp(-Eme*e/(kb*(T+K)))';
            %Electron mobility (cm^2/V/s)
            muv=4*2*e*a^2*nu/(kb*(T+K))*exp(-Emv*e/(kb*(T+K)));
            %Vacancy mobility (cm^2/V/s)
            %Solution of coupled current equation eta
            a1=mue*Ceow-2*muv*Cvom;
            b1=mue*Ceow-mue*Ceom;
            c1=2*muv*Cvow-mue*Ceom;
            delta=b1^2-4*a1*c1;
            eta2=-(b1-delta^0.5)/(2*a1); %eta2 is the only physical solution (see eq.6-16)
        end
    end
end
%Determination of weight gain
```
\[
\gamma_{av} = \mu_v k_b (T+K)/e^* \left( (C_{vow} - C_{vom} \eta_2^2)/(1 - \eta_2^2) \right) \log(\eta_2); \text{ % definition of } \gamma \text{ (see eq. 6-23)}
\]

```matlab
if \eta_2 == 1
    \gamma_{av} = 0;
end

\gamma_{av}(\gamma_{av} < 0) = NaN;
\gamma_{av}(\text{imag}(\gamma_{av}) \neq 0) = NaN;

L(1) = (R_v * t(1) * (3600 * 24) * \gamma_{av});
L1(1) = L(1);
Lt(1) = (2 * L1(1)).^0.5; \text{ % 1st oxide increment calculation}
if \text{ m > 1}
    L(m) = R_v *((t(m) - t(m-1)))*\gamma_{av}; \text{ % m\textsuperscript{th} oxide increment calculation}
end
L1(m) = L(m) * (3600 * 24) + L1(m-1);
Lt(m) = (2 * L1(m)).^0.5; \text{ % Total oxide thickness}

E(m) = (k_b * (T+K) * log(\eta_2) / (e * Lt(m))); \text{ % Electric field (see eq. 6-19)}
J_v(m) = \gamma_{av} / Lt(m); \text{ % Vacancy flux (see eq. 6-22)}
J_z(m) = \mu_v k_b (T+K) / (2 * e) * (C_{vom} - C_{vow}) / Lt(m); \text{ % Flux from Fick's law only, see eq. 6-30)}
\chi(m) = J_v(m) / J_z(m); \text{ % Electric field modification factor (see eq. 6-29)}
end
b(o, p) = Lt(750) .* 10^4; \text{ % Oxide thickness after 75 days of exposure}
c(o, p) = -E(750) * Lt(750); \text{ % Electric potential at the oxide/water interface after 75 days of exposure}
\chi_{it}(o, p) = J_v(750) / J_z(750); \text{ % Electric field modification factor after 75 days of exposure}
end

% Plotting of the results
v = [1.5 1.5; 3.5 3.5];
figure;
surf(Emv, Em, b);
colormap(hsv)
axis square
grid minor
hold on
contour(Emv, Em, b, v);
hold off
figure;
surf(Emv, Em, c);
axis square
```
grid minor

%Output

y={Emeb;Emv;mue;muv;p;c;Chit};
end
function y=HFLPARA(Emv,Eme,Ceom,Cvom,Ceow,Cvow,T,Tr)

%Definition of the different parameters
E=0; %Electric field
Ce=0; %Electron concentration
Cv=0; %Vacancy concentration
L=0; %Oxide thickness
V=0; %Electric potential across the oxide
J_e=0; %Flux of electrons
J_v=0; %Flux of vacancies
J_t=0; %Net flux

%Definition of the different variables
Rv=123.218/(6.02*10^23*5.68); %Volume occupied by one molecule (/cm^3)
u=10^13; %Jump frequency (Hz)
kb=1.3806488*10^(-23); %Boltzmann constant (J/K)
e=1.60217646*10^(-19); %Electron charge (C)
a=5*10^(-8); %Jump distance (cm)
K=273; %Kelvin point (K)
eps=22; %Dielectric constant of zirconia
epso=8.854187817*10^(-12); %Dielectric constant of vacuum

%Definition of the mobilities
for m = 1:Tr

    t(m)=m/10;

    mue=4*(-1)*e*a^2*nu/(kb*(T+K))*exp(-Eme*e/(kb*(T+K)))'; %Electron mobility (cm^2/V/s)
