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ABSTRACT

Zirconium alloy fuel cladding corrosion and the associated hydrogen pickup is a critical life-limiting degradation mechanism for nuclear fuel in existing and advanced nuclear reactors, since the ingress of hydrogen can cause embrittlement. Past studies used destructive techniques, such as hot vacuum extraction, to measure hydrogen but knowledge of the pickup variation with corrosion and the pickup mechanism is lacking. This research investigated the mechanistic link between hydrogen pickup, oxidation rate, alloy chemistry, and microstructure on a wide selection of zirconium alloys. This study combined the non-destructive technique of Cold-Neutron Prompt-Gamma Activation Analysis, with the usual destructive techniques. This technique allows precise determinations of hydrogen content, (and thus the hydrogen pickup fraction at various stages of corrosion), and the ability to perform several measurements on a single sample, thus removing the sample-to-sample variability. The results obtained are discussed and related to the overall corrosion kinetics and to the oxide microstructure. It is shown that the hydrogen pick-up fraction increases before the weight gain transition for Zircaloy-4 and ZIRLO alloys and thus, appears to not depend on the oxidation kinetics. It is also shown that precipitate size plays a role in hydrogen pick-up whereas precipitate volume fraction does not have a significant effect on hydrogen absorption. Finally, the oxidation state of the alloying element in the oxide layer appears to play a role both on oxidation kinetics and hydrogen pick-up.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>LIST OF FIGURES</th>
<th>vi</th>
</tr>
</thead>
<tbody>
<tr>
<td>LIST OF TABLES</td>
<td>xii</td>
</tr>
<tr>
<td>ACKNOWLEDGEMENTS</td>
<td>xiii</td>
</tr>
</tbody>
</table>

**Introduction** .................................................................................................................. 1

**Chapter 1 Bibliographical Review** .................................................................................... 4

1.1. Metallurgy of zirconium alloys ......................................................................................... 4
  1.1.1. Zirconium alloys use in nuclear industry ................................................................. 4
  1.1.2. Alloying elements in common zirconium alloys ...................................................... 7
1.2. Corrosion kinetics ........................................................................................................... 15
  1.2.1. Waterside corrosion of zirconium alloys ................................................................. 15
  1.2.2. Weight gain kinetics ................................................................................................. 24
  1.2.3. Oxide transition ......................................................................................................... 25
1.3. Hydrogen pick-up ............................................................................................................ 28
  1.3.1. Definition .................................................................................................................. 28
  1.3.2. Techniques of hydrogen level assessment in zirconium alloys ............................... 30
    1.3.2.1. Destructive techniques ....................................................................................... 30
    1.3.2.2. Non-destructive techniques ............................................................................... 31
  1.3.3. Hydrogen pick-up characterization .......................................................................... 33
  1.3.4. Parameters influencing hydrogen pick-up ............................................................... 34
    1.3.4.1. External parameters ......................................................................................... 35
      1.3.4.1.1. Temperature ............................................................................................... 35
      1.3.4.1.2. Dissolved gases in solution ......................................................................... 37
      1.3.4.1.3. Chemical environment .............................................................................. 42
      1.3.4.1.4. Irradiation ................................................................................................. 44
      1.3.4.1.5. D$_2$O vs H$_2$O ......................................................................................... 44
      1.3.4.1.6. Effect of flow ............................................................................................. 45
    1.3.4.2. Internal parameters ............................................................................................ 46
      1.3.4.2.1. Alloying element additions ........................................................................... 46
      1.3.4.2.2. Alloy metallurgy ........................................................................................ 50
  1.3.5. Mechanism for hydrogen absorption ....................................................................... 53
1.4. Objective of the study .................................................................................................... 63

**Chapter 2 Experimental procedures** .................................................................................. 64

2.1. Zirconium alloys studied ............................................................................................... 64
2.2. Corrosion procedure ...................................................................................................... 70
2.3. Vacuum Hot Extraction (VHE) ...................................................................................... 71
2.4. Cold Neutron Prompt Gamma Activation Analysis (CNPGAA) ................................... 74
2.4.1. Theory ................................................................................................................. 74
2.4.2. General scheme of CNPGAA apparatus ...................................................... 78
2.4.3. Apparatus at the National Institute of Standard and Technology (NIST) ...... 79
2.4.4. Fitting standard and data analysis .................................................................... 82
   2.4.4.1. Fitting of the gamma-ray spectrum ............................................................ 82
   2.4.4.2. Standards ................................................................................................. 84

Chapter 3 Experimental results ..................................................................................... 87

3.1. CNPGAA benchmarking ..................................................................................... 87
3.2. CNPGAA validation ............................................................................................ 89
3.3. Hydrogen pick-up fraction calculation ............................................................... 91
3.4. Hydrogen pick-up variation as a function of alloying elements determined by
    VHE ......................................................................................................................... 94
   3.4.1. Pure zirconium sponge .................................................................................. 94
   3.4.2. Zr-Sn-Fe-Cr alloys (Zircaloy-4 based) ......................................................... 99
   3.4.3. Binary alloys: Zr-0.5Cu sheet ...................................................................... 108
   3.4.4. Binary alloys: Zr-Cr sheets ......................................................................... 110
   3.4.5. Binary alloys: Zr-Nb .................................................................................. 118
   3.4.6. Ternary alloys: Zr-Fe-Cr sheets .................................................................... 122
   3.4.7. Ternary alloys: Zr-Nb-Cu .......................................................................... 132
   3.4.8. Quaternary alloys: Zr-Nb-Sn-Fe alloys (ZIRLO based) ............................. 135
3.5. Summary of the results ...................................................................................... 141

Conclusions .................................................................................................................... 145

REFERENCES ................................................................................................................. 146
LIST OF FIGURES

Figure 0-1: Hydrogen absorption in the Oxidation Reaction with a theoretical pick-up fraction of 15% [4] .................................................................3

Figure 1-1: Fuel assembly and rod cross section ..................................................5

Figure 1-2: Zircaloy cladding manufacturing sequence [10] ....................................7

Figure 1-3: Phase diagrams: a) Zr-O [11] and b) Zr-Sn [12] ....................................8

Figure 1-4: Phase diagrams Zr-Cr [17] ..................................................................10

Figure 1-5: Phase diagrams Zr-Fe [17] ..................................................................10

Figure 1-6: Phase diagrams Zr-Ni [17] ..................................................................11

Figure 1-7: Phase diagram of Zr-Nb [19] .................................................................12

Figure 1-8: Phase diagram of Zr-H [17] .................................................................14

Figure 1-9: The three crystallographic modifications of ZrO₂ at normal pressure [29, 30] .......15

Figure 1-10: Schematic of the reactions taking place during uniform corrosion of Zr........18

Figure 1-11: Schematic representation of the corrosion of Zircaloy [58] ......................26

Figure 1-12: Oxide layer thickness as a function of exposure time [59] .......................27

Figure 1-13: Different oxidation regime of Zircaloys ..............................................28

Figure 1-14: Oxygen weight gain in function of exposure time in 360°C water + 1000psi oxygen [81]. .........................................................................................37

Figure 1-15: Hydrogen weight gain as function of oxygen weight gain [81] ...............38

Figure 1-16: Hydrogen absorption of Zircaloy-2 and Ni-free Zircaloy-2 in hydrogenated and degassed 343°C water [81] .................................................................40

Figure 1-17: Hydrogen absorption of Zircaloy-2 in hydrogenated and degassed 343°C water [81] .........................................................................................41

Figure 1-18: Hydrogen pick-up as function of hydrogen overpressure after a 14 days exposure in 343° water for both Zircaloy-2 and Zircaloy-4 with different heat treatments [81] ..............................................................................42
Figure 1-19: Hydrogen absorption as function of oxygen weight gain for Zircaloy-2 and - 4 exposed in 360° water replenished with pH 10 lithium hydroxide and approximately 3 psi of hydrogen overpressure [81]..................43

Figure 1-20: Hydrogen pick-up as function oxygen weight gain in static and refreshed autoclave [81]...............................................................45

Figure 1-21: Hydrogen pick-up in sponge based zirconium alloys exposed up to 575 days to static water at 360°C [69]. .................................................................47

Figure 1-22: Hydrogen pick-up fraction as function of Nb content in various Zr-Nb alloys in aged and quenched conditions at 400°C steam under 10Mpa H2O (the error bars are equal to 7% in averaged) [78] ................................50

Figure 1-23: Hydrogen pick-up fraction as a function of exposure time (days) for different metallurgical states of Zircaloy-2 [5] ..................................................51

Figure 1-24: Hydrogen pick-up in Zircaloy-4 [5] ........................................................................52

Figure 1-25: Schematic representation of the corrosion and hydrogen absorption of Zircaloy [81] ..................................................................................54

Figure 1-26: The relationship between oxide surface potential and anion vacancy [93] .........61

Figure 1-27: Corrosion behavior and hydrogen pick-up properties of Zr-4 in pure water at 360°C [65] ..................................................................................62

Figure 2-1: Optical micrographs of etched Zircaloy-4 sheet (50x) ..............................................69

Figure 2-2: Optical micrographs of etched ZIRLO sheet (50x) ................................................69

Figure 2-3: Scheme of VHE apparatus ..................................................................................72

Figure 2-4: Analyzed part of samples for VHE in red (distance are in mm) .........................73

Figure 2-5: Analyzed parts of one sample (in red) to quantify hydrogen content variations...74

Figure 2-6: Mechanism of prompt gamma ray emission by neutron absorption ..............75

Figure 2-7: Scheme of a CNPGAA apparatus (not to scale) ................................................78

Figure 2-8: Plan of the NIST reactor and the Cold Neutron Research Facility. The guide hall dimensions are 30.5 x 61 m .................................................................80

Figure 2-9: Side view of CNPGAA instrument at NIST .....................................................81

Figure 2-10: Gamma ray counts versus gamma ray energy obtained during measurement of a Zr-1Nb-1Sn-0.1Fe sample after 105 days of corrosion in pure water at 360 °C and plotted using GENIE 2000 [120]. The zirconium reference peak (934 keV) and the hydrogen peak (2223 keV) are indicated by arrows ...................................................83
Figure 2-11: Zoom of the gamma ray spectrum (number of counts as a function of gamma ray energy) on the hydrogen energy peak region of Zr-1Nb-1Sn-0.1Fe after 105 days of corrosion in pure water at 360 °C, plotted using GENIE 2000. The hydrogen peak is indicated by an arrow. The calculated hydrogen concentration of this alloy after 105 days of corrosion is 49 mg·kg⁻¹ (or wt·ppm).

Figure 3-1: Hydrogen concentration (wt·ppm) in ZIRLO coupons as function of corrosion time using VHE on sister samples and successive CNPGAA measurements on two different individual coupons, plotted along with the weight gain of the corresponding sample.

Figure 3-2: Weight gain for 16 archived samples of sponge Zirconium sheet (red lozenges mean archived samples and red numbers corresponds to samples presented in Figure 3-3) in 360°C water [125].

Figure 3-3: Weight gain and hydrogen pick-up fraction of 3 zirconium sponge sheet archived samples (early breakaway is represented by red circles).

Figure 3-4: Pure zirconium corroded in 360°C water after 7 days of exposure and 15.1 mg/dm² weight gain (sample #1 in Figure 3-3) A) Polarized light image of cross-section [126], B) Backscattered SEM cross-sections micrographs (x8000), C) Backscattered SEM cross-sections micrographs (x16000) [14].

Figure 3-5: Pure zirconium corroded in 360°C water after 14 days of exposure and 16.3 mg/dm² weight gain (sample #2 in Figure 3-3) A) Polarized light image of cross sections [126] B) Secondary Electron SEM cross-sections micrographs [14].

Figure 3-6: Pure zirconium corroded in 360°C water after 69.3 days of exposure and 51.6 mg/dm² weight gain (sample #2 in Figure 3-3): Secondary Electron SEM cross-sections micrographs.

Figure 3-7: Weight gain for 16 archived samples of Zr-1.3Sn-0.2Fe-0.1Cr (H) sheets (red lozenges mean archived samples and red numbers corresponds to samples presented in Figure 3-9) in 360°C water [14].

Figure 3-8: Weight gain of Zr-Sn-Fe-Cr alloys (red lozenges mean archived samples) in 360°C water.

Figure 3-9: Total hydrogen pick-up fraction of Zircaloy-4: Zr-1.3Sn-0.2Fe-0.1Cr (H) (see Figure 3-7 for corresponding weight gains of archived samples) and weight gain of sample#9 (red lozenge means archived samples).

Figure 3-10: Total hydrogen pick-up fraction and weight gain of Zircaloy-4: Zr-1.45Sn-0.2Fe-0.1Cr sheet (red lozenges mean archived samples).

Figure 3-11: Total hydrogen pick-up fraction and weight gain of Zr-1.45Sn-0.2Fe-0.1Cr cold work stress relieved tube (red lozenges mean archived samples).

Figure 3-12: Hydrogen content in mg/dm² as a function of weight gain of Zircaloy-4 alloys.
Figure 3-13: Weight gain (red=Zr-4 sheet and blue=Zr-4 tube) and instantaneous pick-up fraction using a 15-day step exposure time (red lozenges mean archived samples). .......106

Figure 3-14: Instantaneous pick-up fraction using Zr-4 sheet, comparison between sister samples and one CNPGAA coupon (red lozenges mean archived samples) ..............107

Figure 3-15: Weight gain for 16 archived samples of Zr-0.5Cu sheet (red lozenges mean archived samples and red numbers corresponds to samples presented in Figure 3-16) in 360°C water ...........................................................................................................108

Figure 3-16: Weight gain and hydrogen pick-up fraction of 7 Zr-0.5Cu sheets archived samples chosen for hydrogen pick-up investigation (numbers are related to Figure 3-15) .................................................................................................................................109

Figure 3-17: Weight gain for 16 archived samples of Zr-0.5Cr sheets (red lozenges account for archived samples and red numbers corresponds to samples presented in Figure 3-18) in 360°C water ...........................................................................................................110

Figure 3-18: Weight gain and hydrogen pick-up fraction of three Zr-0.5Cr sheets archived samples chosen for hydrogen pick-up investigation (red numbers are related to Figure 3-17) .................................................................................................................................111

Figure 3-19: SEM cross-section micrographs in backscattered mode of Zr-0.5Cr sample#1 corroded in 360°C for 14 days a) 4000x and b) 8000x [14] ..............................................112

Figure 3-20: SEM cross-section micrographs in backscattered mode of Zr-0.5Cr sample#2 corroded in 360°C for 21 days .........................................................................................112

Figure 3-21: Weight gain for 16 archived samples of Zr-1.0Cr sheets (red lozenges account for archived samples and red numbers corresponds to samples presented in Figure 3-22) in 360°C water ...........................................................................................................114

Figure 3-22: Weight gain and hydrogen pick-up fraction of four Zr-1.0Cr sheet archived samples chosen for hydrogen pick-up investigation .................................................................115

Figure 3-23: SEM cross-section micrographs in backscattered mode of Zr-1.0Cr, sample #3 corroded in 360°C water for 55 days (weight gain = 41.9mg/dm²): A) 4000x, B) 11300x ..................................................................................................................................................116

Figure 3-24: Hydrogen content (mg/dm²) of Zr-0.5Cr and Zr-1.0Cr as a function of weight gain (mg/dm²) ......................................................................................................................117

Figure 3-25: Weight gain of different niobium alloys (red lozenges mean archived samples) corroded in 360°C water ......................................................................................................118

Figure 3-26: Pick-up fraction and weight gain as function of exposure time for Zr-2.5Nb tube corroded in 360°C water (red lozenges mean archived samples) ..............................120

Figure 3-27: Hydrogen content as function of weight gain for different niobium alloys .......120
Figure 3-28: Weight gain for 16 archived samples of Zr-0.2Fe-0.1Cr (L) sheets (red lozenges account for archived samples and red numbers corresponds to samples presented in Figure 3-32) in 360°C water .......................................................... 123

Figure 3-29: Weight gain for 16 archived samples of Zr-0.2Fe-0.1Cr (H) sheets (red lozenges account for archived samples and red numbers corresponds to samples presented in Figure 3-33) in 360°C water .......................................................... 123

Figure 3-30: Weight gain for 16 archived samples of Zr-0.4Fe-0.2Cr (L) sheets (red lozenges account for archived samples and red numbers corresponds to samples presented in Figure 3-34) in 360°C water .......................................................... 124

Figure 3-31: Weight gain for 16 archived samples of Zr-0.4Fe-0.2Cr (H) sheets (red lozenges account for archived samples and red numbers corresponds to samples presented in Figure 3-35) in 360°C water .......................................................... 124

Figure 3-32: Total hydrogen pick-up fraction and weight gain of Zr-0.2Fe-0.1Cr (L) as a function of exposure time ................................................................................. 126

Figure 3-33: Total hydrogen pick-up fraction and weight gain of Zr-0.2Fe-0.1Cr (H) as a function of exposure time ................................................................................. 126

Figure 3-34: Total hydrogen pick-up fraction and weight gain of Zr-0.4Fe-0.2Cr (L) as a function of exposure time ................................................................................. 127

Figure 3-35: Total hydrogen pick-up fraction and weight gain of Zr-0.4Fe-0.2Cr (H) as a function of exposure time ................................................................................. 127

Figure 3-36: Hydrogen content (mg/dm²) as a function of weight gains for Zr-Fe-Cr alloys .......................................................................................................................... 128

Figure 3-37: Weight gain for Zr-2.5Nb, Zr-0.5Cu sheet and Zr-2.5Nb-0.5Cu tube (red lozenges mean archived samples) in 360°C water ......................................................... 133

Figure 3-38: Weight gain for Zr-2.5Nb tube, Zr-0.5Cu sheet and Zr-2.5Nb-0.5Cu tube (red dots account for archived samples) in 360°C water ......................................................... 134

Figure 3-39: Weight gain as a function of exposure time of Zr-Nb-Sn-Fe alloys (red lozenges mean archived samples) ................................................................................. 135

Figure 3-40: Total hydrogen pick-up and weight gain of ZIRLO sheet (red lozenges mean archived samples) .................................................................................................... 136

Figure 3-41: Total hydrogen pick-up and weight gain of ZIRLO tube (red lozenges mean archived samples) ............................................................................................... 137

Figure 3-42: Weight gain (red=ZIRLO sheet and blue=ZIRLO tube) and instantaneous pick-up fraction using a 15 day-step (red lozenges mean archived samples) ................. 139
Figure 3-43: Instantaneous pick-up fraction using ZIRLO sheet, comparison between sister samples and two CNPGAA coupons (red lozenges mean archived samples)..........140
LIST OF TABLES