muv=4*2*e*a^2*nu/(kb*(T+K))*exp(-Emv*e/(kb*(T+K))); %Vacancy mobility (cm^2/V/s)

    %Solution of coupled current equation eta (see Appendix IV-I)
    a1=mue*Ceow-2*muv*Cvom;
b1=mue*Ceow-mue*Ceom;
c1=2*muv*Cvow-mue*Ceom;
delta=b1^2-4*a1*c1;
    eta2=(-b1-delta^0.5)/(2*a1); %eta2 is the only physical solution (see eq.6-16)

    %Determination of weight gain
\[ \text{gammav} = \frac{\mu_v \cdot k_b \cdot (T + K)}{e} \cdot \left( \frac{C_{v_{ow}} - C_{v_{om}} \cdot \eta_2^2}{1 - \eta_2^2} \right) \cdot \log(\eta_2); \]

\text{% definition of gamma (see eq.6-23)}

\[ \text{if } \eta_2 == 1 \]
\[ \text{gammav} = 0; \]
\[ \text{end} \]

\[ \text{gammav} \text{ if } \text{gammav} < 0 = \text{NaN}; \]
\[ \text{gammav} \text{ if } \text{imag}(\text{gammav}) \neq 0 = \text{NaN}; \]

\[ L(1) = (R_v \cdot t(1) \cdot (3600 \cdot 24) \cdot \text{gammav}); \]
\[ L(1) = L(1); \]
\[ L_t(1) = (2 \cdot L(1)).^0.5; \text{ % 1st oxide increment calculation} \]

\[ \text{if } m > 1 \]
\[ L(m) = R_v \cdot ((t(m) - t(m-1)) \cdot \text{gammav}; \text{ % mth oxide increment calculation} \]
\[ L(1, m) = L(m) \cdot (3600 \cdot 24) + L(1, m-1); \]
\[ L_t(m) = (2 \cdot L(1, m)).^0.5; \text{ % Total oxide thickness} \]
\[ \text{end} \]

\text{% Determination of electrical field and fluxes}

\[ \text{x}_n(m) = L_t(m) / (2 \cdot a); \text{ % Position in the oxide} \]
\[ E(m) = \frac{k_b \cdot (T + K) \cdot \log(\eta_2) / \left( e \cdot L_t(m) \right)}{\text{; % Electric field (see eq.6-19)} \]
\[ J_e(m) = \mu_e \cdot E(m) \cdot \left( \frac{C_{e_{ow}} - C_{e_{om}} / \eta_2}{1 - 1 / \eta_2^2} \right); \text{ % Electron flux} \]
\[ J_v(m) = \text{gammav} / \text{L_t(m)}; \text{ % Vacancy flux (see eq.6-22)} \]
\[ J_t(m) = 2 \cdot J_v(m) - J_e(m); \text{ % Net flux} \]
\[ J_z(m) = \mu_v \cdot k_b \cdot (T + K) / \left( 2 \cdot e \cdot (C_{v_{om}} - C_{v_{ow}}) / L_t(m) \right); \text{ % Flux from Fick’s law only, see eq.6-30)} \]
\[ \text{Chi}(m) = J_v(m) / J_z(m); \text{ % Electric field modification facto (see eq.6-29)} \]

\[ \text{if } J_t(m) < 1000 \]
\[ J_t(m) = 0; \]
\[ \text{end} \]

\[ \text{for } n = 1 : \text{x}_n(m) \]
\[ x(n, m) = n / \text{x}_n(m); \text{ % Position in the oxide in %} \]
\[ V(n, m) = -E(m) \cdot 2 \cdot a \cdot n; \text{ % Electric potential} \]
\[ C_{e}(n, m) = C_{e_{om}} \cdot \exp(-2 \cdot a \cdot n \cdot e \cdot E(m) / (k_b \cdot (T + K))) + J_e(m) / (\mu_e \cdot E(m)) \cdot (1 - \exp(-2 \cdot a \cdot n \cdot e \cdot E(m) / (k_b \cdot (T + K)))); \text{ % Electron concentration} \]
\[ C_{v}(n, m) = C_{v_{om}} \cdot \exp(4 \cdot a \cdot n \cdot e \cdot E(m) / (k_b \cdot (T + K))) + J_v(m) / (\mu_v \cdot E(m)) \cdot (1 - \exp(4 \cdot a \cdot n \cdot e \cdot E(m) / (k_b \cdot (T + K)))); \text{ % Vacancy concentration} \]
\[ \text{qtot}(n, m) = 2 \cdot a \cdot (2 \cdot C_{v}(n, m) - C_{e}(n, m)); \text{ % Concentration difference} \]