Table 1-1: ASTM Specifications for Zircaloy-2, Zircaloy-4 and Zr-Nb [6]. The normal choice of compositions for the advanced ZIRLO™ and M5™ alloys used nowadays in the nuclear industry (wt%) [7] are also shown..............................................................6

Table 1-2: Model alloys pre-transition kinetics constants in 360°C water autoclave experiments [7, 14]. .........................................................................................................................25

Table 1-3: Cladding environment in different reactors [6]..............................................................35

Table 1-4: Chemical compositions of Zircaloy-2, Ni-free Zircaloy-2 and Zircaloy-4 in [8]..............................................................................................................................................35

Table 1-5: Post transition hydrogen pick-up fraction of the Zircalloys [5]. ..............................36

Table 2-1: Chemical composition, geometry, process temperature and origin of alloys used in this study [14]. ........................................................................................................65

Table 2-2: Alloy fabrication procedure [14]...................................................................................66

Table 2-3: Grain sizes of some of the I-NERI alloys [14]................................................................66

Table 2-4: Hydrogen content on different samples of a given alloy corroded for 60 days.....74

Table 2-5: Calculated activities and dose rates for the end of irradiation of 1g of Zicaloy-4 after a decay period of 3hours and a neutron flux of $8 \times 10^8 \text{ cm}^{-2}.\text{s}^{-1}$ ..............................77

Table 2-6: Hydrogen and zirconium sensitivities and hydrogen background determine for CNPGAA measurements .............................................................................................................86

Table 3-1: Hydrogen concentration in wt-ppm obtained with VHE and CNPGAA on 10 Zr alloys (25 mm x 20 mm x 0.8 mm). ..............................................................89

Table 3-2: Weight gain and oxide thickness at transition for Zr-Sn-Fe-Cr alloys...................101

Table 3-3: $n$ value for different Nb contents in Zr-Nb alloys [14]. ..............................................119

Table 3-4: Weight gain and critical oxide thickness for protective behavior for Zr-Fe-Cr alloys .................................................................................................................................129

Table 3-5: Effect of Zr(Cr,Fe)$_2$ precipitate size and Zr(Cr,Fe)$_3$ precipitate volume fraction on corrosion behavior and hydrogen pick-up fraction for ZrFeCr alloys. .....................131

Table 3-6: Weight gain and critical oxide thickness for protective behavior for Zr-Nb-Sn-Fe alloys .........................................................................................................................136
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Introduction

Materials used in the nuclear reactor core need to perform within acceptable limits of mechanical properties, heat transfer capabilities and also withstand radiation damage, corrosion, as well as elevated temperatures and pressures for long exposures. Furthermore, these materials need to have a low neutron absorption cross section. That is why zirconium alloys are currently used in thermal nuclear reactors as fuel cladding. The cladding is the primary barrier to fission product release by physically separating the fuel pellet from the primary coolant. Indeed, zirconium alloys are known for their low neutron absorption cross section [1], their good high temperature corrosion resistance and microstructural stability under irradiation. However, zirconium alloys undergo waterside corrosion in the high temperature coolant water leading to the formation of an oxide layer and to the release of hydrogen gas in the coolant according to Equation 1:

\[
Zr + 2H_2O \rightarrow ZrO_2 + 2H_2
\]  

Although the oxide layer formed is protective, and acts as a barrier to hydrogen ingress, some of the hydrogen generated during corrosion can enter the metal and form brittle hydrides, which degrade mechanical properties.

The absorption of hydrogen in zirconium alloys cladding through the oxide layer formed during waterside corrosion has been extensively researched since the beginning of the nuclear power era. The existing commercial alloys were formulated largely through empirical methods of alloy addition, testing, optimization and thermo-mechanical processing. The research led to the development of new alloys which absorb less hydrogen such as Zircaloy-4, ZIRLO® and M5® that are currently used in PWR. One of the questions that has to be answered is whether or not the hydrogen is actually absorbed at a constant rate over the entire exposure time, if the absorption
rate varies among alloys and if it is related to the oxidation kinetics. It has been proposed that for Zircaloy-4, approximately 15% of the hydrogen generated by the corrosion reaction is absorbed by the metal [2] (see Figure 0-1). On the other hand, the Boiling Water Reactor’s (BWR) cladding, called Zircaloy-2, exhibits higher hydrogen absorption under water corrosion at 350°C, which is the temperature of the reactor primary coolant as a function (the inner wall surface being at 400°C).

In current conditions, the hydrogen level in the cladding rods at the end of cycle does not exceed 800 wt.ppm and thus does not exceed the Nuclear Regulatory Commission (NRC) limit of 1000 wt.ppm ($\approx$ 9.2 at%) [3]. However, new challenges arise today since the nuclear industry would like to extend fuel burnup and have it work in a more corrosive and higher temperature cladding environment. These factors could lead to an increase in the hydrogen content of cladding rods at the end of cycle.

The mechanism of absorption of hydrogen during corrosion reaction of zirconium alloys is not well understood. Indeed, the characterization of hydrogen transport in the oxide layer is particularly difficult due to the difficulty in reliably measuring hydrogen content. Also, most techniques are not performed in-situ but are often performed after cooling, which is very problematic in the case of hydrogen detection because of the very high mobility of hydrogen in the matrix. Finally, there are numerous parameters that could influence the hydrogen absorption such as the mass fraction of alloying elements, precipitate size, coolant chemistry and temperature, zirconium metal microstructure, irradiation dose, etc.

The objective of this study was to give a better understanding on how can we reliably and precisely detect hydrogen in zirconium alloys. Then, the study focused on the characterization of the hydrogen pick-up variations as a function of exposure times and alloy compositions. Finally, the hydrogen absorption rate was related to the oxidation kinetics.
Figure 0-1: Hydrogen absorption in the Oxidation Reaction with a theoretical pick-up fraction of 15\% [4]
Chapter 1

Bibliographical Review

This chapter presents a bibliographical review to develop relevant aspects of hydrogen absorption in zirconium alloys during water corrosion.

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, we the waterside corrosion kinetics in reactor and in autoclave is presented. The influence of different parameters, such as alloying element mass fraction and temperature, on the oxidation kinetics are discussed. The hydrogen pick-up fraction is defined and characterized and the various parameters that influence it are discussed.

1.1. Metallurgy of zirconium alloys

1.1.1. Zirconium alloys use in nuclear industry

The fuel in BWRs and PWRs is in the form of uranium dioxide (UO₂) pellet stacked in a tube cladding made of zirconium alloys. These fuels rods (approximately 4 m height for 9.6 mm diameter) are gathered to form fuel assemblies, and several such assemblies compose the nuclear core (Figure 1-1).
The alloying element mass fraction in zirconium alloys is usually low 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 [5]. 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.

Table 1-1: ASTM Specifications for Zircaloy-2, Zircaloy-4 and Zr-Nb [6]. The normal choice of compositions for the advanced ZIRLO™ and M5™ alloys used nowadays in the nuclear industry (wt%) [7] 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>
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<td>1.2-1.7</td>
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<td>-</td>
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<tr>
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<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.

However, nickel has been associated with high hydrogen absorption and thus Zircaloy-2 was not a good candidate for PWRs fuel cladding [8]. Consequently, the Zircaloy-4 (Zr-Sn-O-Fe-Cr) was developed, in which the nickel has been removed and replaced by iron.

Zircaloy-2 and Zircaloy-4 have similar properties. They are composed of an αZr matrix (low temperature, hexagonal compact phase of zirconium). 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 P63/mmc. At 865°C, Zr undergoes an allotropic transformation from hcp α phase to a bcc β phase and finally melts at 1860°C [9].

The microstructure of the alloys largely depends on the heat treatment they undergo during alloy fabrication and processing. Figure 1-2 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**

In the αZr matrix of Zircaloy-2 and Zircaloy-4 both Sn and O elements are found in solid solution, respectively in substitution for the former and insertion for the latter [9]. Figure 2-3 presents the phase diagram for Zr-O and Zr-Sn. The phase diagram of this Zr-Sn system shows three compounds SnZr₄, Sn₂Zr₅, Sn₇Zr, which should be present at room temperature. However, even if thermodynamics predict their formation, they are not observed in normal Zr alloys probably because of slow kinetics of formation.

Figure 1-2: Zircaloy cladding manufacturing sequence [10]
Figure 1-3: Phase diagrams: a) Zr-O [11] and b) Zr-Sn [12]
The other alloying elements (Fe, Cr, Ni) have a very low terminal solubility in αZr and thus precipitate as Zr(Fe,Cr)_2 and Zr_2(Fe,Ni) in Zircaloy-2 and as Zr(Fe,Cr)_2 in Zircaloy-4. These second phase particles (SPP) are Laves phases both inter and intra granular [13]. 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 [14]. It has been shown that their optimal size to improve resistance to corrosion in PWRs was around 150 nm [15] while finely distributed small precipitates seem to improve the corrosion resistance in BWRs [6]. 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 [6]. Charquet [16] studied the solubility limit of iron and chromium in Zr-1.4Sn matrix. The maximum solubilities are 120 ppm for iron at 820°C, 200 ppm for chromium 860°C and 150 ppm for iron plus chromium at 810°C. The phase diagrams of Zr-Fe, Zr-Cr and Zr-Ni are presented in Figure 1-4, 1-5 and 1-6. The first precipitates to form are of ZrCr_2 and Zr_2Ni types. Iron precipitates at a slightly lower temperature and prefers to precipitate as Zr(Cr,Fe)_2 or Zr_2(NiFe) instead of Zr_3Fe [9].
Figure 1-4: Phase diagrams Zr-Cr [17]

Figure 1-5: Phase diagrams Zr-Fe [17]
Niobium is also found in Zr-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 Zr up to 0.4 at%–0.5 at% at which point β-Nb precipitates. These precipitates contain approximately 85% of Nb and have a size of 50 nm which is usually smaller than Zr(Fe,Cr)$_2$ and Zr$_2$(Fe,Ni) precipitates. 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' supersaturated hcp phase. If this is followed by heat treatment below the monotectoid temperature precipitation of β'–Nb occurs at twin boundaries of the α' needles [18].
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 thermal 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 [20]. Terminal solid solubility (TSS) of hydrogen in αZr, Zircaloy-2 and Zircaloy-4, below 550°C, is given by Kearns et al. as:

\[ C_H = 9.9 \times 10^4 e^{-8250/RT} \text{ ppm} \]  

where T is the temperature in Kelvins and R the universal gas constant. The hydrogen solubility in αZr first increases with the oxygen content and then decreases at higher oxygen contents. The hydrogen solubility in the βZr(O) solid solution first decreases with the oxygen content and then
increases slightly. The presence of interstitial oxygen varied the enthalpy of solution of hydrogen into both the αZr(O) and βZr(O) solid solutions. 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 little solubility of hydrogen in the zone containing a high concentration of oxygen [21]. The hydrogen solubility is 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 [22]. Assuming the oxides 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 [21] on preoxidized samples exposed to tritium. This low solubility of hydrogen in zirconia is also confirmed by Miyake et al. [23] where the hydrogen concentration ranged between $10^{-4}$ and $10^{-5}$ moles of hydrogen per moles of oxide and decreases with increasing temperature. This situation might be quite different in porous oxide films [24]. The authors also observed a significant 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 or if it is due to favored hydride precipitation sites during the cooling process (stress effect of the oxide) has not been clarified.

In steam at 300°C-400°C, the rate of hydrogen uptake decreases when the TSS in the metal is exceeded during the oxidation of zirconium alloys [25]. 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 at the entry site and to counter effect the hydrogen diffusion rate 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.
The hydrides do not change too much the mechanical properties of the material at high temperature. However, at room temperature, hydrogen precipitates as hydride particles, which can embrittle the metal by lowering the fragile/ductile transition temperature [26]. Furthermore, hydrogen is also a $\beta$-stabilizer. Thus, in the case of a loss of coolant accident (LOCA), high hydrogen content could lower the $\alpha \rightarrow \beta$ transition. Since the $\beta$ phase is very susceptible to irradiation creep, high hydrogen content can lead to a problematic 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.

Figure 1-8: Phase diagram of Zr-H [17]
1.2. Corrosion kinetics

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. On the particular subject of zirconium oxidation Cox [27] and the IAEA [6, 26] (International Atomic Energy Agency Technical Document) have published complete and detailed reviews.

A native thin layer of so called air-formed 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 \( \text{Zr}_2\text{O} \) were reported to be seen (\( \text{ZrO}, \text{Zr}_3\text{O} \) and \( \text{Zr}_3\text{O}_{1.3} \)) accompanied by the oxide of \( \text{ZrO}_2 \) [28]. 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 [27].

The stable zirconium oxide (\( \text{ZrO}_2 \)) exists in three crystallographic modifications at normal pressure. These are monoclinic, tetragonal and cubic, see Figure 1-9.

Figure 1-9: The three crystallographic modifications of \( \text{ZrO}_2 \) at normal pressure [29, 30].
In reactor or autoclave oxidation conditions (below 500°C), the most stable oxide phase is monoclinic (see Figure 1-9c). 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-stoechiometry and/or alloying elements (especially iron) [31].

As a consequence of the thermodynamics of the zirconium oxidation system being considered and the environmental conditions to which the material is exposed, defect concentrations will be established at the two interfaces of the oxide layer (oxide/water and oxide/metal interfaces). These defects concentration gradients are the driving force for the diffusion of the species across the oxide film. The mobile species can be some combination of cation interstitials or vacancies, anion interstitials or vacancies and electrons or holes.

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 reaction given in equation (1) cannot happen directly, but the oxidizing species have to travel through the oxide layer. In the absence of external applied potentials on the specimen there can be no net current through the oxide. Thus, the negative and positive oxidation currents must be equal and opposite. If this is not the case initially, then a potential will develop across the oxide that will equalize these currents. It requires either the cations or the anions to be transported through the oxide layer (that is, either the oxygen atoms have to arrive at the oxide/metal interface or the zirconium atoms have to arrive at the oxide/water interface). In ceramic zirconia specimens oxygen was established to have much higher diffusion rates than zirconium ions [32]. From the observation of the zirconium oxide system it has been proposed that the corrosion of zirconium and its alloys in high temperature environment occurs by oxygen anion migration throughout the corrosion film, with the formation of new oxide at the metal/oxide interface [32, 33]. The observed sub-stoechiometry gradient (or oxygen activity gradient) of the zirconium oxide would
be the driving force for the oxygen anion diffusion. However, this amount of sub-stoechiometry has not been precisely determined. The diffusion of zirconium ions in ZrO\(_2\) is expected to be low, based on its immobility during the growth of anodic oxide films and thus Zr ions do not diffuse through the oxide layer during water corrosion at 360°C [32]. However, reports of some Zr mobility at very high temperatures under LOCA conditions showed that there might be some small zirconium ion migration [34].

The series of reactions are schematically shown in Figure 1-10.

The oxidation can be divided in four steps. Firstly, oxygen dissolved in the water is adsorbed onto the oxide layer surface:

\[
2\text{H}_2\text{O} \xrightarrow{\text{dissociation}} 4\text{H}^+ + 2\text{O}^{2-}_{\text{adsorbed}} \tag{3}
\]

\[
\text{O}^{2-}_{\text{adsorbed}} + \text{V}_0 \xrightarrow{\text{absorption}} \text{O}^{2-}_{\text{adsorbed}} \tag{4}
\]

In reactor hydrogen is also generated by radiolysis according to the following reaction:

\[
\text{H}_2\text{O} \xrightarrow{\text{radiolysis}} \text{HO}^- + \text{H}^+ \tag{5}
\]

It has been proposed that the lower energy created by oxygen vacancies in the oxide layer could lower the enthalpy of the dissociation reaction of water in an oxygen ion and two protons [27]. Then, because of the defect concentration gradient which is the driving force (see concentration profile of anions in blue in Figure 1-10). When the oxygen anion arrives at the oxide/metal interface it can react with Zr cations to form new oxide.

\[
\text{Zr} \xrightarrow{\text{oxidation}} \text{Zr}^{4+} + 4\text{e}^- \tag{6}
\]

\[
\text{Zr}^{4+} + 2\text{O}^{2-}_{\text{adsorbed}} \xrightarrow{\text{oxide formation}} \text{ZrO}_2 \tag{7}
\]

The formation of this new oxide releases electrons which then, migrate through the oxide to reduce the hydrogen ions in the outer layer (black arrow in Figure 1-10).
The driving force of this diffusion is the electrical gradient through the oxide layer.

Figure 1-10: Schematic of the reactions taking place during uniform corrosion of Zr

The driving force of this diffusion is the electrical gradient through the oxide layer.
However, some hydrogen atoms do not recombine with electrons at the oxide/water interface but are instead absorbed by the oxide layer. These atoms then diffuse through the oxide layer to the metal, where they are found either in solid solution of αZr or as hydride precipitate (diffusion is marked by an orange arrow in Figure 1-10). This phenomenon is called hydrogen pick-up and is discussed in more detailed in the following sections. The hydrogen ingress through the oxide layer and the electron diffusion are two competing processes. The scheme detailed above allows for the possibility of any of the steps being rate-limiting. That is, the slowest reaction controls the corrosion kinetics.

It is well known that the corrosion rate decreases as the thickness of the oxide layer increases. Thus, it is unlikely that any surface reactions steps are rate limiting. So either oxygen ion diffusion or electron diffusion is rate-limiting. If we assume that the rate limiting step is the oxygen ion diffusion through the oxide layer, we can develop a parabolic scaling law for the oxidation kinetics; however, if the transport of electrons through the oxide is the rate-limiting step, an electrical gradient would appear that would slow down the diffusion of oxygen (and then a lower power law will be observed). The rate limiting step is likely influenced by the type of alloying elements, the environment (temperature, coolant chemistry, etc.) and the thickness of the oxide. Even if some models have been proposed [35], a complete understanding is still lacking and it is possible that a combination of these mechanisms may contribute to determine the overall oxidation rate. Several experiments have been done to quantify the ion and electron diffusion.

From anodic oxidation experiments, it was concluded that the equations which best fit the anodic (ionic transport) and cathodic (electron transport) processes are different [35]. The former fits a diffusion controlled process; the latter appears to be best fitted to a Schottky emission process with the emission taking place at a few localized sites in the oxide [36]. However, information about the ionic transport process during oxidation cannot be obtained from
potential measurements alone, and that because of the differences between the transport processes for ions and electrons. Both processes should be studied separately if possible to deduce how each process is influenced by oxidation conditions. The potentials measured across the oxide film are apparently determined by the kinetics of the processes occurring, and are not necessarily related to the thermodynamics of the system [37].

If the two processes do not initially proceed at identical rates, a potential will develop across the oxide such as will slow down the faster process and accelerate the slower process to equalize the two rates. The magnitude of the resulting potential difference will be determined by the polarizability of the two diffusion processes (i.e. the slopes of their respective I–V curves) and the half-cell potentials of the anodic (oxygen migration) and cathodic (electron migration) half-cells [35].

The overall potential driving the oxidation reaction has been established from the energy involved to be approximately equal to 2.34V [38], but the respective half-cell potentials must be determined experimentally.

To study the electron transport process we need a method of forming an electrical contact with the outer surface of the oxide which would satisfy the following criteria [39]:

- It should not affect the oxidation rate of the surface beneath the contact
- It should contact the whole specimen area or a known fraction of that area so that the current density could be measured.
- It should be as near as possible to an ohmic reversible contact for both ionic and electronic processes.
- No additional contributions to the measured current (i.e. from processes other than specimen oxidation) should be present.

Measuring the potentials developed across the oxide film during oxidation without affecting the oxidation reaction is not easy. Experiments at high temperatures (600–800°C) using a point probe
pressed on the outer oxide surface often results in a local short-circuit, especially in the thin film region, as a result of oxide cracking or a lack of oxygen accessibility (or both) at the point of contact. Measurements made with evaporated metal layers, even if these are porous, also suffer from possible changes in local oxygen access [40]. Measurements in high-temperature aqueous solutions at 300°C may be affected by the already noted lack of reversibility of the cathodic processes at the oxide/metal interface [27]. At low polarization rates cyclic tests in fused salts (pure electrolytes) have the merit that they give results at typical reactor temperatures (without the complications due to surface electrochemical reactions) and show potentials across the oxide film that are similar to those measured by the other techniques during high temperature (600–800°C) oxidation. Using this technique, it is possible to measure the current-voltage (I-V) characteristics of growing oxide films, and to separate these curves into their ionic and electronic components. Results suggest that the anodic half-cell potential (E_a) is 1.0 ± 0.1V, and the cathodic half-cell potential (E_c) is 1.35 ± 0.1V. The results also show that the electronic transport can often be approximated to a Schottky emission process. It also appears that the electron transport process may differ at different locations on the specimen surface. Both electron and hole conduction have been identified under different conditions, again showing the variability of the electron conduction processes which occur. 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 [41]. Thus, it has been proposed that the conduction was mainly localized at intermetallic particles in Zircaloy type alloys and that this is also the main route for electron conduction during oxidation. From observations in a number of oxidizing media of differing conductivity, and from direct measurement Cox [39] deduced that surface resistivity is a major part of the overall electronic resistance, especially for unalloyed zirconium. Putting this evidence together he found that in zirconium and the Zircaloys the electronic component of the oxidation current flows primarily at a few sites, commonly identified
with the intermetallic particles. Since the reduction of oxygen and its diffusion through the oxide occur more uniformly over the surface (because of the small crystallite size) the electrical circuit should be closed by surface conduction. The oxidation field across the oxide is set by that voltage needed to equalize the two components of the oxidation current. In practice, because of the steeply rising nature of the electronic current as a function of increasing voltage, this oxidation field is determined largely by the electronic conduction. The ionic flux is controlled by this field, and hence the oxidation rate is fixed, within limits set by the oxygen diffusion process, by the electronic properties of the oxide. In such situation neither process can be said to uniquely control the oxidation.

Measurements in fused salts does show a drop in the negative potential at the oxide/metal interface as the oxides thicken which is not seen in the high temperature measurements. This drop has been ascribed to the formation of an iron oxide layer on surface intermetallics, which enhances the oxide electronic conduction [42].

Before putting much weight on these measurements of the voltage across the oxide during oxidation, the question of whether they are determined by the kinetics of migration of charged species through oxide, as described above, or are thermodynamic potentials determined by the free energies of the anodic and cathodic processes should be addressed. That they are kinetically determined is shown by the observations that, at the start of oxidation, the potential is zero and increases to the equilibrium value over a significant time, returning to zero if the oxidation is stopped [38].

Thus, a picture emerges in which the growth of the oxide initially is controlled by the electronic conductivity of the film formed. During high temperature gaseous oxidation this control by electronic conduction continues to be evident, whereas at temperatures close to reactor temperatures it appears that the oxide may become more ion conducting as it thickens so that the electronic and ionic resistivities are more balanced. However, the potential measured on the metal
is always negative (even though it may sometimes be small) indicating that electron transport is usually the more difficult (and hence rate determining) process.

The valence state of alloying elements incorporated in the oxide can change the concentration of $O^{2-}$ vacancies in the oxide if these elements are oxidized. If the valence state of the cation is higher than the valence state of Zr, extra oxygen vacancies in the system are consumed by these cations in order to maintain the charge balance in the system. If the alloying elements have lower valence state than Zr, in this case, more oxygen vacancies are generated for the same reason. The solid solution elements used in the Zr-based alloys are Sn and Nb. The valence states of these elements are $Sn^{2+}$, $Sn^{3+}$, $Sn^{4+}$, $Nb^{2+}$, $Nb^{4+}$ and $Nb^{5+}$. If, for example, the valence state of Sn is +2 and valence state of Nb is +5 in the oxide, the presence of Sn will generate oxygen vacancies per atom and that of Nb$^{5+}$ will reduce the vacancy concentrations.

The alloy components of zirconium-based alloys are nobler than Zr, which means that they are generally incorporated unoxidized and undergo oxidation after some residence time in the oxide. When Zr is oxidized, the alloying elements in the Zr matrix can segregate to zirconia grain boundaries [43, 44]. Takeda and Anada [44] observed Sn segregation to the monoclinic ZrO$_2$ grain boundaries. Sn has also been reported as SnO or Sn$_2$O$_4$ forms [7]. Foord et al. [43] also observed Sn segregation in the oxide grain boundaries of Zircaloy-4 oxide. Pêcheur et al. [45] observed metallic Sn near the oxide/metal interface and $Sn^{5+}$ and $Sn^{4+}$ in the oxide, in addition to Fe$^{2+}$ and Fe$^{3+}$.

Although both $Sn^{2+}$ and $Sn^{4+}$ are observed in pre-transition oxides, $Sn^{4+}$ was principally observed in the post-transition oxides. Anada et al. [46] also observed both $Sn^{2+}$ and $Sn^{4+}$ in ZrO$_2$.

Barberis et al. [47] observed background level differences between Zircaloy-4 with 0% Sn and Zircaloy-4 with 1.2% Sn in Raman spectra. While Zircaloy-4 with 1.2% Sn alloy oxide shows high background in the spectrum, the background level of Zircaloy-4 with 0% Sn alloy oxide is lower and closer to that of Zr-1% Nb alloy oxide spectrum. The authors explained that
electrons would be trapped in the vacancies near low valence state atoms (Sn$^{2+}$), and thus perturb the Raman signal, indicating that Sn generates extra vacancies in the oxide layers.

The effects of alloying elements on the $O^{2-}$ ion vacancy concentration were discussed by Beie et al.[48]. Near the oxide/metal interface, the anion vacancy concentration is higher and decreases linearly towards the oxide/water interface, since the stoichiometry of the oxide is fixed at the oxide/metal and oxide/water interface. In this region, oxide growth is controlled by ion diffusion and this region is called as intrinsic region. This linearity can be changed by extrinsic vacancies created by oxidation of aliovalent alloying elements (i.e. Sn, Cr, Fe). Therefore, in the outer oxide, oxide growth is not controlled by ion diffusion but, rather, electron transport is the rate limiting step [48].

**1.2.2. Weight gain kinetics**

It can be easily shown that if the rate limiting step is the diffusion of oxygen anions and if the oxide is stoichiometric at the oxide/water interface and sub-stoechiometric at the oxide/metal interface, a parabolic law for the oxide thickness is obtained:

$$\delta = Kt^{1/2}$$  \hspace{1cm} (9)

However, it has been often reported that the corrosion kinetics follow a cubic law instead of a parabolic law [49]. Some explanations for this change in kinetic law have been proposed [50], such as grain boundary diffusion combined with a linear change in the grain size with oxide thickness or apparition of cracks in the oxide layer. Indeed, the oxygen anion diffusion at grain boundaries has been reported to be much faster than the bulk diffusion [32, 51]. By measuring the $O^{17}$ concentration profile on a zirconium sample oxidized in natural $O_2$ and then in 50% $^{17}O_2$ at 400-500°C using a ion microprobe mass spectrometer the lattice diffusion coefficient for oxygen in zirconia was found to be about $10^4$ lower than the process that determines oxide growth [32].
It has been reported that depending on the alloying elements chosen, the general oxidation kinetics follow Equation (10) [14]:

\[ \delta = K t^n \]  

(10)

This exponent \( n \) has been carefully measured in various zirconium alloys at the beginning of the corrosion 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 [7, 14].

<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-25 Nb-0.5Cu</td>
<td>8.4</td>
<td>0.31</td>
</tr>
</tbody>
</table>

The reasons why \( \bar{n} \) is varying from 0.18 to 0.45 are not clear but the precipitates and the extrinsic compensating defects due to aliovalent cations might play a role [52, 53].

1.2.3. 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 [6, 31, 54-56]. 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. This protective oxide film is often called the barrier layer.

With a closer observation at 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 cyclic nature of post-transition corrosion has been observed and noted for some time [57] and this nature of corrosion is common among Zr alloys and is also widely reported in the literature. After approximately 70-100 µm, the oxide can start to spall off.

Figure 1-11: Schematic representation of the corrosion of Zircaloy [58].

In PWR conditions, it has been noticed that after that the oxide reaches a thickness of 5 to 10 µm, a second oxide transition occurs, which is totally different from the first as it is presented in Figure 1-12 [59].
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 (see Figure 1-13).

Figure 1-12: Oxide layer thickness as a function of exposure time [59]
When breakaway occurs, the oxide becomes white (grey for transition) which is characteristic of a porous, non-protective oxide and which allows stoichiometric ZrO\(_2\) (white in color and very powdery in aspect) to be formed and oxide spallation can occur. Some models have been proposed [9, 60-62] but a complete understanding of the oxide transition and of the parameters leading to breakaway are still lacking.

1.3. Hydrogen pick-up

1.3.1. Definition

The hydrogen pick-up fraction is defined as the ratio of the hydrogen absorbed over the total hydrogen that is generated by the corrosion reaction:
As a function of exposure time, it has been 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 [63]. However, a significant spread of the pick-up fraction results exists in the literature. For instance, for a given alloy, we still do not clearly know if the pick-up fraction is a constant [2], if it varies as a function of exposure time following the cyclical behavior of oxidation kinetics [64] or not [65]. 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 try to refer the different important conclusions that have been found in the past.

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, \( f_H \) determination is not enough to judge of the hydrogen absorption behavior of a given alloy. Consequently, in this study the authors tried as much as possible to provide results on hydrogen pick-up and weight gain at the same time. 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 12.5% of the corrosion weight gain!

\[
f_H = \frac{H_{absorbed}}{H_{generated}}
\]
1.3.2. Techniques of hydrogen level assessment in zirconium alloys

1.3.2.1. Destructive techniques

Most of the time, the quantity of hydrogen absorbed in the metal has been measured by Vacuum Hot Extraction (VHE) or Inert Gas Fusion (IGF) [66-69]. These techniques offer the advantage of a fixed calibration which can provide good precision for the determination of hydrogen content. The fixed calibration also allows for accurate hydrogen determination at lower sample mass. In these destructive techniques, the hydrogen is extracted from the sample by heating (VHE) or melting (IGF) the sample. Then the hydrogen is collected within the system and measured using a McLeod gauge. These techniques are well developed, fast and inexpensive. In these experiments, zirconium samples are heated either to approximately 1200 °C in the case of VHE (causing significant alloy microstructure changes, since the zirconium transition from α to β phase occurs at 865 °C) or to a temperature above the melting point in the case of IGF. Thus, both VHE and IGF are destructive techniques, which preclude further analyses on the sample. 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) used in autoclave experiments. Thus, spot-to-spot hydrogen concentration variations within the coupon may skew the results. Finally the precision of these destructive techniques at these low hydrogen concentration levels is not well established.

Thus, one can understand how it is important to find precise and reliable non-destructive techniques to detect even low levels of hydrogen in order to characterize the hydrogen pick-up
fraction variations as a function of exposure time. The possibility to derive a comprehensive
mechanism of hydrogen pick-up is dependent on the availability of such a technique.

1.3.2.2. Non-destructive techniques

Various non-destructive techniques have been used for evaluating hydrogen content in
zirconium alloys.

First, researchers have used wave induction techniques to detect hydrogen. The EMAR
method (electromagnetic acoustic resonance) [70] is ideal for in situ measurements. This
experiment consists of an ultrasonic resonance and an electromagnetic acoustic transducer
(EMAT). The EMAT creates a permanent static magnetic field for an electrically conductive
specimen. As a result of the Lorentz forces induced at the sample surface, shear and longitudinal
waves are created, which propagate in the sample in different directions. Then the resonance
frequencies of the system are recorded. The difference in resonance frequencies in different
specimens with different amount of hydrogen charging are plotted as a function of hydrogen
charging for calibration. With the same kind of apparatus, one can also perform ultrasonic
measurement of induced waves coupled with eddy current testing [71]. These systems are non-
contact systems and are of course non-destructive. However, the effects of oxide microstructure,
alloying elements and hydride precipitation on the resonance frequencies and ultrasonic
measurements are very hard to characterize and a proper evaluation of the experimental error is
lacking.

Neutron transmission techniques [72] have also been applied to this problem. In this case
the sample is placed in front of a collimated neutron beam and a detector is placed at the exit. The
detector counts the neutrons that emerge from the sample without interacting. Due to the high
cross section of hydrogen compared to that of other elements, the sample transmission varies
considerably even for small variations of the hydrogen concentrations. These techniques assumed that the change in neutron transmission is only due to hydrogen content variations from sample to sample. The scattering cross section of hydrogen being at least one order of magnitude higher than most of the elements, this assumption looks correct. However, the main drawback of this technique is that one needs to know the total cross section of the hydrogen atom to perform a quantitative analysis. This total cross section depends on the chemical state of the hydrogen atom, which is particularly difficult to model, increasing the error range of the technique.

Electrode-based techniques consist in the ionization of the hydrogen atoms and a further determination of the current produced by the movement of hydrogen ions. They allow a resolution of approximately 1 wt.ppm in steels. However in zirconium, hydrogen forms hydrides and thus is not easily ionizable. The solubility of hydrogen in zirconium alloys being very low at room temperature, these techniques cannot be applied in the case of zirconium alloys.

Techniques that are based on nuclear reactions with an incident beam of helium have been used [73]. He nuclei with energies in the order of 1MeV are elastically scattered and the hydrogen nuclei removed from the sample are detected in coincidence. This method is highly sensitive and allows a determination of concentrations in the range of 1 atomic ppm. However the sample must be very thin (25 µm or less) and the incident beam damages the sample. These techniques are thus not of great use for our non-destructive purposes.

Neutron scattering techniques [74-76] are also interesting. They make use of the considerable energy loss of the neutrons dispersed by hydrogen nuclei (inelastic scattering), as opposed to the essentially elastic nature of atom dispersion in high atomic masses. These techniques are non-destructive and a sensitivity of approximately 0.4 wt.ppm has been reported. However, these determinations are particularly recommended for massive samples, since the neutrons penetrate deeply in the matter and thus the signal obtained comprises information of the total sample and precise neutron energy detectors are needed. According to Couvreur [75], the
hydrogen incoherent cross-section gives rise to a continuous background in diffraction spectra, which is proportional to the hydrogen content, and is (nearly) independent of scattering angle. Zirconium is a favorable element for this study, because its neutron absorption coefficient and incoherent scattering cross-sections are very weak: the diffraction spectra of hydrogen-free samples show very low background. Neutron scattering also gives us the phases present in the sample with a better sensitivity than classic X-Ray diffraction. Thus, theoretically, if the beam size was small enough, it could be possible to correlate the local hydrogen content to the different zirconia phases or intermetallic precipitates.

One can see that none of these techniques has the level of reliability and precision required to detect low hydrogen mass fractions in zirconium alloys (with the exception of neutron scattering techniques).

In this study we used another neutron-based hydrogen measurement technique. While transmission and scattering techniques have been used on zirconium alloys, neutron absorption techniques have yet been used for this purpose. We used a particular neutron absorption technique called Cold Neutron Prompt-Gamma Activation Analysis (CNPGAA) to analyze low levels of hydrogen in zirconium. Although, CNPGAA is time consuming and can only be performed in a specialized facility, it is a valuable technique as it is non-destructive, precise, measures the average hydrogen concentration in the whole sample and can detect very low levels of hydrogen (as low as 5 wt·ppm) [77].

1.3.3. Hydrogen pick-up characterization

In spite of significant experimental uncertainties it is possible to describe the hydrogen pick-up evolution in three different steps [63, 67]:

- At the very start of corrosion, the hydrogen absorbed and the pick-up fraction are high.
After several tenth of microns of oxide layer is formed, the kinetics of hydrogen absorption slow down until almost no more hydrogen is absorbed by the metal. The pick-up fraction goes down.

- After the oxide transition, the pick-up fraction increases again to reach a constant value.

Pure zirconium is known to have a high pick-up fraction in the post transition regime (>50%) [63, 67].

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 [8]. 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% [63, 67].

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 [78, 79].

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 are reviewed in the following.

### 1.3.4. Parameters influencing hydrogen pick-up

One of the main problems of the study of hydrogen pick-up in zirconium alloys is the difficulty in separating the different effects of external and internal parameters. The following review attempts to distinguish the effects on hydrogen absorption of the most relevant parameters.
1.3.4.1. External parameters

Table 1-3 shows the different cladding environments in most of the nuclear reactors [6].

Table 1-3: Cladding environment in different reactors [6].