\[ \text{Esp}(1, m) = e \cdot 4 \cdot \pi / (\varepsilon_s \cdot \varepsilon_{s_{0}}) \cdot \text{qtot}(1, m); \text{ % Total space charge} \]

\[ \text{if } n > 1 \]
\[ \text{Esp}(n, m) = \text{Esp}(n-1, m) + e \cdot 4 \cdot \pi / (\varepsilon_s \cdot \varepsilon_{s_{0}}) \cdot \text{qtot}(n, m); \text{ % Electric field due to space charge} \]
\[ \text{end} \]
end
if xn(m) > 50000
    break
end

%Plotting of the results
[graph,slope,intercept]=logfit(t,Lt.*10^4);
exponent=slope;
factor=10^(intercept);

u=round(m/10)
cmap = hsv(round(m/u));

figure;
for i=1:1:m/u
    plot(x(:,u*i),V(:,u*i),’Color’,cmap(i,:));title(’Electrical
potential in oxide layer’);xlabel(’Normalized Oxide
thickness’);ylabel(’Electrical potential (V)’);
    hold on
    legendInfo{i} = [’L= ’, num2str(10^4*Lt(:,u*i))];
end
legend(legendInfo);
hold off

figure;
for i=1:1:m/u
    semilogy(x(:,u*i),Cv(:,u*i),’Color’,cmap(i,:),’LineStyle’,’--’);
    hold on
    semilogy(x(:,u*i),Ce(:,u*i),’Color’,cmap(i,:));title(’Electron and
vacancy concentrations in oxide layer’);xlabel(’Normalized Oxide
thickness’);ylabel(’Electron and vacancy (-- ) concentrations
(particles/cm3)’);
    hold on
    legendInfo{i} = [’L= ’, num2str(10^4*Lt(:,u*i))];
end
legend(legendInfo);
hold off

figure;
for i=1:1:m/u
    plot(x(:,u*i),qtot(:,u*i),’Color’,cmap(i,:));title(’Space
charge’);xlabel(’Normalized Oxide thickness’);ylabel(’Monolayer space
charge density (/cm2)’);
    hold on
    legendInfo{i} = [’L= ’, num2str(10^4*Lt(:,u*i))];
end
legend(legendInfo);
hold off

figure;
for i=1:1:m/u

subplot(2,1,1); plot(x(:,u*i), Esp(:,u*i), 'Color', cmap(i,:), 'Marker', 'o', 'LineStyle', 'none', 'MarkerSize', 3); title('Space charge contribution to the electric field'); ylabel('Electric field due to space charge (V/cm)'); hold on

legendInfo{i} = ['L= ', num2str(10^4*Lt(:,u*i))];
end
legend(legendInfo);

subplot(2,1,2); semilogy(t,E, 'b'); xlabel('Exposure time (d)'); ylabel('Electric field (V/cm)');
hold off

figure;
for i=1:1:m/u

semilogy(x(:,u*i), sigmae(:,u*i), 'Color', cmap(i,:)); title('Electronic conductivity in oxide layer'); xlabel('Normalized Oxide thickness (microns)');
hold on
legendInfo{i} = ['L= ', num2str(10^4*Lt(:,u*i))];
end
legend(legendInfo);
hold off

figure;
plot(t,Lt*10^4, 'b'); xlabel('Exposure time (d)'); ylabel('Oxide thickness (microns)');

figure;
plot(t,Chi, 'b'); xlabel('Exposure time (d)'); ylabel('Electric field modification factor');

figure;
semilogy(t,Je, 'r'); title('Flux of particles');
hold on
semilogy(t,Jv, 'b'); xlabel('Exposure time (d)'); ylabel('Particle flux (particles/cm2/s)');
hold on
legend('Electron flux', 'Vacancy flux');
hold off

figure;
subplot(2,1,1); plot(t,Jt, 'b'); xlabel('Exposure time (d)'); ylabel('Total flux');
subplot(2,1,2); plot(t,E, 'b'); xlabel('Exposure time (d)'); ylabel('Electric field (V/cm)');
%Output

y={t; mue; muv; eta2; gammav; L; Lt; E; Je; Jv; Jt; Ce; Cv; exponent; factor; Esp; Chi; Jz; qtot};
end
Appendix E-IV

Matlab code for the non-homogeneous field space charge model (NHFSC):