<table>
<thead>
<tr>
<th>Reactor type</th>
<th>Environment</th>
<th>pH (25°C)</th>
<th>P (bars)</th>
<th>T (°C)</th>
<th>H₂ (ppm)</th>
<th>O₂ (ppm)</th>
<th>LiOH (ppm)</th>
<th>H₃BO₃ (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PWR</td>
<td>H₂O</td>
<td>parameter</td>
<td>155</td>
<td>285-325</td>
<td>1.5-5</td>
<td>&lt;5</td>
<td>0.7-2</td>
<td>0-2500</td>
</tr>
<tr>
<td>BWR</td>
<td>H₂O</td>
<td>7</td>
<td>70</td>
<td>216-286</td>
<td>&lt;25 ppb</td>
<td>200-400</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>VVER</td>
<td>H₂O</td>
<td>10</td>
<td>140</td>
<td>270-320</td>
<td>2-6</td>
<td>&lt;5</td>
<td>-</td>
<td>0-13.5</td>
</tr>
<tr>
<td>CANDU</td>
<td>D₂O</td>
<td>10-11</td>
<td>-</td>
<td>280-320</td>
<td>0.5-4</td>
<td>50</td>
<td>0-2</td>
<td>-</td>
</tr>
</tbody>
</table>

1.3.4.1.1. Temperature

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 [8]. The chemical compositions of the alloys used in this study are presented in Table 1-4.

Table 1-4: Chemical compositions of Zircaloy-2, Ni-free Zircaloy-2 and Zircaloy-4 in [8].

<table>
<thead>
<tr>
<th>Element</th>
<th>Zircaloy-2</th>
<th>Ni-free Zircaloy-2</th>
<th>Zircaloy-4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn</td>
<td>1.20%to 1.70%</td>
<td>1.20%to 1.70%</td>
<td>1.20%to 1.70%</td>
</tr>
<tr>
<td>Fe</td>
<td>0.07% to 0.2%</td>
<td>0.12% to 0.18%</td>
<td>0.18% to 0.21%</td>
</tr>
<tr>
<td>Cr</td>
<td>0.05% to 0.15%</td>
<td>0.05% to 0.15%</td>
<td>0.07% to 0.13%</td>
</tr>
<tr>
<td>Ni</td>
<td>0.03% to 0.08%</td>
<td>&lt;0.007%</td>
<td>&lt;0.007%</td>
</tr>
</tbody>
</table>
In Ni free Zircaloy-2 and Zircaloy-4 the Ni concentration was fixed at a maximum impurity level of 70 ppm. Ni-free Zircaloy-2 is essentially Zircaloy-2 without the Ni addition whereas Zircaloy-4 contains the same Sn and Cr levels as Zircaloy-2 but additional iron has been added to compensate for the volume of intermetallic phases reduced by the removal of Ni. In Zircaloy-4 and Ni-free Zircaloy-2, a greater quantity of hydrogen per unit of oxygen weight gain is absorbed in 400°C steam than in 360°C water. However, this trend is reversed for Zircaloy-2 as shown in Table 1-5. The alloys presented in Table 1-5 have been α annealed at a temperature of 750°C for 4 hours in evacuated bulbs and furnace cooled and then corroded in two different environments: 360°C pure water and 400°C steam autoclaves.

Table 1-5: Post transition hydrogen pick-up fraction of the Zircaloys [5].

<table>
<thead>
<tr>
<th>Alloy</th>
<th>360°C pure water</th>
<th>400°C steam</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zircaloy-2</td>
<td>78%</td>
<td>77%</td>
</tr>
<tr>
<td>Ni-free Zircaloy-2</td>
<td>26%</td>
<td>46%</td>
</tr>
<tr>
<td>Zircaloy-4</td>
<td>22%</td>
<td>53%</td>
</tr>
</tbody>
</table>

It seems that there is no temperature effect on Zircaloy-2 whereas a strong effect is noticed in Ni-free Zircaloy-2 and Zircaloy-4. It has been reported that for temperatures higher than 420°C (in steam), the Zircaloy-2 hydrogen pick-up fraction remains stable while the Zircaloy-4 hydrogen pick-up fraction is getting closer to the Zircaloy-2 one [8, 63].

In niobium alloys, the different studies do not agree on the effect of temperature on hydrogen pick-up. In the pre-transition regime, it seems that the hydrogen pick-up of alloys Zr-1.0Nb and Zr-2.5Nb does not depend on temperature and would be close to 10% [80]. However, in the post transition regime, at 500°C, the hydrogen pick-up could reach 100%, 30% at 450°C [80] or 10% at 500°C.
The results above show that the effect of temperature is not completely characterized and that previous researches do not agree on its influence on hydrogen pick-up. As a result, it was decided to maintain a constant temperature in this study.

1.3.4.1.2. Dissolved gases in solution

A precise study to record the effect of dissolved oxygen was performed by Hillner [81]. The results are presented in Figure 1-14 and 1-15. An overpressure of 1000 psi of oxygen was added to the water pressure.

![Graph](image)

Figure 1-14: Oxygen weight gain in function of exposure time in 360°C water + 1000psi oxygen [81].

The remaining coupons from the survey experiment were reinserted into freshly prepared test solution and the experiment has been repeated (such coupons are shown with open symbols). The solid line represents the weight change information for the exposure of Zircaloy (all three
types of alloys, see Table 1-4 for alloy chemical compositions) to 360°C pure degassed water (since they approximately follow the same oxidation kinetics), whereas the dashed lines indicate upper and lower 2σ limits (95% confidence levels) for the standard curve. With the exception of early exposure data, the results show that the weight gain changes observed for all three alloys lie just outside of the upper 2σ limit of the degassed water curve for the entire length of exposure (the reproducibility look also quite good). 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.

Figure 1-15: Hydrogen weight gain as function of oxygen weight gain [81].

Figure 1-15 shows the hydrogen accumulation in the corrosion coupons as a function of oxygen weight gain, plotted on a linear set of coordinates. The quantity of hydrogen absorbed by the
corrosion specimens is an average value of at least two separate analyses performed on a single corrosion coupon. Typical behavior for Zircaloy-2 and Ni-free Zircaloy-2 in 360°C degassed water, as well as the 100% hydrogen pick-up fraction line are included for comparison with the test data. While the oxygen overpressure has no effect on oxidation kinetics, its effect on hydrogen pick-up is very striking. Zircaloy-2 shows the largest reduction in $f_H$, and Ni-free Zircaloy-2 the smallest change. Moreover, a single linear relationship appears best to represent all the data generated under the high oxygen overpressure, regardless of alloy composition. In oxygenated water, Zircaloy-2, Ni-free Zircaloy-2 and Zircaloy-4 absorb approximately 6% of the hydrogen generated (the theoretical line of 6% has been added to the plot). In degassed water at 360°C, during the pre-transition regime the hydrogen pick-up was equal to 78%, 22% and 26% respectively against 40%, 15% and 25% in the post transition regime [5]. In the oxygenated water all three alloys absorb approximately 5% to 7% of theoretical after the initial stages of oxidation.

The effect of dissolved hydrogen in water has also been studied on Zircaloy 2. At 315°C, for short exposure times (up to 14 days) an addition of 300 psi of H$_2$ leads to an appreciable increase in hydrogen pick-up (72%) compared to that experienced for degassed water (15%) (1 psi H$_2$ at 343°C is equivalent to 2 ppm of hydrogen [82]). The presence of hydrogen in the corroding medium does not appear to influence the observed weight gains for the test specimens. Kass and Kirk have performed experiments at an H$_2$ overpressure of 700psi [8] (Figure 1-16).
It is clearly demonstrated that enhanced hydrogen pick-up rates are obtained in the hydrogenated water environments. They observe an average increase of 75% in $f_H$ for Zircaloy-2, while Ni-free Zircaloy-2 show an increase of 93%. Without exception, the hydrogen pick-up value at any given weight gain is higher for the hydrogenated environment. These results are also confirmed at higher H$_2$ pressure [83] (see Figure 1-17).
In Figure 1-16 and 1-17, the hydrogen weight gain is plotted against the total oxygen absorption for exposure to 343°C water. These figures clearly indicate that the presence of large quantities of hydrogen in the corroding medium lead to hydrogen content well in excess of the maximum theoretical value governed by the corrosion reaction. No effect of hydrogen overpressure on oxidation kinetics has been noticed by any of the authors.

Lustman et al. [83] also subjected Zircaloy-2 and Zircaloy-4 corrosion coupons to a 14 days exposure in 343°C water under pressures of 0, 500, 1000, 1500, and 200 psi hydrogen (see Figure 1-18, where the hydrogen pick-up after 14 days of exposure is plotted against the total hydrogen overpressure). Weight gains were found to vary from 14 to 22 mg/dm² whereas, in degassed water, the anticipated weight gain is approximately 15mg/dm². The hydrogen pick-up was found to be a linear function of hydrogen pressure for both materials (Zircalo-2 and Zircaloy-4) and heat treatments (either as-rolled or beta quenched) and that Zircaloy-4 is almost not
sensitive to hydrogen overpressure whereas Zircaloy-2 shows a great sensitivity to hydrogen overpressure. The impact of metallurgy on hydrogen pick-up fraction will be discussed later.

Figure 1-18: Hydrogen pick-up as function of hydrogen overpressure after a 14 days exposure in 343° water for both Zircaloy-2 and Zircaloy-4 with different heat treatments [81].

1.3.4.1.3. Chemical environment

The pH-value is one of the important parameters for the oxidation behavior of zirconium alloys inside a reactor. A low pH-value results in more corrosion products (crud) in the primary water and a pH-value higher than 12 dramatically accelerates the general corrosion rate. To optimize corrosion behavior a constant pH-value of 7.2 and 7.4 is currently recommended [6]. It is also common to add some dissolved hydrogen to maintain a low content of oxygen. Indeed,
oxygen radicals can be formed due to irradiation and their concentration can significantly increase with burn-up and alter the corrosion process.

Kass [5] confirms that the addition of hydrogen in the coolant has almost no effect on Zircaloy-4 as seen in Figure 1-18. In contrast, the Zircaloy-2 hydrogen pick-up fraction can exceed 100% in these conditions which indicates that Zircaloy-2 is absorbing some dissolved hydrogen [84]. Hillner et al. [85] investigated the combined effect of hydrogenated and lithiated solutions on the Zircaloy corrosion and hydrogen pick-up behavior in 360°C replenished systems. No adverse effects on the Zircaloy corrosion kinetics were noted in pH 10 lithiated solutions. The results on hydrogen absorption are displayed in Figure 1-19.

![Figure 1-19: Hydrogen absorption as function of oxygen weight gain for Zircaloy-2 and -4 exposed in 360°C water replenished with pH 10 lithium hydroxide and approximately 3 psi of hydrogen overpressure [81].](image)

The data points represent the information obtained by Hiller et al. while the solid lines indicate the anticipated behavior in replenished, degassed, neutral water at 360°C. The good agreement between the experimental data produced in lithiated and hydrogenated solutions and those
obtained in neutral, degassed, water, strongly suggests that lithium hydroxide concentrations of pH 10 and added hydrogen contents to the extent of 3 psi do not affect the Zircaloy hydrogen pick-up characteristics.

However, if the concentration in lithium hydroxide is increased from a few ppm to tens of ppm (concentrated lithium solutions – pH 12 and above), the oxidation kinetics and hydrogen pick-up fraction dramatically increase. For instance, whereas the Zry-4 cladding usually picks up 16-18% of the hydrogen generated by the corrosion reaction the pick-up fraction amounts to 80% during corrosion in 0.5M LiOH at 34 °C and 160 bar [86].

1.3.4.1.4. Irradiation

Irradiation seems to slightly accelerate the oxidation kinetics when compared to an identical experiment performed in out-of-pile autoclaves [87]. 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 [88]. 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) [87]. This second transition is totally different from the first, would not depend on temperature but would be only due to the neutron flux and thermal heat flux [59]. It is worth noticing that M5 alloy (see composition in Table 1-1) does not undergo this second acceleration of the oxidation kinetics under irradiation observed Zircalloys [64].

1.3.4.1.5. D₂O vs H₂O

Several studies have been done comparing the hydrogen pick-up in D₂O (heavy-water) and H₂O (light-water) in Zr-2.5Nb alloys [81]. They all conclude that the oxidation kinetics of
Zircaloy-2 in the two media are not significantly different. To be able to compare their hydrogen absorption behavior, it is more meaningful to use the hydrogen equivalent (atomic basis) than the total weight of absorbed species. Using mg.dm$^{-2}$ for hydrogen pick-up and mg.dm$^{-2}$/2 for deuterium pick-up, they show that the amount of deuterium absorbed from either heavy-water or steam corrosion is significantly lower than the corresponding hydrogen pick-up from light-water corrosion.

1.3.4.1.6. Effect of flow

During the corrosion test of zirconium alloys in static autoclave degassed water, the hydrogen released as hydrogen gas (H$_2$) was allowed to accumulate in the environment until completion of the cycle.

![Graph showing hydrogen pick-up as function oxygen weight gain in static and refreshed autoclave](image)

Figure 1-20: Hydrogen pick-up as function oxygen weight gain in static and refreshed autoclave [81].
Figure 1-20 shows us the evolution of the hydrogen weight gain as function of oxygen absorption in static and refreshed autoclaves for Zircaloy-2 and Ni-free Zircaloy-2. The 100% theoretical hydrogen pick-up fraction value has been added. In Figure 1-20, even after 1 year of exposure, there is a general equivalence between refreshed and static water autoclave testing on hydrogen pick-up (the authors also showed the equivalence of the oxidation kinetics). Then, a possible acceleration in hydrogen pick-up coming from the build-up of hydrogen in the static autoclave should not occur.

1.3.4.2. Internal parameters

1.3.4.2.1. Alloying element additions

The hydrogen absorption during corrosion was studied for Zircaloy-2 and some binary alloys in water at 316-400°C [69]. Figure 1-21 shows the hydrogen pick-up fraction for various binary alloys as a function of alloying element content.
Figure 1-21: Hydrogen pick-up in sponge based zirconium alloys exposed up to 575 days to static water at 360°C [69].

The tin effect has also been reported elsewhere [67, 89]. Figure 1-21 shows that below 0.5% mass fraction the tin has also no effect on hydrogen pick-up. When the tin content exceeds 0.5% mass fraction, it is known to increase the oxidation kinetics although with little effect on hydrogen absorption [5, 89-91].

The addition of iron at the order of tenths of wt%, to pure zirconium or to zirconium-tin alloys, improves the alloy resistance to oxidation. However, the hydrogen pick-up increases linearly with the iron content to reach an average of 80% for Zr-1.54Fe [66-68] either in Zr-Fe or Zr-Sn-Fe alloys. According to Berry et al., there is a slight decrease of the hydrogen pick-up fraction at low level of iron mass fraction (25% at 0.25 wt% Fe) but it increases dramatically at higher iron content as shown in Figure 1-21. The same detrimental effect of iron on hydrogen pick-up has been observed in Zr-2.5%Nb at 360°C, at impurity level of 1000 ppm [92]. However, contradictory results have been found by Kakiuchi et al in 673K in steam [93]. In their study, they
compared the hydrogen pick-up of Zircaloy-2 to HiFi alloy (same as Zircaloy-2 but with an iron content increased to 0.4wt%). The hydrogen pick-up went down from 50% for Zircaloy-2 to 28% for HiFi. In conclusion, the sizes, types and distributions of ZrFe type of precipitates can play a role in the hydrogen absorption behavior of a given alloy.

In Figure 1-21, it is clear that the addition of nickel in zirconium as single alloying element significantly increases the hydrogen pick-up fraction. Kass and Kirk studied the hydrogen absorption as a function of nickel content [8]. The absorption of hydrogen, produced during the corrosion process, decreased in the Ni-free Zircaloy-2 compared to standard Zircaloy-2. However, the role of Ni of Zr\(_2\)(Fe,Ni) precipitates on hydrogen pick-up fraction has not been clearly clarified.

In autoclave at 360°C after 127 days of exposure in pure water, the hydrogen pick-up fraction for Zr-Cr binary alloys (0.2 < wt%Cr < 4.07) was approximately 12±3% [68]. It has also been reported that for the alloy Zr-1.0Cr oxidized in 360°C pure water the hydrogen pick-up fraction is almost zero with oxidation kinetics close to the ones of Zircalloys [66]. However, for higher chromium content (Zr-10wt%Cr), the hydrogen pick-up increases to reach 50% but the oxidation kinetics are very high. It is also interesting to note that in autoclave, the addition of chromium in ternary alloys such as Zr-Sn-Fe does not affect the oxidation kinetics or the hydrogen pick-up [89, 94]. However, for a constant volume fraction of Fe and Cr, the replacement of Fe by Cr reduces significantly the hydrogen pick-up [94]. 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.

Baur et al. have studied the mechanism for hydrogen pick-up in water at 350°C using electrochemical techniques [95]. Cathodic polarization was used to clarify the influence of the
precipitate size on the oxide layer electrical resistivity. They found that one important 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%) has a lower electrical resistance 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 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. [96] on which bigger precipitates are supposed to increase the hydrogen uptake. The relationship between electrical resistance and hydrogen pick-up seems clear 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 of the barrier layer.

Concerning the Zr-Nb alloys corroded in autoclave, Zr-2.5Nb and Zr-1.0Nb show much less hydrogen pick-up than Zircaloy-4 [97, 98]. However, it seems that depending on the thermal treatments of the alloys, the hydrogen pick-up could increase. Indeed, as shown in Figure 1-22, Choo [78], for a significant range of Nb additions (Zr-1.0Nb, Zr-2.5Nb, Zr-5Nb, Zr-10Nb and Zr-15Nb) after 58 days of oxidation at 400°C under 10MPa H2O steam, has shown that a Zr-Nb quenched alloy (annealed at 1000°C for 15 minutes then quenched in water) picks-up less hydrogen than a Zr-Nb aged alloys (same as quenched but followed by an ageing at 550°C for 10 days and then air cooled).
In the literature, it seems established that niobium has a beneficial effect on hydrogen absorption. In general, percentage pick-up values from specimens from tubes of β-quenched material (2.5% to 5%) are lower than those from tubes made of non β-quenched material (2% to 8%) [88].

1.3.4.2.2. Alloy metallurgy

During their processing zirconium alloys undergo different annealing and shaping processes. These processes affect the degree of recrystallization, the size, shape and orientation of the grains and also the size and repartition of intermetallics precipitates. According to that a recrystallized alloy oxidizes more slowly than a cold work stress relieved alloy [6, 64]. In Figure 1-23, it is shown that, for Zircaloy-2, the hydrogen uptake performance can be altered by fabrication techniques and thermal treatments [5]. The material quenched at 788°C (from α phase, annealed for 4 hours before quenching) initially absorbs small quantities of hydrogen in 360°C water, but after a period of time the quantity absorbed increases. Material quenched at 843°C
(α+β phase annealed for 15 minutes before quenching), on the other hand, does not show significant increases in the absorption rate. Initially the 788°C fabricated material shows a lower amount of absorbed hydrogen, but at 220 days of exposure in 360°C water, the 843°C fabricated material shows lower hydrogen absorption values.