```matlab
function y = NHFLSC(Emv,Eme,Ceom,Cvom,Ceow,Cvow,T,max)

%Definition of the different variables
nu = 10^13; % Jump frequency (Hz)
kb = 1.3806488*10^(-23); % Boltzmann constant (J/K)
e = 1.60217646*10^(-19); % Electron charge (C)
a = 5*10^(-8); % Jump distance (cm)
K = 273; % Kelvin point (K)
tol = 10^(-6); % Tolerance of the coupled current solution
eps=22; % Dielectric constant of zirconia
epso=8.854187817*10^(-12); % Dielectric constant of vacuum
Rv = 123.218/(6.02*10^23*5.68); % Volume of zirconia molecule

% Vector initialization
p = cputime; % Computation time after a monolayer increment
tElapsed = zeros(max,1); % Jacobian computation time
Nlayers = zeros(max,1); % Number of oxide monolayers
Cc = zeros(2*max-1,max); % Concentration vector
Sc = zeros(2*max-1,max); % Residual vector
Jvv = zeros(max,1); % Vacancy flux
Jee = zeros(max,1); % Electron flux
Espp = zeros(2*max-1,max); % Electric field due to space charge
N = 1;
Nlayers(1) = 1;

% 1st monolayer growth

if N==1
    Espp(1,1) = 8*pi*a*e/(eps*epso)*(2*Cvow-Ceow); % Electric field due to space charge in the case of a monolayer oxide thickness
    [E,fval] = fsolve(@(E) 2*exp(-Emv*e/(kb*(T+K)))*(Cvom*exp(e*a*(E+Espp(1,1))/(kb*(T+K)))^2-Cvow*exp(e*a*(E+Espp(1,1))/(kb*(T+K))))^(-2)-exp(-Eme*e/(kb*(T+K)))*(Ceom*exp(e*a*(E+Espp(1,1))/(kb*(T+K)))^(-1)-Ceow*exp(e*a*(E+Espp(1,1))/(kb*(T+K)))),10^5); % solve cc equation
    E0(1) = E; % Surface electric field
    Jvv(1) = 2*a*nu*exp(-Emv*e/(kb*(T+K)))*(Cvom*exp(e*a*(E0(1)+Espp(1,1))/(kb*(T+K))))^2-Cvow*exp(e*a*(E0(1)+Espp(1,1))/(kb*(T+K)))^(-2)); % vacancy flux
    Jee(1) = 2*a*nu*exp(-Eme*e/(kb*(T+K)))*(Ceom*exp(e*a*(E0(1)+Espp(1,1))/(kb*(T+K)))^(-1)-Ceow*exp(e*a*(E0(1)+Espp(1,1))/(kb*(T+K)))); % electron flux
    Jt(1) = 2*Jvv(1)-Jee(1); % Net flux
    dT(1) = 2*a/(Jvv(1)*Rv); % Time increment to grow the 1st monolayer
    Tt(1) = dT(1); % Total time to grow the 1st monolayer
end
```
% Initialization of matrices necessary to store the data up to N oxide monolayers

for N=2:max
    N % Oxide monolayer number
    Nlayers(N) = N; % Vector of the number of oxide monolayers
    mue = zeros(N,1); % Electron mobility vector
    mvu = zeros(N,1); % Vacancy mobility vector
    Esp = sym(zeros(N,1)); % Electric field due to space charge vector
    beta = sym(zeros(N,1)); % Effect of local electric field on mobilities vector
    JV = sym(zeros(N,1)); % Vacancy flux vector
    Je = sym(zeros(N,1)); % Electron flux vector
    F = sym(zeros(2*N-1,1)); % Set of non-linear equations vector
    Cv = 10^15*ones(N-1,1); % Initial guessed vacancy concentration vector
    Ce = 10^15*ones(N-1,1); % Initial guessed electron concentration vector
    g=1;
    Ei = 10^3; % Initial guessed homogeneous electric field

    % Initial concentration in particles/cm3 in the N layers in symbolic variables (necessary to compute the Jacobian in Matlab)
    sym E; % Electric field is a symbolic variable