![Graph showing hydrogen pick-up fraction as a function of exposure time (days) for different metallurgical states of Zircaloy-2](image)

**Figure 1-23**: Hydrogen pick-up fraction as a function of exposure time (days) for different metallurgical states of Zircaloy-2 [5]

In the case of Zircaloy-4, alpha annealed material absorbs greatest amount of hydrogen while the beta-quenched material absorbs less amount of hydrogen (see Figure 1-24).
The differences between different thermal treatments could be due to the intermetallic precipitates. A β quench could result in more alloying elements in super saturation relative to the matrix [99]. The fabrication process and especially the different annealing treatments have a significant effect on hydrogen absorption [8]. The grain size does not seem to influence the oxidation and hydrogen pick-up behavior; but the precipitate size seems to play a significant role.

The optimal size (regarding the corrosion resistance) of the SPP’s depends on the environment: in a PWR it is recommended to have SPP’s of 150 nm diameter (for uniform corrosion resistance) whereas in a BWR a diameter inferior to 100 nm is preferable (for nodular corrosion resistance) [6].

Hatano has shown that in pre-transition regime, the alloys containing coarse precipitates (long annealing time in α phase after a rapid quench or slow cooling from β phase) always absorb more hydrogen than the ones with fine precipitates (smaller annealing time in α phase) even if

Figure 1-24: Hydrogen pick-up in Zircaloy-4 [5]
their oxidation kinetics are faster [96, 100]. In the case of coarse precipitates, the Zircaloy-4 seems to absorb more hydrogen than Zircaloy-2, which is opposed to usual observations [96].

In conclusion, alloy metallurgy and especially second phase precipitates have a significant role on hydrogen pick-up. Alloy processing, alloying element content and second phase particles characterization are of primary importance to characterize hydrogen pick-up fraction.

1.3.5. **Mechanism for hydrogen absorption**

Although the transport mechanism of hydrogen through the oxide layer is not fully understood, various hypotheses have been proposed to explain the ingress of hydrogen. Hillner [81] has suggested a model to describe the mechanism for hydrogen absorption. This model considers that the oxide film growth proceeds via anion vacancy diffusion through the oxide layer, which is a good assumption (see previous section on waterside corrosion). The generation of anion vacancies occurs at the metal/oxide interface due to the fact that the metal has a large chemical affinity for oxygen. Oxygen atoms in the oxide diffuse from a lattice position to an interstitial position in the underlying metal, thus forming oxygen vacancies according to Equation (12):

\[
\text{Null} \rightarrow (xO_l)_Zr + (ZrO_{2-x} + xV_o^* + 2xe^-)_{ZrO_2} \tag{12}
\]

where \((xO_l)_Zr\) represents an oxygen atom in interstitial solid solution in \(\alpha\)Zr.

It is also possible that the oxide forms directly with a stoechiometry of \(ZrO_{2-x}\). If the metal is not saturated by oxygen, the reaction rate depends only on temperature. Oxygen ions move inwards by jumps between anion vacancies and an anion vacancy gradient is thus established in the oxide as shown in the curve OA of Figure 1-25.
The anion vacancy gradient can also be described in terms of almost stoichiometric oxide at the outer surface and large deviations from stoichiometry at the inner oxide interface. The dissociation of a water molecule caused by the oxidation or the radiolysis reaction of water will give protons (Equations (13) and (14)). These will be neutralized by electrons:

\[ \text{H}^+ + \text{e}^- \xrightarrow{\text{neutralization}} \text{H}^0 \]  

(13)

The hydrogen atoms formed can either recombine to form molecular hydrogen (\(\text{H}_2\)) or enter the oxide by:

\[ \text{H}^0 + V_{0^*} \rightarrow \text{H}_{0^*}^0 \]  

(14)

where \(\text{H}_{0^*}^0\) represents a hydrogen atom sitting in an anion vacancy. It is undecided if the hydrogen atom enters the oxide as a charged or neutral particle. However, work by Smith [101] has shown that the hydrogen atom was too big to enter the oxide through the gap between oxygen and zirconium oxide ions, but anion vacancies would be an excellent site for hydrogen atoms.

The hydrogen atom sitting at the anion vacancy could diffuse through the oxide by a jumping
mechanism from anion vacancy to anion vacancy or, even if less favorable, form interstitial sites to interstitial sites.

Murgatroyd and Winton [84] studied the hydrogen pick-up in Zircaloy-2 in the presence of LiOH. The result from this investigation showed that approximately 65% of the hydrogen generated during the corrosion process was picked up by the metal. This value was not affected by the thickness of the oxide layer or by the LiOH concentration.

Wanklyn et al. [102] determined the hydrogen uptake of zirconium and its alloys in steam at 400-600°C. The instantaneous hydrogen pick-up fraction increased during corrosion and reached almost 100% for some alloys. They suggest three possibilities for the entrance of hydrogen into the metal through the protective oxide. The water molecules react with oxygen vacancies and:

1. Both protons are removed and, taking up two of the electrons which accompany the vacancies, form hydrogen molecules (Equation (8)).
2. One proton is removed and OH$^-$ ion enters the oxide. The proton forms a H$_2$ molecule together with an electron and a second proton from another water molecule.
3. OH$^-$ ion enters the oxide, while the second proton is captured by a negative site on the surface, then moving to an O$^{2-}$ ion to form a second OH$^-$. The negative site is suggested to be an O$^{2-}$ ion or a site resulting from the presence of foreign cations in the oxide.

Wanklyn et al. [102] further suggest that when the protons are inside the oxide they jump from O$^{2-}$ to O$^{2-}$ towards the metal. The OH$^-$ ion is not believed to jump because then the hydrogen uptake could not exceed 50%. The small number of OH$^-$ groups found with Infra-Red measurements in the oxide is explained by the fast diffusion of protons through the oxide.
Klepfer [68] suggested that the significant differences in hydrogen pick-up among the alloys could be explained by two competing processes of charge transport through the oxide film: the surface hydrogen discharge:

\[ e_{metal} \rightarrow e_{oxide} \quad (15) \]
\[ e_{oxide} \rightarrow e_{surface} \quad (16) \]
\[ 2e_{surface} + 2H^+_{surface} \rightarrow H_2 \quad (17) \]

and the metal hydrogen uptake:

\[ H^+_{surface} \rightarrow H^+_{oxide} \quad (18) \]
\[ H^+_{oxide} \rightarrow H^+_{metal} \quad (19) \]
\[ H^+_{metal} + e + Zr \rightarrow ZrH \quad (20) \]

The diffusion of hydrogen ions in the oxide must proceed by thermally activated diffusion and would be expected to be speeded up by an increase in temperature or in hydrogen pressure and slowed down by the oxide thickness. The hydrogen pick-up variations would be explained by some kind of electron valve: a metal/doped oxide junction, a negative-positive junction in the oxide itself, or the potential energy barrier due to the anion vacancy gradient across the film.

Hatano [103] studied the impact of fine and coarse intermetallic precipitates such as Zr(Fe,Cr)$_2$ and Zr$_2$(Fe,Ni) on hydrogen uptake for two types of Zircaloy-2 [100] and Zircaloy-4 [96] during pre-transition oxidation at 350°C to 450°C in steam water. It was concluded that, for smaller precipitates (β quenched alloy) with diameter inferior to 50 nm, the hydrogen permeability of the oxide was lower and showed no temperature dependence of oxidation. The samples with larger particles with a mean size of approximately 1.1µm diameter and obtained from a slow cooling process showed high hydrogen uptake and the uptake increased with decreasing oxidation temperature. It has been proposed that SPP’s remain in the metallic state in the oxide film and act as an ingress route for hydrogen (it is well known that Zr(Fe,Cr)$_2$ and
$\text{Zr}_2(\text{Fe},\text{Ni})$ can absorb up to three hydrogen atoms and remain stable \cite{104-106}. The unoxidized metallic state of SPP’s in the oxide layer as a function of exposure time has been extensively studied \cite{107}. These intermetallic precipitates would localize the recombination of electrons and protons and then release the hydrogen atoms to the oxide once oxidized. The hydrogen uptake was reported to be higher in Zircaloy-4 than in Zircaloy-2 specimens containing coarse precipitates of comparable size \cite{103}. The coarse particles found in Zircaloy-4 remained unoxidized closer to the oxide/metal interface compared to the coarse particles found in Zircaloy-2 samples. According to the authors, the oxidation of the precipitates will dissolve sub-cations in the matrix (such as Fe$^{3+}$). It is known from studies on binary metal oxides that sub-cations increase the vacancy concentrations to compensate their relative negative charges. If it is supposed that zirconium oxide is of n-type under the oxidizing conditions, then the charged vacancies will reduce the electronic conductivity. Indeed, they have shown that the cathodic current density was smaller at high temperature (more sub-cations in the oxide) compared to lower temperature. However, experiments in which Zircaloy-2 still showed higher initial hydrogen uptake rates than Zircaloy-4, even though all $\text{Zr}_2(\text{Fe},\text{Ni})$ particles in the surface had been dissolved during an initial pickling of the specimens, suggests that the intermetallics themselves do not participate directly in the hydrogen uptake process \cite{25}.

The spatial distribution of hydrogen in Zircaloy-2 oxidized in $\text{H}_2\text{O}$ steam has been studied using a technique of tritium micro-autoradiography \cite{108,109}. Tritium was introduced in the oxide layer by cathodic charging and the radiograph of the cross-section was then studied using scanning electron microscope. Hydrogen present in the oxide layer was mainly found in SPP’s embedded in the oxide. The authors also observed that the hydrogen content embedded in the SPP’s seemed to decrease closer to the oxide/water interface, which is probably due to the intermetallic oxidation process. In the metal, hydrogen was densely distributed along the grain boundaries, but was also present in the grains. However, it is not possible to conclude from this
that SPP’s are a possible favorable path for hydrogen since the presence of hydrogen inside of SPP’s at room temperature could be due to its redistribution during the cooling process. The heat of solution and solubilities for hydrogen in the intermetallics phases compared with the matrix, suggests that these redistributions into the intermetallics could occur during the cooling of the specimens.

SIMS measurements of the depth profile of deuterium in the oxide layer have shown the existence of a deuterium gradient from the oxide surface to the metal/oxide interface [103]. Higher concentrations of deuterium were found in samples with large intermetallic precipitates than in samples with fine particles. However, the sensitivity of the technique could change closer to the oxide/metal interface or could be dependent on the oxide stoichiometry, which could lead to wrong analyses of the results.

Recently, Cox has proposed that pores/small cracks in the oxide layer act as the ingress route for hydrogen [25]. He suggests that in these small cracks a microscopic steam process takes place, and hydrogen is accumulated close to the metal/oxide interface. The passive oxide at the bottom of the crack is thought to break down during this process and hydrogen enters the metal. This assumes that the bottom of the crack is in contact with the metal, which is not proved in his paper. In the experiment performed to support the model, the oxidation test was performed on thin Zircaloy-2 plates in steam at 300-400°C. When the terminal solid solubility (TSS) of hydrogen in the zirconium metal was reached, which occurred during the pre-transition oxidation, the uptake rate of hydrogen decreased. To locate the flaws in oxide films formed on different zirconium alloys, Cox and Wong [110] have used cathodic polarization to deposit small copper balls on the active cathodic sites in the oxide film. In Zircaloy-2 the copper deposit was observed invariably at cracks or small holes in the oxide film. No association with intermetallics in the initial surface was found.
Smith has suggested that the mechanism of hydrogen uptake is diffusion of hydrogen through the oxide along easy diffusion paths such as dislocation lines and grain boundaries [101]. TEM investigation of thin oxide films formed on pure zirconium (400°C after 24 h) have shown that pores may form an interconnected network up to 10 nm wide, following the oxide equiaxed grain boundaries [111]. The permeation is believed to occur via the pore network rather than by bulk diffusion. He measured the diffusion coefficient for hydrogen in zirconium oxide films by exposing preoxidized specimens to a low pressure hydrogen gas. However, it is well known that the oxide undergoes rapid breakdown if the sample is transferred from an oxygen to a hydrogen atmosphere.

Charquet et al. [112] studied the hydrogen uptake in steam as a function of oxidation behavior for Zircaloy-4 at 400 and 500°C. The hydriding kinetics increases with corrosion rate, however, the relative absorption ratio decreases with increasing oxidation rate. This indicates the existence of a mechanism that limits the penetration of hydrogen through the barrier oxide layer. This mechanism is suggested to be the diffusion of hydrogen through the oxide layer, a process which may be slower than the oxygen diffusion. By decreasing the oxidation rate the hydrogen absorption rate is also decreased.

Bossis et al. [113] made the hypothesis of the location of the reduction reaction at the interface oxide/water because of the doping in electrons due to the presence of Nb$^{5+}$ in the oxide layer. This mean that the hydrogen, in the case of M5, is rejected due to the presence of Nb$^{5+}$ unlike Zircaloy-4, where the hydrogen is reduced and diffuses via non-oxidized precipitates present in the oxide layer, near the metal/oxide interface.

Kakiuchi et al [93] discussed the relationship between iron addition and electrical potential across the oxide film. From electrochemical approach of binary metal oxides, it is known that acceptor aliovalent impurities such as iron will be compensated by anion vacancies in zirconium oxide (however, this supposed that Schottky disorder is the primary intrinsic ionic
defect in zirconium oxide). Comparing Zircaloy-2 and HiFi (Zircaloy-2 +0.4wt%Fe) alloys, the concentration of anion vacancy in the oxide film should be higher for HiFi due to higher iron concentration. Thus, the reaction between anion vacancy and oxygen is more active in the oxide film surface of HiFi and consequently the amount of surface electrons consumed in the reaction is larger in HiFi. Measurements of contact potential difference, which is directly related to the relative electrical potential across the oxide film, even if there are subject to caution [35], are indeed higher in HiFi compared to Zircaloy-2. If the oxide surface is more positive, electrons that are created at the oxide/metal interface can diffuse faster toward the oxide/water interface, decreasing the electrical gradient. The authors assumed that the amount of protons that transport through the oxide film inward to the metal/oxide interface will relatively reduce when the electrical gradient over the oxide film decreases. This model, summarized in Figure 1-26 could explain why hydrogen absorption of HiFi alloy is reduced compared to Zircaloy-4.
Harada et al. [65] have shown that the hydrogen pick-up fraction in Zircaloy-4 and Zircaloy-2 was not constant as a function of the exposure time but varied. In the pre-transition phase, although the corrosion rate gradually decreased, the calculated hydrogen pick-up percentage increased. At transition, the corrosion rate increased but the hydrogen pick-up percentage decreased (see Figure 1-27). In Figure 1-27, the weight gain (on left), total hydrogen pick-up fraction (at the top) and instantaneous hydrogen pick-up fraction (on right) are plotted as
a function of exposure time. The different weight gain transitions are clearly visible such the variations of instantaneous hydrogen pick-up fraction.

They proposed that the hydrogen in the oxide may cause the interface layer to consist of distorted ZrO$_2$ and sub-oxide before the transition, and also assist the growth of a uniform and defect-free oxide after the transition. Hydrogen is thought to have two opposite effects on the corrosion process. One is to suppress the transport of the oxygen ion through the oxide by stabilizing the interface layer prior to transition, and the other is to degrade the interface layer at the transition. However, satisfactory explanations of this change in hydrogen effect are lacking.

Figure 1-27: Corrosion behavior and hydrogen pick-up properties of Zr-4 in pure water at 360°C [65]
1.4. **Objective of the study**

As it has been detailed previously, a non-destructive and precise technique to detect low level of hydrogen in zirconium alloys is lacking. We propose a novel use of a non-destructive technique to quantitatively assess hydrogen concentration in zirconium alloys. The technique, called Cold Neutron Prompt Gamma Activation Analysis (CNPGAA), is based on measuring prompt gamma rays following the absorption of cold neutrons, and comparing the rate of detection of characteristic hydrogen gamma rays to that of gamma rays from matrix atoms. Because the emission is prompt, this method has to be performed in a close proximity to a neutron source such as the one at the National Institute of Technology (NIST) Center for Neutron Research. Using this non-destructive technique couple with usual VHE technique, this study methodically and carefully evaluated the hydrogen pick-up fraction for various zirconium alloys in an attempt to understand the role of alloying elements in hydrogen pick-up in zirconium alloys. The study particularly focuses on the hydrogen pick-up fraction variations as a function of exposure time and relates it to the oxidation kinetics.
Chapter 2

Experimental procedures

This chapter reviews the experimental procedures used in this study. Before explaining the experimental procedures, the zirconium alloys used in this study are detailed.

2.1. Zirconium alloys studied

Three type of alloys were selected for this study: ZrSnFeCr (Zircaloy-4), NbSnFe (ZIRLO) and ZrNb (Zr-2.5Nb).

Alloys currently used in the industry such as cold worked-stress relieved Zircaloy-4, ZIRLO and Zr-2.5Nb were selected to be investigated in this project. Also, a wide range of model alloys prepared in a previous study [14] were available to be investigated to understand the effect of alloying microstructure and microchemistry on hydrogen pick-up. Indeed, it has been shown in previous studies that microstructure and microchemistry have a strong influence on hydrogen pick-up and corrosion kinetics of zirconium alloys [66, 68, 69]. The different alloys studied in this work are summarized in Table 2-1.

For the US I-NERI [14] and ROK I-NERI alloys [14], chemical analysis was performed on the model alloys by using ICP-OES (Inductively Coupled Plasma Optical Emission Spectroscopy) and the target compositions were met for all of the model alloys. The fabrication process followed
the steps shown in Table 2-2. Buttons were vacuum arc melted four times to promote chemical homogeneity and then beta annealed followed by water quenching.

Table 2-1: Chemical composition, geometry, process temperature and origin of alloys used in this study [14].