    Cv = sym(zeros(N,1)); % Vacancy concentration is a symbolic variable
    Ce = sym(zeros(N,1)); % Electron concentration is a symbolic variable

    % Definition of a symbolic vector gathering all unknowns (vacancy and electron concentrations and surface electric field)
    for k = 1:N-1
        Cv(k,1) = sym(sprintf('Cv%d', k));
        Ce(k,1) = sym(sprintf('Ce%d', k));
        C(k,1) = Cv(k,1); % Store vacancy concentration
        C(k+N-1,1) = Ce(k,1); % Store electron concentration
    end

    C(2*N-1,1)=E; % Store electric field

    Cv(N,1) = double(Cvow); % Boundary conditions at the O/W interface
    Ce(N,1) = double(Ceow); % Boundary conditions at the O/W interface

    Elsp(1,1) = 8*pi*a*e/(eps*epso)*(2*Cv(1)-Ce(1)); % Space charged electric field in the 1st monolayer
    Esp(1,1) = Elsp(1,1); % Total electric field due to space charges in a given location in the oxide
\[
\begin{align*}
mue(1) &= \exp\left(-\frac{Em_e e}{kb(T+K)}\right) ; \\
muv(1) &= \exp\left(-\frac{Em_v e}{kb(T+K)}\right) ; \\
\beta(1) &= \exp\left(\frac{e a (E + Esp(1))}{kb(T+K)}\right) ; \\
Jv(1) &= \muv(1)^2 (Cvom \beta(1)^2 - Cv(1) \beta(1)^{-2}) ; \% vacancy flux \\
Je(1) &= mue(1)^2 (Ceom \beta(1)^{-1} - Ce(1) \beta(1)) ; \% electron flux at the 1st monolayer \\
F(1) &= 2Jv(1) - Je(1) ; \% cc equation \\
\end{align*}
\]

\%Electric field due to space charge in the N monolayers \\
% and effect of electric field on migration energy barriers \\

\% for \ i = 2:N \\
\begin{align*}
\operatorname{Elsp}(i,1) &= 8\pi a e/(\varepsilon \varepsilon_0) \times (2Cv(i) - Ce(i)) ; \% Electric field due to space charge at the i^{th} monolayer \\
mue(i,1) &= \exp\left(-\frac{Em_e e}{kb(T+K)}\right) ; \\
muv(i,1) &= \exp\left(-\frac{Em_v e}{kb(T+K)}\right) ; \\
Esp(i,1) &= Esp(i - 1) + \operatorname{Elsp}(i) ; \% Total electric field due to space charge \\
\beta(i,1) &= \exp\left(\frac{e a (E + Esp(i))}{kb(T+K)}\right) ; \\
Jv(i,1) &= \muv(i)^2 (Cv(i-1) \beta(i)^2 - Cv(i) \beta(i)^{-2}) ; \% vacancy flux at the i^{th} monolayer \\
Je(i,1) &= mue(i)^2 (Ce(i-1) \beta(i)^{-1} - Ce(i) \beta(i)) ; \% electron flux at the i^{th} monolayer \\
F(i,1) &= Jv(i-1) - Jv(i) ; \% steady state flux equations \\
F(i+N-1,1) &= Je(i-1) - Je(i) ; \% steady state flux equations \\
\end{align*}

\% Jacobian calculation of F vector gathering all non linear equations \\
F = vpa(F,3) \% Approximation of the symbolic value of the set of non-linear equations \\
tStart = tic; \% Clock starts \\
J = vpa(jacobian(F, C),3); \% Exact Jacobian determination and approximation of the symbolic value of the Jacobian \\
tElapsed(N,1) = toc(tStart); Clock stops \\

\% Numerical expression of the initial concentrations and surface electric field used at the beginning of each routine \\
\% for j=1:N-1 \\
\begin{align*}
&\% In the case of two monolayers, the initial vector is taken in the routine \\
&\text{if } N==2 \\
&\% The vector of unknowns is rewritten in parametric