<table>
<thead>
<tr>
<th>Alloy system</th>
<th>Alloy composition (wt%)</th>
<th>Sample geometry</th>
<th>Process temperature °C</th>
<th>Origin</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure Zr</td>
<td>Zr sponge</td>
<td>Sheet</td>
<td>580</td>
<td>US I-NERI</td>
</tr>
<tr>
<td>Zr-Fe-Cr</td>
<td>Zr-0.2Fe-0.1Cr (L)</td>
<td>Sheet</td>
<td>(L): 580 (H): 720</td>
<td>US I-NERI</td>
</tr>
<tr>
<td></td>
<td>Zr-0.2Fe-0.1Cr (H)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Zr-0.4Fe-0.2Cr (L)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Zr-0.4Fe-0.2Cr (H)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zr-Cr</td>
<td>Zr-0.5Cr</td>
<td>Sheet</td>
<td>650</td>
<td>US I-NERI</td>
</tr>
<tr>
<td></td>
<td>Zr-1.0Cr</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zr-Cr-Fe</td>
<td>Zr-1.0Cr-0.2Fe</td>
<td>Sheet</td>
<td>650</td>
<td>US I-NERI</td>
</tr>
<tr>
<td>Zr-Cu</td>
<td>Zr-0.5Cu</td>
<td>Sheet</td>
<td>580</td>
<td>US I-NERI</td>
</tr>
<tr>
<td></td>
<td>Zr-1.0Cu</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zr-Nb</td>
<td>Zr-0.2Nb</td>
<td>Sheet</td>
<td>580</td>
<td>ROK I-NERI</td>
</tr>
<tr>
<td></td>
<td>Zr-0.4Nb</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Zr-1.5Nb</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Zr-2.5Nb</td>
<td>Sheet and tube</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zr-Nb-Cu</td>
<td>Zr-2.5Nb-0.5Cu</td>
<td>Tube</td>
<td>580</td>
<td>Hydrogen program</td>
</tr>
<tr>
<td>Zr-Sn-Fe-Cr</td>
<td>Zr-1.3Sn-0.2Fe-0.1Cr (H)</td>
<td>Sheet</td>
<td>720</td>
<td>US I-NERI</td>
</tr>
<tr>
<td>Zr-Nb-Sn-Fe</td>
<td>Zr-1.0Nb-1.0Sn-0.1Fe</td>
<td>Tube</td>
<td>580</td>
<td>Hydrogen program</td>
</tr>
<tr>
<td></td>
<td>Zr-1.0Nb-0.6Sn-0.4Fe</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Zr-0.9Nb-0.4Sn-0.4Fe</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Zr-0.9Nb-0.9Sn-0.1Fe</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ZIRLO</td>
<td>Zr-1.0Nb-1.0Sn-0.1Fe</td>
<td>Sheet and tube</td>
<td>580</td>
<td>Hydrogen program</td>
</tr>
<tr>
<td>Zircaloy-4</td>
<td>Zr-1.45Sn-0.2Fe-0.1Cr</td>
<td>Sheet and tube</td>
<td>580</td>
<td>Hydrogen program</td>
</tr>
</tbody>
</table>

The buttons were rolled at different temperatures depending on the desired final microstructure.

The grit blasted and pickled hot rolled strip was then vacuum annealed, which was followed by two iterations of cold rolling and vacuum annealing to produce final strip in a fully recrystallized condition with a thickness of about 0.8 mm. The majority of the alloys were processed at 580°C.
This was required in order to stay below the two-phase temperature range for the Nb-bearing alloys, minimize grain growth for commercially pure zirconium (sponge) and to maintain small precipitates in two Zr-Fe-Cr alloys (denoted by (L)). An intermediate process temperature of 650°C was selected for the Zr-Cr-Fe alloy while a high process temperature of 720°C was used to grow large precipitates in two Zr-Fe-Cr alloys and Zr-1.3Sn-0.2Fe-0.1Cr. Each button provided material for about 60 to 70 corrosion coupons (25 mm x 20 mm x 0.8 mm). The fabrication of the Zr-Nb alloys was completed in the spring of 2003 at KAERI (Korea Atomic Energy Research Institute) in the Republic of Korea (South Korea) while the US alloy fabrication was completed in August of that same year at Westinghouse Electric Co. in Pittsburgh, PA. After completion of the manufacturing in KAERI, 30 corrosion coupons per each alloy were transferred to US for corrosion tests and characterization efforts. All the alloys (US-INERI and ROK-INERI) are in

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Vacuum arc melt</td>
<td>Melt 4 times to promote chemical homogeneity</td>
<td>Melt 4 times to promote chemical homogeneity</td>
</tr>
<tr>
<td>Beta Treatment</td>
<td>No canning β-anneal Water quench</td>
<td>Can in 304 stainless steel β-anneal Water quench</td>
</tr>
<tr>
<td>Hot roll</td>
<td>580, 650, or 720°C Roll to ~4m</td>
<td>580°C Roll to ~4 mm</td>
</tr>
<tr>
<td>Condition</td>
<td>Grit blast to remove oxide Pickle</td>
<td>Remove SS can Grit blast to remove oxide Pickle</td>
</tr>
<tr>
<td>Vacuum anneal</td>
<td>58, 650, or 720°C for 4 hours</td>
<td>560-580°C for 5-10 hours</td>
</tr>
<tr>
<td>Condition</td>
<td>Pickle</td>
<td>-</td>
</tr>
<tr>
<td>Cold roll</td>
<td>Roll to ~2 mm</td>
<td>Roll to ~2 mm</td>
</tr>
<tr>
<td>Vacuum anneal</td>
<td>580, 650, or 720°C for 4 hours</td>
<td>560-580°C for 5-10 hours</td>
</tr>
<tr>
<td>Condition</td>
<td>Pickle</td>
<td>-</td>
</tr>
<tr>
<td>Cold roll</td>
<td>Roll to ~0.8 mm</td>
<td>Roll to ~0.8 mm</td>
</tr>
<tr>
<td>Final vacuum anneal</td>
<td>580, 650, or 720°C for 2-4 hours</td>
<td>560-580°C for 5-10 hours</td>
</tr>
</tbody>
</table>
fully recrystallized state. This processing procedure resulted in different microstructure. Regarding the I-NERI samples, the grain structure revealed by etching was observed using polarized light microscopy in reflection mode. The average grain size was measured for a representative sample of the alloys: the reference alloys (sponge Zr, crystal bar Zr and Zr-1.3Sn-0.2Fe-0.1Cr (H)), Zr-0.2Fe-0.1Cr (L) and Zr-0.2Fe-0.1Cr (H). The optical micrographs from the alloys show predominantly equiaxed grains and a homogeneous microstructure, as would be expected from a recrystallizing heat treatment. The average grain sizes were measured in a previous study [14] as reported in Table 2-3. As expected, the average measured grain size for the Zr-0.2Fe-0.1Cr (L) alloy is smaller, since the alloy was annealed at lower temperature.

The typical manufacturing procedure of the alloys from the Hydrogen program is described in the following [7]. The production of sheet alloys was the same as the one used in the US I-NERI program. The production of Zircaloy-4 tubing from an extrusion involved α-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 β-annealed, air cooled, conditioned to remove the oxide film, and then pilgered to TREXs. All TREXs were α-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 α range to recrystallize the tubing, with the exception of the final stress-relief anneal. The recrystallization anneals of Zircaloy-4 were characterized by a cumulative annealing parameter using a value for Q/R of 40,000K. The Cumulative Annealing Parameter (CAP) value of Zircaloy-4 alloy was about 6.2 × 10^{-18}h [114]. A lower recrystallization temperature was used for Nb containing alloys to achieve a distribution of fine particles in the final size tubing. The recrystallization anneals were performed in the temperature range of 853 to 873K for approximately 4 hours [115, 116]. Final conditioning of all 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 grain size of ZIRLO sheet is also much smaller compared to Zircaloy-4 as seen in Figures 2-1 and 2-2. The cross sections have been prepared from bare coupons cut with a low speed diamond saw. After subsequent silicon grit polishing, the coupons were further polished under 6µm diamond, 1µm diamond and finally 0.05 µm colloidal silica. An etching solution of nitric and hydrofluoric acid (45% water, 45% HNO₃, 10% HF) was used to reveal the grain boundaries under polarized light microscopy. The white spots on Figure 2-1 are the Zr(Cr,Fe)₂ precipitates.

Table 2-3: Grain sizes of some of the I-NERI alloys [14]

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Average grain size (µm)</th>
<th>StDev</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr-0.2Fe-0.1Cr (L)</td>
<td>9.7</td>
<td>2.6</td>
</tr>
<tr>
<td>Zr-0.2Fe-0.1Cr (H)</td>
<td>14.5</td>
<td>3.4</td>
</tr>
<tr>
<td>Zr sponge</td>
<td>11.3</td>
<td>2.0</td>
</tr>
<tr>
<td>Zr-1.3Sn-0.2Fe-0.1Cr (H)</td>
<td>14.2</td>
<td>2.9</td>
</tr>
</tbody>
</table>
Figure 2-1: Optical micrographs of etched Zircaloy-4 sheet (50x)

Figure 2-2: Optical micrographs of etched ZIRLO sheet (50x)
2.2. Corrosion procedure

All the alloys were corroded in 360°C pure water in a single static autoclave of 4 liters in saturated pressure condition at 2708.6 psi (18.7 MPa) according to ASTM G2-88 [117] (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 coolant temperature is approximately 310°C at a pressure of 2250 psi (15.5 MPa). In fact, there are more severe operating conditions than the ones found in the PWR operation, in terms of temperature and pressure, 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 done at Westinghouse Laboratory in Monroeville, PA. After every cycle, the autoclave was opened and the water was refreshed, so that the dihydrogen gas in water was released. Indeed, if the water was not refreshed, the hydrogen gas would gradually accumulate (approximately 155 cc/(kg of H₂O) after a growth of 1μm of oxide if all the hydrogen produced by corrosion is assumed to be released in water), and could alter the corrosion process. If, however, hydrogen level in water was kept between 25-50 cc of H₂/(kg of H₂O) there should be no effect [26].
2.3. Vacuum Hot Extraction

Vacuum Hot Extraction (VHE) and Cold Neutron Prompt Gamma Activation Analysis (CNPGGA) were used to determine the hydrogen content of a large set of different zirconium alloys. Since CNPGGA has not been routinely used on zirconium alloys in the past, it was necessary to benchmark the technique using VHE.

The VHE technique has been routinely used to determine the hydrogen content of corroded zirconium alloys. A weighed sample is introduced through a vacuum lock into a molybdenum crucible in a vacuum line system. The sample is cleaned with ether and allowed to dry prior to weighing to remove any surface contamination. Heat is then applied to the crucible through an induction coil, the sample and crucible are heated to 1200°C and with the aid of high speed diffusion pumps, and hydrogen is extracted from the sample and collected within the system. Gas pressure is then measured using a McLeod gauge and the change in gas conductivity is related to hydrogen concentration and results are reported in parts per million by weight. A scheme of the apparatus is presented in Figure 2-3.
Calibration is verified with NIST or NIST-traceable standard reference materials of known hydrogen content. The apparatus used in this study is a NRC Model 917 (ASTM E146-83) [118]. The vacuum hot extraction technique offers the advantage of a fixed calibration which can determine hydrogen content with good precision. The fixed calibration also allows for accurate hydrogen determination at lower sample mass. Since the sample is not consumed, vacuum hot extraction provides opportunity for retrieval of samples for additional analyses. However, the microstructure is altered during heat up (for instance at 1200°C, the transformation $\alpha Zr \rightarrow \beta Zr$ has already occurred and thus this is a destructive method). Figure 2-4 shows which part of the samples (sheet and tube shapes) has been analyzed:
Hydrogen analysis using this technique was done at LUVAK, MD. As mentioned above, although this technique is fast and reasonably accurate, it is also destructive. Thus, to measure the evolution of hydrogen content, it is necessary to perform several measurements on different samples (sister samples), which is intrinsically a cause of measurement dispersion. Also, the error range is not well defined. The average experimental error is approximately ±5%, as confirmed by different studies [65, 119]. The area of the analyzed samples was 8 mm x 8 mm (see Figure 2-4), which corresponds to an approximate mass of 280 mg. This corresponds approximately to the size and mass limit defined by the VHE apparatus. The analyzed samples were as big as possible to minimize any local area-to-area variations of hydrogen content. To evaluate the range of this variation of hydrogen content within the sample, several smaller samples of the same alloy were analyzed. The results for ZIRLO sheet, Zircaloy-4 sheet and Zr-2.5Nb tube are presented in Table 2-4 and the different analyzed parts are presented in Figure 2-5.
Table 2-4: Hydrogen content on different samples of a given alloy corroded for 60 days

<table>
<thead>
<tr>
<th>Alloys</th>
<th>H content (wt.ppm) Test 1</th>
<th>H content (wt.ppm) Test 2</th>
<th>H content (wt.ppm) Test 3</th>
<th>H content (wt.ppm) Test 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZIRLO sheet</td>
<td>18</td>
<td>21</td>
<td>19</td>
<td>20</td>
</tr>
<tr>
<td>Zircaloy-4 sheet</td>
<td>15</td>
<td>17</td>
<td>16</td>
<td>17</td>
</tr>
<tr>
<td>Zr-2.5Nb tube</td>
<td>19</td>
<td>20</td>
<td>17</td>
<td>18</td>
</tr>
</tbody>
</table>

Figure 2-5: Analyzed parts of one sample (in red) to quantify hydrogen content variations

The results in Table 2-4 indicates that the variability of hydrogen content in the sample within the experimental error of the technique (which is \( \approx \pm 1 \text{ wt.ppm} \) for that level of hydrogen).

2.4. Cold Neutron Prompt Gamma Activation Analysis (CNPGAA)

2.4.1. Theory

The CNPGAA detection technique is based on the emission of characteristic prompt gamma rays emitted by a given nucleus when it absorbs a neutron [1]. The mechanism of prompt gamma emission is explained by Figure 2-6. Thermal neutrons exit the reactor (\( \bar{E}_{neutrons} \approx \))
0.025eV) and enter a liquid hydrogen cold moderator \( T_{\text{moderator}} \approx 25K \), which shifts the neutron spectrum to lower energy \( E_{\text{neutrons}} \approx 5\,\text{meV} \). Using these cold neutrons increases the sensitivity of the technique and lowers the hydrogen background, allowing us to detect very low levels of hydrogen content \((\leq 5\,\text{wt.\,ppm})\) [77]. Cold neutrons are then absorbed by hydrogen atoms which emit a characteristic gamma ray by de-excitation of the nucleus. This gamma ray is then detected and with proper calibration the signal can be converted to the hydrogen content of the sample. This technique is non-destructive and does not alter the sample, as discussed later. Also, its error is lower than usual destructive techniques (VHE or IGF) and does not increase with the amount of hydrogen in the sample.

The CNPGAA technique is based on the detection of the prompt gamma ray from hydrogen nucleus (they are called prompt since their emissions happen less than \(10^{-9}\)s after the formation of the compound nucleus). One should not mix up CNPGAA with the better known

![Figure 2-6: Mechanism of prompt gamma ray emission by neutron absorption](image-url)
Neutron Activation Analysis (NAA), which is based on the detection of delayed gamma rays following the beta decay of the activated nucleus. One of the advantages of CNPGAA is that it can detect the low atomic number elements (such H, Li, B), which do not form activated nuclei and thus are not detectable by NAA. However, three major drawbacks of CNPGAA have to be overcome:

- The de-excitation time being very short so the gamma-rays must be counted while sample is irradiated.
- The detector needs to be placed very close to the neutron target due to the low source strength, while still avoiding experimental noise coming from the emission of gamma rays from the chamber or even from the neutron source (a nuclear thermal reactor).
- The sample is activated at the end of the experiment. However, zirconium alloys do not activate much since the zirconium neutron capture cross section is very low and the alloying elements are not in a high concentration. Simulations have been run to confirm the low activation of the sample after its analysis (see Table 2-5). Since the total sample activity is less than 1 mCi, we were able to retrieve our samples almost directly after the experiment.

The neutron capture cross section is strongly dependent on the type of nucleus and the energy of the incoming neutron. The absorption rate $F_a$ is given by:

$$ F_a = \phi_n \left( \sum_i N_i \sigma_{ai} \right) $$

where:

$F_a = $ Absorption reaction rate (absorption.cm$^{-3}$),

$\phi_n = $ neutron flux (neutrons.cm$^{-2}.s^{-1}$) which is almost monoenergetic,

$N_i = $ atomic density of the $i^{th}$ element (atoms.cm$^{-3}$), and
\(\sigma_{ai}^a\) = Microscopic absorption cross section of the \(i^{th}\) element (cm\(^2\)) at the neutron energy.

Table 2-5: Calculated activities and dose rates for the end of irradiation of 1g of Zicaloy-4 after a decay period of 3 hours and a neutron flux of \(8 \times 10^8\) cm\(^{-2}\).s\(^{-1}\).

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Target Mass (g)</th>
<th>Isotope Activity (mCi)</th>
<th>Gamma Exposure Rate on contact (mrem/hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr-95</td>
<td>1.71E-1</td>
<td>2.24E-3</td>
<td>8.91E-3</td>
</tr>
<tr>
<td>Zr-97</td>
<td>2.76E-2</td>
<td>7.71E-2</td>
<td>3.40E-1</td>
</tr>
<tr>
<td>Sn-113</td>
<td>1.16E-4</td>
<td>1.77E-5</td>
<td>5.34E-5</td>
</tr>
<tr>
<td>Sn-113m</td>
<td>1.16E-4</td>
<td>1.70E-6</td>
<td>1.16E-6</td>
</tr>
<tr>
<td>Sn-117m</td>
<td>1.74E-3</td>
<td>2.68E-5</td>
<td>4.53E-5</td>
</tr>
<tr>
<td>Sn-119m</td>
<td>2.91E-3</td>
<td>3.12E-6</td>
<td>2.88E-6</td>
</tr>
<tr>
<td>Sn-123</td>
<td>5.56E-4</td>
<td>9.29E-6</td>
<td>3.13E-7</td>
</tr>
<tr>
<td>Sn-123m</td>
<td>5.56E-4</td>
<td>6.45E-5</td>
<td>5.15E-5</td>
</tr>
<tr>
<td>Sn-125</td>
<td>6.95E-4</td>
<td>1.09E-5</td>
<td>1.69E-5</td>
</tr>
<tr>
<td>Mn-54</td>
<td>1.16E-4</td>
<td>2.59E-7</td>
<td>1.34E-6</td>
</tr>
<tr>
<td>Cr-51</td>
<td>1.16E-4</td>
<td>5.43E-4</td>
<td>3.72E-4</td>
</tr>
<tr>
<td>Mn-56</td>
<td>1.83E-3</td>
<td>1.07E-5</td>
<td>8.72E-5</td>
</tr>
<tr>
<td>Fe-59</td>
<td>5.60E-6</td>
<td>3.58E-6</td>
<td>2.15E-5</td>
</tr>
<tr>
<td>TOTAL</td>
<td>2.07E-1</td>
<td>8.00E-2</td>
<td>3.50E-1</td>
</tr>
</tbody>
</table>

Then, all the neutrons absorbed do not necessarily emit a prompt gamma ray. The gamma ray emission rate of the sample \(R_s\) is given by:

\[
R_s = N_A \phi_n \left( \sum_i \frac{m_i \gamma_i \sigma_{ai}}{M_i} \right)
\]  

(22)

where:

\(\gamma_i\) = Gamma – Ray yield of the \(i^{th}\) element (photons/capture),

\(m_i\) = mass of the \(i^{th}\) element (g),

\(M_i\) = Atomic weight of the \(i^{th}\) element (g.mol\(^{-1}\)), and

\(N_A\) = Avogadro’s number (mol\(^{-1}\)).