\( C_t(j,1) = \text{subs}(C(j,1), C_{vi}(j,1)) \);
\( C_t(j+N-1,1) = \text{subs}(C(j+N-1,1), C_{ei}(j,1)) \);
\( C_t(2*N-1,1) = \text{subs}(C(2*N-1,1), E_i) \);
end

% In the case of more than two monolayers, the previous result vector is taken as the initial vector in the routine
if \( N>2 \)
% The vector of unknowns is rewritten in parametric
\( C_t(j,1) = \text{subs}(C(j,1), C_{c}(j,N-1)) \);
\( C_t(j+N-1,1) = \text{subs}(C(j+N-1,1), C_{c}(j+N-1,N-1)) \);
\( C_t(2*N-1,1) = \text{subs}(C(2*N-1,1), C_{c}(2*N-1,N-1)) \);
end

\( C_t = \text{vpa}(C_t,3) \) % Approximation of the symbolic value of the concentrations and surface charge field used in the routine
\( S = \text{zeros}(2*N-1,1) \); % Initialization of the solution increment
\( X(m+1)-X(m) \) vector
\( C_{tt} = \text{zeros}(2*N-1,1) \); % Initialization of the \( X(m) \) vector
stop = 0;

% Newton routine
while ~stop % Newton routine start
  \( g = g+1 \)
  \( F_{_C_t} = \text{vpa}(\text{subs}(F, C, \text{eval}(C_t)), 3) \); % Approximation of the numeric value of the set of linear equations
  \( F_{\text{prime}_C_t} = \text{vpa}(\text{subs}(J, C, \text{eval}(C_t)), 3) \) % Approximation of the numeric value of the Jacobian
  \( d_{F_{C_t}(g)} = \text{norm}(F_{C_t}) \); % Evaluation of the norm of \( F_{C_t} \)
  \% Newton formula (see eqs.6-52 to 6-55)
  \( d_{C_t} = \text{mldivide}(F_{\text{prime}_C_t}, F_{C_t}) \);
  \( C_t = C_t - d_{C_t} \);
  \% End of Newton formula

  \( \text{vpa}(C_t,3) \); % Approximation of the solution at the next iteration
  \( h = \text{norm}(\text{eval}(d_{C_t})) \) % Norm of the increment
  \( S(:, end+1) = d_{C_t} \); % Save of the increment at this oxide thickness and this iteration
  \( C_{tt}(:, end+1) = C_t \); % Save of the solution at this oxide thickness and this iteration
%Check for divergence of the solution
if isnan(Ct)
    stop = 1;
    char('no convergence found')
end

%Check for root convergence and break parameter
if norm(d_Ct) < 10 | abs((norm(d_F_Ct(g)) - norm(d_F_Ct(g-1))))< 10^(-2)
    stop = 1;
end

end

w(N,1)=g;  %Total number of iterations necessary for convergence
Jvv(N,1) = 2*a*nu*subs(Jv(N),C,Ct);  %Vacancy flux at each oxide thickness
Jee(N,1) = 2*a*nu*subs(Je(N),C,Ct);  %Electron flux at each oxide thickness
Jt(N,1) = 2*Jvv(N,1) - Jee(N,1);  %Net flux at each oxide thickness

%Results of the Newton routine are saved at this oxide thickness
for i=1:2*N-1
    Cc(i,N) = Ct(i,1);  %Save concentration vector
    Sc(i,N) = d_Ct(i,1);  %Save increment vector
end

Lt(N,1)= 2*a*Nlayers(N);  %Total oxide thickness
dT(N,1) = 2*a/(Jvv(N,1)*Rv);  %Time increment to grow the Nth monolayer
Tt(N,1) = Tt(N-1,1)+dT(N,1);  %Total exposure time
E0(N) = Cc(2*N-1,N);  %Surface electric field
V0(N) = E0(N)*2*a*Nlayers(N);  Electric potential from surface electric field

%Electric field due to space charge at every monolayer
for i=1:N-1
    qtot(i,N) = 2*a*(2*Cc(i,N)-Cc(i+N-1,N));