Finally, all the gamma rays emitted by the sample are not detected by the gamma ray detector.

The final detection rate \(R_d\) is given by:

\[
R_d = R_s \varepsilon \Omega
\]  

(23)
where:

\[ \varepsilon = \text{detection efficiency for the gamma ray (photopeak counts/photon), and} \]

\[ \Omega = \text{solid angle between the target and the detector.} \]

One can conclude that theoretically there is a strong influence of the neutron flux, the target (mass, absorption cross section, gamma-ray yield) and the general apparatus (type of detector and geometry) on the prompt gamma ray detection rate.

### 2.4.2. General scheme of CNPGAA apparatus

A scheme of a classic CNPGAA apparatus is presented in Figure 2-7.

The thermal neutrons come out from the thermal reactor \(E_{\text{neutrons}} \approx 0.025eV\) and enter the cold moderator \(T_{\text{moderator}} < 50K\), which causes the neutron spectrum to shift towards lower energy: the neutrons are called cold \(E_{\text{neutrons}} \approx 5meV\). The cold neutrons are focused in a neutron guide (approximately 40 meters), which has the target at its end. Some neutrons are absorbed by the sample; some by the chamber; some do not interact and travel through the chamber without being absorbed. Some of the nuclei that absorb neutrons emit characteristic gamma rays isotropically. Finally, some of these gamma rays are collected by the

![Figure 2-7: Scheme of a CNPGAA apparatus (not to scale)](image-url)
detector. The detector efficiency is called detection rate ($\varepsilon$ in Equation (23)). Physically several system design parameters can be tweaked to increase this rate for a given element:

- The use of cold neutrons increases absorption rate. Indeed, cold neutrons are used since the absorption cross sections of the different elements vary as the inverse of neutron velocity. Thus the colder the neutrons, the higher the absorption cross sections, which causes $R_s$ to increase.

- Simply moving the detector closer to the sample will increase the solid angle, but at the cost of higher backgrounds and other consequences of operating instruments in high radiation areas. Thanks to cold neutrons the signal-to-noise ratio is high, since the coldest neutrons from the reactor are reflected with high efficiency from the guide walls (their wavelength is higher than that of thermal neutrons such that as a result, their reflection coefficient is higher), while the fast neutrons and gamma rays decrease as $1/r^2$.

Furthermore, the neutron guide is slightly curved so that the fast neutrons and gamma rays that are not reflected by the wall do not impact the sample.

- A convergent focused beam is desirable to increase the flux. To achieve this it is necessary to collimate the beam as much as possible by the use of focusing lenses.

### 2.4.3. Apparatus at the National Institute of Standard and Technology (NIST)

The author performed CNPGGA at the National Institute of Standards and Technology (NIST). An illustration of the whole NIST beam and guide hall is given in Figure 2-8 and a more precise side view of the CNPGAA apparatus is shown in Figure 2-9.
Figure 2-8: Plan of the NIST reactor and the Cold Neutron Research Facility. The guide hall dimensions are 30.5 x 61 m.
The cold moderator at NIST is made of liquid hydrogen at a temperature of 25 K. The neutron guide is a super mirror guide made of a nickel alloy and its length is 41 m. The thermal equivalent neutron fluence rate at the CNPGGA target position is approximately $8 \times 10^8$ cm$^{-2}$ s$^{-1}$. The collimation is achieved with Li apertures, and the neutrons are incident on the sample on a circular area of approximately 3.14 cm$^2$ (2 cm diameter).

The inner chamber (24.1 cm x 17.1 cm x 24.8 cm) is made of aluminum and magnesium alloys which have small neutron absorption cross section. This minimizes the gamma ray background from neutron capture by the walls of the sample box. The chamber is purged with helium to minimize the gamma ray background due to neutron capture by nitrogen and hydrogen in atmospheric water vapor. Samples irradiated inside the chamber are suspended by Teflon strings between the prongs of an aluminum fork (again to minimize the instrumental background). The samples are thin enough to avoid gamma ray attenuation and neutron self-shielding by the sample.

Gamma rays emitted by the sample are measured using a high-purity germanium detector ($\varepsilon = 26\%$) mounted vertically into a bismuth germanate (BGO) Compton suppressor (which

Figure 2-9: Side view of CNPGAA instrument at NIST
improves the signal-to-noise ratio by decreasing the baseline background coming from Compton gamma rays).

Accounting for all of these features, the maximum background noise at the hydrogen gamma-ray energy is 5 mg·kg⁻¹ (or wt·ppm explained in Section 2.4.4.2), and the sensitivity is such that very low concentrations of hydrogen in the samples are detectable (approximately 5 mg·kg⁻¹). This background originates principally from other gamma-rays produced by neutron capture in hydrogenous materials present in the germanium and BGO detectors.

2.4.4. Fitting standard and data analysis

2.4.4.1. Fitting of the gamma-ray spectrum

During the experiment a gamma-ray spectrum is acquired in which each peak is originated from a given gamma ray of a given nucleus de-excitation. Although the hydrogen nucleus undergoes only one characteristic nuclear de-excitation (at 2223 keV), zirconium undergoes multiple de-excitations which generate numerous peaks in the gamma-ray spectrum. A typical example of the full gamma ray spectrum of a hydrided zirconium alloy is shown in Figure 2-10, with a zoom-in on the hydrogen peak energy region given in Figure 2-11.
Even at an apparent concentration of 49 wt.ppm of hydrogen (which is actually equal to 19 wt.ppm after corrections as explained in Section 3.1), the hydrogen peak is clearly distinct from the noise.

The zirconium 934 keV peak has been chosen as the reference zirconium peak. Different types of fitting programs have been used to analyze the results. Indeed, since the detected
hydrogen concentrations can be very low, the choice of the fitting programs can affect the results (especially the background correction routines used). To verify this, three different fitting programs were used: an algorithm for hand fitting of peaks (SUM) written at NIST [121], GENIE 2000, a standard commercial peak search program which locates peaks and integrates peaks automatically, and the program PEAKFIT 4.0, a manual program in which the fitting is made peak by peak and is used to double check the automatic fitting processes used in the other programs. One significant difference between the SUM algorithm and GENIE 2000 is that using SUM, the background and peak regions are chosen by hand, while the peak search program chooses a few channels on either side of the peak for background calculation. This different way to consider the background affects the results of GENIE 2000, which are always a few wt.ppm lower than the results obtained by SUM.

2.4.4.2. Standards

The first major obstacle to performing quantitative hydrogen analysis is that no certified NIST standards of hydrogen in zirconium exist (actually one standard exists but as detailed in Section 3.1 there are questions on the indicated hydrogen value [122]). The peaks have different sensitivities to the neutron absorption. Sensitivities (the number of counts per seconds per milligrams of the considered element exposed to the beam) are directly related to the neutron absorption cross sections and to the probability of a given de-excitation path compared to another one (for instance going from Energy Level 1 to 3 directly, by passing Energy Level 2). The hydrogen mass fraction in mg·kg⁻¹ in a zirconium sample \( C_H \) is given by Equation 24:

\[
C_H = \left( \frac{A_{Zr} - H}{S_{2223}} \right) \left( \frac{S_{934}}{S_{934}} \right) 10^{-6} \frac{\omega_{Zr}}{\omega_{Zr}} \text{mg·kg}^{-1} \tag{24}
\]
where \( C_H \) is the hydrogen concentration in the sample in mg·kg\(^{-1}\) (or wt.ppm), \( A_{2223} \) is the area of the 2223 keV peak in counts, \( H_b \) is the hydrogen background in counts per second, \( S_{2223}^H \) is the hydrogen sensitivity in cps·mg\(^{-1}\), \( t \) is the acquisition time in seconds, \( S_{934}^{Zr} \) is the 934 keV reference zirconium peak sensitivity, \( A_{934} \) is the area of the 934 keV reference peak and \( \omega_{Zr} \) is the mass fraction of zirconium. Considering the low concentration of alloying elements in a sample, and the low effect of the oxide formation on the total mass of the sample, it was assumed that \( \omega_{Zr} \cong 1 \) for all alloys at any time of the corrosion process (and thus mg·kg\(^{-1}\) is approximately equal to wt·ppm).

Thus, the determination of the sensitivities was of primary importance to the determination of hydrogen concentration. These sensitivities were determined using standards.

Because NIST certified standards of hydrogen into zirconium do not exist (only reference values exist), a combination of different standards had to be used: a pure zirconium foil \( (m_{Zr} = 218 \text{ mg}) \), a titanium foil \( (m_{Ti} = 14 \text{ mg}) \) and a graphite/urea/titanium powder sample \( (%Ti = 12.55 \% \text{ and } %H = 3.171 \% \text{ mass fractions}) \). Using this combination of standards, the sensitivities were calculated using Equations 25 to 29:

\[
S_{1381}^{Ti} = \frac{A_{1381}}{(m_{Ti} \times t)} \quad (25)
\]

where \( S_{1381}^{Ti} \) is the sensitivity of the 1381 keV titanium peak, \( A_{1381} \) is the area of the 1381 keV peak and \( t \) the acquisition time.

\[
S_{934}^{Zr} = \frac{A_{934}}{(m_{Zr} \times t)} \quad (26)
\]

where \( S_{934}^{Zr} \) is the sensitivity of the 934 keV zirconium peak.

The hydrogen background \( H_b \) was determined before running the samples by acquiring a spectrum for 48 hours with no sample inserted in the chamber:

\[
H_b = \frac{A_{2223}^b}{t} \quad (27)
\]
where $A_{2223}^b$ is the area of the peak for this experiment.

The ratio of Ti and H sensitivities were determined using the graphite/urea/titanium powder according to:

$$
\frac{S_{2223}^H \text{ powder}}{S_{1381}^{Ti \text{ powder}}} = \left( \frac{A_{2223}^b - H_b}{\%H} \right) \left( \frac{\%Ti}{(A_{1381} \times t)} \right) \quad (28)
$$

Finally:

$$
S_{2223}^H = \frac{S_{2223}^H \text{ powder}}{S_{1381}^{Ti \text{ powder}}} S_{1381}^{Ti} \quad (29)
$$

The results obtained using the various fitting programs for the analysis and calculation of area were in good agreement with each other. GENIE 2000 gives the smallest error range and consequently the best confidence. Thus, in the study, only the results given by GENIE 2000 are presented. The sensitivities are given in Table 2-6.

Table 2-6: Hydrogen and zirconium sensitivities and hydrogen background determine for CNPGAA measurements

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Peak centroid (keV)</th>
<th>GENIE 2000</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zirconium sensitivity (counts·s⁻¹·mg⁻¹)</td>
<td>934</td>
<td>$9.91 \times 10^{-2}$ $\pm 7.8 \times 10^{-4}$</td>
</tr>
<tr>
<td>Hydrogen sensitivity (counts·s⁻¹·mg⁻¹)</td>
<td>2223</td>
<td>13.12 $\pm 2.9 \times 10^{-1}$</td>
</tr>
<tr>
<td>Hydrogen background (counts·s⁻¹)</td>
<td>2223</td>
<td>$6.3 \times 10^{-2}$ $\pm 1.1 \times 10^{-3}$</td>
</tr>
</tbody>
</table>
Chapter 3

Experimental results

In this chapter, the possibility to assess low level of hydrogen concentration in zirconium alloys using Cold Neutron Prompt Gamma Activation is discussed. Then, the hydrogen pick-up of various zirconium alloys is discussed and related to the amount of alloying element in solid solution and to the corrosion kinetics.

3.1. CNPGAA benchmarking

Using the sensitivities of every peak of interests determined in the last chapter, the hydrogen content of any zirconium alloys could be determined. The first goal was to benchmark the CNPGAA with the VHE results since again no reliable standards of hydrogen in zirconium exist.

The H content in Zr samples by CNPGAA were calculated using the hydrogen peak at 2223keV and the Zr peak at 934keV as references. The approximate hydrogen content of the sample in wt.ppm $C_{H}^{\text{Sample}}$ is given by Equation 24, reproduced here:

$$C_{H} = \left( \frac{A_{2223}}{A_{934}} - H_b \right) \left( \frac{S_{Zr}^{2223}}{S_{934}} \right)$$

One of the advantages of the CNPGAA technique is that it does not require precise information on the thickness or on the mass of the sample since only the ratios are measured. Using the element ratio method also largely negates the effect of uncertainties concerning neutron...
interactions (absorption, scattering, etc.) on the results. Indeed, quantities associated with the neutron flux such as beam attenuation, temporal differences in the neutron flux, variation in sample area coverage by the beam or attenuation of the beam into the sample due to neutron absorption will vary from experiment to experiment. However, in a single experiment, uncertainties in these quantities are divided, since both the hydrogen and the zirconium peaks are equally affected [123].

The uncertainty in VHE is the total experimental uncertainty taking into account error coming from the VHE technique and from other uncertainties such as the area-to-area variation of hydrogen concentrations in a coupon. This error is difficult to evaluate but, equating the error with the stated experimental precision of the VHE apparatus given by the company [124] and using VHE on various spots of the same coupon, the overall error was estimated to be ±5% of the hydrogen content as confirmed by other studies [65, 119]. The error in CNPGAA comes from the error in \( A_x \) given by the different fitting programs, the composition errors of the standards and the counting statistics. Using error propagation formulas, the final error is given by Equation 30:

\[
\Delta C_H = C_H \left( \left( \frac{(\frac{\Delta A_{2223}}{t} + \Delta H_b)^2}{\frac{A_{2223}}{t} - H_b} \right)^2 + \left( \frac{\Delta S_{H_{2223}}^{2223}}{S_{H_{2223}}^{2223}} \right)^2 \right) \left( \left( \frac{\Delta S_{Zr_{34}}^{2223}}{S_{Zr_{34}}^{2223}} + \left( \frac{\Delta A_{34}}{A_{34}} \right)^2 \right)^2 \right)^{1/2} \tag{30}
\]

where \( \Delta X \) denotes the error associated with \( X \). Evaluating \( \Delta C_H \) using equation 30 (and shown in Table 3-1), we obtain an error varying between ±0.5% and ±2%, depending on the hydrogen content of the sample. For benchmarking, ten uncut corrosion coupons were examined using first CNPGAA and then VHE. The results are shown in Table 3-1.

A consistent difference of 29.4 ± 1.1 wt·ppm between the VHE and CNPGAA results was noticed. This difference is rationalized and explained in the next chapter as caused by an unidentified zirconium peak underneath the hydrogen peak. The following results given by
CNPGAA were corrected for this difference. Taking into account this consistent offset, the CNPGAA technique accurately matches the results given by conventional destructive techniques such as VHE, but with a smaller error range.

Table 3-1: Hydrogen concentration in wt·ppm obtained with VHE and CNPGAA on 10 Zr alloys (25 mm x 20 mm x 0.8 mm).

<table>
<thead>
<tr>
<th>Alloys</th>
<th>Exposure time (days)</th>
<th>Hydrogen concentration (wt·ppm) by VHE</th>
<th>Hydrogen concentration (wt·ppm) by CNPGAA (not corrected)</th>
<th>Hydrogen concentration (wt·ppm) by CNPGAA (corrected)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr-0.2Fe-0.1Cr</td>
<td>0</td>
<td>11 ± 0.5</td>
<td>39.8 ± 0.6</td>
<td>10.6 ± 1.0</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>24 ± 1.2</td>
<td>52.9 ± 1.0</td>
<td>23.7 ± 1.2</td>
</tr>
<tr>
<td></td>
<td>173</td>
<td>64 ± 3.2</td>
<td>92.0 ± 1.3</td>
<td>62.8 ± 1.8</td>
</tr>
<tr>
<td>Zr-0.4Fe-0.2Cr</td>
<td>493</td>
<td>129 ± 6.5</td>
<td>160.0 ± 2.1</td>
<td>131.2 ± 1.9</td>
</tr>
<tr>
<td>Zr-1.3Sn-0.2Fe-0.1Cr (H)</td>
<td>0</td>
<td>9 ± 0.5</td>
<td>37.3 ± 0.6</td>
<td>8.1 ± 0.9</td>
</tr>
<tr>
<td></td>
<td>28</td>
<td>23 ± 1.1</td>
<td>50.0 ± 0.8</td>
<td>20.8 ± 1.2</td>
</tr>
<tr>
<td></td>
<td>55</td>
<td>25 ± 1.2</td>
<td>55.4 ± 0.9</td>
<td>26.2 ± 1.4</td>
</tr>
<tr>
<td></td>
<td>240</td>
<td>75 ± 3.8</td>
<td>108.0 ± 1.7</td>
<td>78.3 ± 1.9</td>
</tr>
<tr>
<td>Zr-0.2Nb</td>
<td>326</td>
<td>69 ± 3.4</td>
<td>96.9 ± 1.6</td>
<td>67.7 ± 2.0</td>
</tr>
<tr>
<td>Zr-2.5Nb</td>
<td>326</td>
<td>134 ± 6.7</td>
<td>165.0 ± 2.2</td>
<td>135.2 ± 2.3</td>
</tr>
</tbody>
</table>

3.2. CNPGAA validation

Since the measurements in Table 3-1 show that CNPGAA technique and VHE techniques agree once the offset is taken into account, CNPGAA was used to measure hydrogen content on two individual ZIRLO coupons (2.5 mm x 3.0 mm x 0.8 mm) at different times during the corrosion process. The ZIRLO coupons were corroded in 360 °C pure water in a single static autoclave of four liters in saturated pressure condition at 18.7 MPa (2708.6 psi). Several ZIRLO sister samples were inserted in the autoclave to study the evolution of hydrogen uptake using VHE. The results are presented in Figure 3-1, which plots the weight gain (mg·dm⁻², red lozenges
on the right vertical scale) caused by oxygen ingress during the corrosion reaction for all samples
analyzed by VHE or CNPGAA at that particular corrosion time. The hydrogen contents (on the
left vertical axis) were measured using both CNPGAA (circles and triangles) and VHE (crosses),
and the error bars calculated as described above.

![Graph]

Figure 3-1: Hydrogen concentration (wt-ppm) in ZIRLO coupons as function of corrosion time
using VHE on sister samples and successive CNPGAA measurements on two different individual
coupons, plotted along with the weight gain of the corresponding sample.