    Elspp(i,N) = 4*pi*e/(eps*epso)*qtot(i,N);
end

Espp(1,N) = Elspp(1,N);

%Total electric field due to space charge at every monolayer
for i=2:N-1
    Espp(i,N) = Espp(i-1,N)+Elspp(i,N);
end
%Total electric potential due to space charge at every monolayer

for i=1:N-1
    Vsp(i,N) = (E0(N)+Espp(i,N))*2*a*i;
end
end

%Plotting of the results

[graph,slope,intercept] = logfit(Tt/(3600*24),Lt.*10^4);
exponent = slope;
factor = 10^(intercept);
figure;
plot (Nlayers,tElapsed);xlabel('Number of oxide monolayers');ylabel('Time to compute the Jacobian');

figure;
plot(Tt,Lt*10^4,'-o');xlabel('Exposure time (d)');ylabel('Oxide thickness (microns)');

figure;
semilogy(Nlayers,Jee,'r');title('Flux of particles');
hold on
semilogy(Nlayers,Jvv,'b');xlabel('Number of oxide monolayers');ylabel('Particle flux (particles/cm2/s)');
hold on
legend('Electron flux','Vacancy flux');
hold off

figure;
subplot(2,1,1); plot(Nlayers,Jt,'b');xlabel('Number of oxide monolayers');ylabel('Total flux');
subplot(2,1,2); plot(Nlayers,E0,'b');xlabel('Number of oxide monolayers');ylabel('Electric field (V/cm)');

e = cputime - p

%Output

y = {mue;muv;Jvv;Jee;Sc;Cc;dT;Tt;factor;exponent;tElapsed;qtot;Elsp;Espp;E0;V0;Vsp;k;Nlayers};
save('NHFLSC.mat');
end
VITA

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EDUCATION

• 2011 – 2014 **PhD in Nuclear Engineering** – Mechanical and Nuclear Engineering Department of Penn State University (PA, USA) on the subject of hydrogen pickup behavior in zirconium alloys.

• 2009 – 2011 **Master of Science degree in Nuclear Engineering** – Mechanical and Nuclear Engineering Department of Penn State University. GPA of 3.9. [https://etda.libraries.psu.edu/paper/12311/](https://etda.libraries.psu.edu/paper/12311/)

• Spring 2011 **Master of Engineering degree** – “Ecole Centrale de Lyon” (France) with further development in the nuclear engineering sector.

• 2004 - 2006 **Post-secondary intensive preparatory school** – Lycée Michelet, Paris (France).
Major in Physics, Mathematics and Chemistry.

• June 2004 High school graduation for entry to university (major in Sciences) with honors.

WORK EXPERIENCE

• 2009 – 2014 **Graduate research assistant** – Nuclear Engineering Department of Penn State University (PA, USA):
  • Study of the hydrogen pickup mechanism in zirconium alloys under the supervision of Dr. Arthur T. Motta, chair of the Nuclear Engineering Department.
  • On secondment since January 2013 at the Research and Development department of Materials and Mechanics of Components (MMC) of Electricité de France (EDF, France) under the supervision of Dr. A. Ambard.

  Study of the atomistic simulation of helium bubbles in silicon-carbide through molecular dynamics under the supervision of Dr. J.-P. Crocombette.

• Jun.-Sep. 2008 **Research assistant** – Laboratory of Applied Sciences of Doshisha University (Kyoto, Japan) on the plasma-surface interactions in nuclear field under the supervision of Dr. M. Wada.