The hydrogen measurement results in Figure 3-1 show that measurements with the
different techniques yield consistent results. In particular, the fact that the CNPGAA
measurements fall on top of the VHE measurement indicates that removing ZIRLO coupons,
performing CNPGAA on them and then inserting them back to the autoclave does not alter the
corrosion process. For instance, after 75 days of corrosion, the hydrogen content measured in one
of the sister samples using VHE (cross) and in coupon two using CNPGAA (circle) are the same, even though coupon two underwent two CNPGAA measurements (one at 35 days and one at 75 days) prior to the measurement. The examination of the evolution of hydrogen content among the different samples allows us to conclude that CNPGAA coupons behave similarly to sister samples, and thus that the CNPGAA measurement does not alter the corrosion and hydriding process of ZIRLO samples. One should note that the uncertainty in CNPGAA measurements decreases with hydrogen content whereas the uncertainty of VHE increases, which indicates that CNPGAA is more precise than VHE for levels of hydrogen higher than 40 wt.ppm.

### 3.3. Hydrogen pick-up fraction calculation

In this section the hydrogen pick-up fraction of a sample was calculated from the measurement of its weight gain and its hydrogen content.

The following assumptions are made:

1. Oxide films are assumed to have theoretical density,
2. No correction is made to account for local dissolution of oxygen in metal,
3. The results do not take into account for hydrogen ingress,
4. No loss of oxide occurs by any process (spallation, dissolution, etc.), so that the measured weight change measured comes only from the oxygen reacted,
5. The volume increase due to oxide formation occurs mainly normal to the sample surface, and thus 1µm of metal consumed yields 1.56µm of oxide, and
6. The amount of hydrogen in the oxide is negligible compared to the hydrogen content in the bulk.

Assumptions 1, 2 and 4 are generally verified by the measurement of oxide thickness and comparison to weight gain. Assumption 3 is valid as long as the hydrogen pick-up fraction is
small (for a 100% hydrogen pick-up the weight gain due to hydrogen will be equal to 12.5% of
the total weight gain). The concentration (wt.ppm) of hydrogen in the sample $C_H$ is given by the
following formula:

$$C_H = \frac{m_H^i + m_H^f}{m_s}$$  \hspace{1cm} (31)

where:

$m_s$ = final mass of the sample,

$m_H^i$ = initial mass of hydrogen in the sample,

$m_H^f$ = mass of H picked up by the sample during corrosion = $m_H^c = \frac{2N_0 f_H}{N_A} M_H$,

$f_H$ = total hydrogen pick-up fraction,

$N_A$ = Avogadro’s number,

$M_H$ = atomic mass of hydrogen atom,

$N_O$ = number of oxygen atoms = $\frac{m_O}{M_O} N_A = \frac{w_g}{M_O} N_A$ oxygen atoms,

$w_g$ = weight gain due to corrosion,

$M_O$ = atomic mass of oxygen atom, and

$m_O$ = mass of oxygen picked up by the sample during corrosion.

So finally:

$$m_H^c = \frac{2(m_s - m_s^i)f_H}{M_O} M_H \text{ grams}$$  \hspace{1cm} (32)

where:

$m_s^i$ = initial mass of the bare sample.

The initial mass of hydrogen in the sample is given by Equation 33:

$$m_H^i = c_H 10^{-6} m_s^i$$  \hspace{1cm} (33)

where:
$C_H^i$ = initial concentration of hydrogen in the sample (wt. ppm).

Hence:

$$C_H \times 10^{-6} = \frac{2(m_s - m_s^i) f_H M_H}{M_O} m_s + m_s^i C_H^i \times 10^{-6}$$  \hspace{1cm} (34)

In terms of the weight gain $w_o$ the total hydrogen pick-up fraction $f_H$ is:

$$f_H = \frac{10^{-6}(m_s C_H - m_s^i C_H^i)}{2\left(\frac{m_s - m_s^i}{M_O}\right) M_H}$$  \hspace{1cm} (35)

The total hydrogen pick-up fraction error is given by:

$$\Delta f_H = f_H \sqrt{A + \frac{B + C}{D}}$$  \hspace{1cm} (36)

where:

$$A = \frac{\Delta m_s^2 + \Delta m_s^i}{(m_s - m_s^i)^2},$$  \hspace{1cm} (37)

$$B = (m_s C_H)^2 \left(\frac{\Delta m_s^i}{m_s}\right)^2 + \left(\frac{\Delta C_H}{C_H}\right)^2,$$  \hspace{1cm} (38)

$$C = (m_s^i C_H^i)^2 \left(\frac{\Delta m_s^i}{m_s^i}\right)^2 + \left(\frac{\Delta C_H^i}{C_H^i}\right)^2,$$  \hspace{1cm} (39)

$$D = \left(m_s C_H - m_s^i C_H^i\right)^2.$$  \hspace{1cm} (40)

From Equation 35 it is also possible to calculate a theoretical hydrogen concentration from weight gain measurements and a given pick-up fraction. This could be useful if one wants to extrapolate the hydrogen concentration of a sample after long term exposure using the pick-up fraction determined for short term exposure. However, this assumes that the pick-up fraction does not vary with exposure time.
The instantaneous pick-up fraction \( f_{H}^{i} \), which is defined as the pick-up fraction between two different exposure times \( (t_1 \text{ and } t_2) \) can also be used. Its calculation can be very useful to quantify the variation of the pick-up fraction. However, because the calculation involves small differences in mass, the instantaneous pick-up fraction can significantly vary so that the numbers should be interpreted with caution.

\[
\begin{align*}
    f_{H}^{i} &= \frac{10^{-6}(m_{s}^{t_2}C_{H}^{t_2} - m_{s}^{t_1}C_{H}^{t_1})}{2 \left( \frac{m_{s}^{t_2} - m_{s}^{t_1}}{M_{O}} \right) M_{H}} \\
\end{align*}
\]

where:

\( m_{s}^{t_2} \) = sample mass at exposure time \( t_2 \) (g),

\( m_{s}^{t_1} \) = sample mass at exposure time \( t_1 \) (g),

\( C_{H}^{t_2} \) = hydrogen concentration in the sample at exposure time \( t_2 \) (wt. ppm), and

\( C_{H}^{t_1} \) = hydrogen concentration in the sample at exposure time \( t_1 \) (wt. ppm).

3.4. Hydrogen pick-up variation as a function of alloying elements determined by VHE

3.4.1. Pure zirconium sponge

Pure zirconium metal was first investigated. This alloy is defined as pure since no alloying element has been voluntarily added. However, even a very low level of acceptor or donor impurities in zirconium (such as iron and others) can dramatically change the corrosion behavior and possibly the hydrogen pick-up, as discussed in Chapter 1. The weight gain results for “pure” Zr are presented in Figure 3-2.
From Figure 3-2, it seems clear that the pure sponge Zirconium is not consistently protective. Either the corrosion weight gain takes off immediately (most common) or eventually goes into breakaway after an initially protective layer. This is why zirconium alloys were developed in the first place. However, one can notice that coupons behave in a more protective fashion than others, although any good explanations have explained this discrepancy among sister samples. It is possible that the concentration of impurities is different from sample to sample. Small differences in impurity concentrations among samples could explain why some samples are more protective than others (see Chapter 1). It is noted that “pure” Zr, in the instances when it has low corrosion rate at the beginning, (when the weight gain does not increase suddenly right at the start) has $n$ (defined in equation 10) varying between 0.20 and 0.25 [125]. The pick-up fractions of three different samples indicated in Figure 3-2 have been determined and the results are presented in Figure 3-3.
Typically “pure Zr” exhibits wide sample to sample variability, so that sister samples behave quite differently (e.g. at 14 days of corrosion one has gone into breakaway (3) – red circle - while another one is still protective (2)). In the protective regime (weight gain inferior to 20 mg/dm²) sample 1 and 2 show a pick-up fraction equal to 18%. The pick-up fraction between 7 and 14 days does not change, suggesting that the pick-up fraction is a constant (close to 20%) as long as the oxide is protective. The protectiveness of the oxide is confirmed in Figure 3-4 and 3-5-B since no cracks are detected in the oxide. However, once protectiveness is lost the pick-up fraction increases dramatically to exceed even 100%. According to our pick-up fraction definition this should be only possible if (i) there is oxide spallation (loss of oxide but the hydrogen remains in the metal), (ii) if the oxidation reaction is not the only source of hydrogen or (iii) if hydrogen released from corrosion reaction with other samples is available. Oxide spallation after breakaway is seen on Figure 3-6-A and B, so it is possible that pick-up fraction determinations after breakaway are not reliable. The oxide-metal interface is irregular, showing big dendrites, likely along the metal grain boundaries [126] as shown in Figure 3-5-A. Although the hydrogen pick-up fraction of sample #2 is the same as sample #1 (close to 20%), one can see on Figure 3-5-A that dendrites are starting to form on the metal grain boundaries. Figure 3-5-B confirms that the
oxide is still protective (no cracks or spallation are visible). Thus the single formation of dendrites is not apparently followed by an increase in hydrogen pick-up fraction so that dendrites are not necessarily easy paths for hydrogen uptake by the metal.

Figure 3-4: Pure zirconium corroded in 360°C water after 7 days of exposure and 15.1 mg/dm² weight gain (sample #1 in Figure 3-3) A) Polarized light image of cross-section [126], B) Backscattered SEM cross-sections micrographs (x8000), C) Backscattered SEM cross-sections micrographs (x16000) [14].
Figure 3-5: Pure zirconium corroded in 360°C water after 14 days of exposure and 16.3 mg/dm² weight gain (sample #2 in Figure 3-3) A) Polarized light image of cross sections [126] B) Secondary Electron SEM cross-sections micrographs [14].
Pure zirconium exhibits significant sample-to-sample variability so it is not a good reference material to compare other zirconium alloys with. On the other hand, Zircaloy-4 shows less variability, as shown in the next part.

### 3.4.2. Zr-Sn-Fe-Cr alloys (Zircaloy-4 based)

Several Zr-Sn-Fe-Cr alloys have been studied: Zr-1.3Sn-0.2Fe-0.1Cr (H) fully recrystallized sheet and Zr-1.45Sn-0.2Fe-0.1Cr recrystallized sheet and tubes. Only the weight gain of archived samples is represented in the case of Zr-1.45Sn-0.2Fe-0.1Cr sheet and tube because the standard deviations in their weight gain were lower than 1mg/dm². However, since the standard deviation for Zr-1.3Sn-0.2Fe-0.1Cr (H) weight gain was higher, the usual weight gain representation is used for this alloy. The weight gains of Zr-1.3Sn-0.2Fe-0.1Cr (H) samples are presented in Figures 3-7.

Figure 3-6: Pure zirconium corroded in 360°C water after 69.3 days of exposure and 51.6 mg/dm² weight gain (sample #2 in Figure 3-3): Secondary Electron SEM cross-sections micrographs.
The weight gains of Zr-1.45Sn-0.2Fe-0.1Cr (sheet and tube) are presented in Figure 3-8 as well as the weight gain of Zr-1.3Sn-0.2Fe-0.1Cr (H) sample #4 (see Figure 3-7) for comparison. The $n$ value for Zircaloy-4 is equal to 0.22, which is close to that of “pure” Zr [125].

A comparison of the alloys plotted in Figure 3-8, shows that the two Zircaloy-4 oxidation rates are approximately the same. However the first transition of Zr-1.45Sn-0.2Fe-0.1Cr sheet alloy happens the earliest and the one of Zr-1.3Sn-0.2Fe-0.1Cr (H) sample #4 happens the latest.

Figure 3-7: Weight gain for 16 archived samples of Zr-1.3Sn-0.2Fe-0.1Cr (H) sheets (red lozenges mean archived samples and red numbers corresponds to samples presented in Figure 3-9) in 360°C water [14].
The weight transition and time as well as the oxide thickness at transition are presented in Table 3-2.

Table 3-2: Weight gain and oxide thickness at transition for Zr-Sn-Fe-Cr alloys

<table>
<thead>
<tr>
<th>Alloys</th>
<th>Exposure time at breakaway (days)</th>
<th>Weight gain at breakaway (mg/dm²)</th>
<th>Oxide thickness at breakaway (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr-1.3Sn-0.2Fe-0.1Cr (H)</td>
<td>120</td>
<td>39.9</td>
<td>2.7</td>
</tr>
<tr>
<td>Zr-1.45Sn-0.2Fe-0.1Cr sheet</td>
<td>75</td>
<td>29.9</td>
<td>2.0</td>
</tr>
<tr>
<td>Zr-1.45Sn-0.2Fe-0.1Cr tube</td>
<td>105</td>
<td>35.8</td>
<td>2.4</td>
</tr>
</tbody>
</table>

The hydrogen pick-up fractions of Zr-Sn-Fe-Cr (H) alloy are presented in Figures 3-9, 3-10 and 3-11. The weight gain of Zr-1.3Sn-0.2Fe-0.1Cr (H) sample #9 is displayed in Figure 3-9 to show the general oxidation behavior of those samples. On Figure 3-10, one can notice that the hydrogen pick-up fractions of non-archived samples are also available, as a result of the use of CNPGAA to determine hydrogen content on these samples.
Figure 3-9: Total hydrogen pick-up fraction of Zircaloy-4: Zr-1.3Sn-0.2Fe-0.1Cr (H) (see Figure 3-7 for corresponding weight gains of archived samples) and weight gain of sample#9 (red lozenge means archived samples).

Figure 3-10: Total hydrogen pick-up fraction and weight gain of Zircaloy-4: Zr-1.45Sn-0.2Fe-0.1Cr sheet (red lozenges mean archived samples).
Unfortunately, as shown in Figure 3-12, no data are available before a weight gain of 15mg/dm$^2$, so that the early hydrogen pick-up behavior cannot be characterized in these samples.

In the case of Zr-1.45Sn-0.2Fe-0.1Cr alloys, in the pre-transition regime, the hydrogen pick-up fraction increases from 3% to approximately 6%. This increase being relatively small, we can conclude that Zr-1.45Sn-0.2Fe-0.1Cr alloys do not seem to pick-up more hydrogen until they reach a weight gain close to the weight gain transition value (see Table 3-2). The total hydrogen pick-up fraction of the sheet $f_H$ seems to increase close to the weight gain transition (approximately 30 mg/dm$^2$). The same trend is observed with the tube version of the same alloy showing an increase of $f_H$ just before the weight gain transition. However, instantaneous hydrogen pick-up fraction calculations should better reveal the changes in hydrogen pick-up behavior of these alloys. After their transitions, Zr-1.45Sn-0.2Fe-0.1Cr hydrogen pick-up fractions slowly increase from 6% to 15%. In the case of Zr-1.3Sn-0.2Fe-0.1Cr alloy, the scarcity of data makes it difficult to precisely analyze variations in hydrogen pick-up fraction. Compared
to Zr-1.45Sn-0.2Fe-0.1Cr alloys, it seems that the total hydrogen pick-up fraction is close to 15% at the beginning of corrosion and slowly decreases to reach approximately 9% before transition. After the first transition, it seems that its value is closer to the Zr-1.45Sn-0.2Fe-0.1Cr ones (close to 15%).

Figure 3-12: Hydrogen content in mg/dm² as a function of weight gain of Zircaloy-4 alloys.

The hydrogen pick-up varies in the pre-transition regime and increases in the weight gain transition region for every Zircaloy-4 based alloys studied. However, according to Figure 3-9, after the first transition, \( f_H \) remains at a constant value, between 15% and 20%. Subsequent transitions do not seem to affect \( f_H \), since a steady state has apparently been reached. If \( f_H \) depended on oxide microstructure, then it should show periodic variations and reproduce the same pattern from one transition to another since the growth of the protective barrier layer is
periodic, which apparently is not the case. However, in the overall hydrogen pick-up fraction plots, these periodic variations could be hidden and instantaneous hydrogen pick-up fraction should rather be considered. Thus, precise measurements of Zr-1.45Sn-0.2Fe-0.1Cr hydrogen pick-up fraction in the next transition regimes should yield a more detailed picture on the hydrogen pick-up fraction variations.

Close to the transition, the hydrogen pick-up seems to increase before the weight gain transition (see Figure 3-12). However, it has not been proven that this particular hydrogen pick-up fraction increase is related to the transition phenomenon. It is likely that these two phenomena (transition and hydrogen pick-up increase) are unrelated because:

- No significant increase of the hydrogen pick-up fraction is observed in subsequent transitions, and
- The hydrogen pick-up fraction increases also before breakaway and not only before transition (as shown later). However it should be noted that transition and breakaway might come from the same causes, the breakdown being a transition without recovering of protectiveness.

The hydrogen pick-up fraction of Zr-1.45Sn-0.2Fe-0.1Cr was precisely determined by performing measurements every 15 days. The fine measurement steps were particularly useful to calculate the instantaneous hydrogen pick-up fraction from a time \( t \) to a time \( t+15 \) days: \( f^i_{H} \), and to thoroughly quantify its variations with exposure time. Thus, it is possible to compare the instantaneous hydrogen pick-up fraction variation to the oxidation rate. These results are presented in Figure 3-13.
Figure 3-13: Weight gain (red=Zr-4 sheet and blue=Zr-4 tube) and instantaneous pick-up fraction using a 15-day step exposure time (red lozenges mean archived samples).
A significant increase in the instantaneous hydrogen pick-up fraction is observed around 30 mg/dm$^2$. This increase does not seem to be related to the weight gain transition. Indeed the transition in the tube sample occurs later than in the sheet sample, whereas the instantaneous hydrogen pick-up fraction spikes exactly at the same weight gain for the two different shapes. In the case of the sheet sample, this increase is masked by the transition since both events (weight gain transition and hydrogen pick-up increase) occur at the same time. This is not the case for the tube sample; the two events happen at different times and thus can be distinguished. Since the instantaneous pick-up fraction is quite sensitive to weight gain and hydrogen content variations, the previously observed variations could be due to small differences in behavior among sister samples. This is where CNPGAA is particularly useful (see Figure 3-14).

![Figure 3-14: Instantaneous pick-up fraction using Zr-4 sheet, comparison between sister samples and one CNPGAA coupon (red lozenges mean archived samples)]
The instantaneous pick-up fraction of Z4S2 coupon (red “x”) was determined every 30 days using CNPGAA and compared it to instantaneous pick-up fraction in the sister samples (green “x”). In Figure 3-14, the previously observed increase of $f_H^I$ in sister samples just before the weight gain transition is also observed on a given sample (red “x” in Figure 3-14). In conclusion, the hydrogen pick-up fraction increase is not an artifact due to the use of sister samples, since it is also observed on a given sample. Thus measurements on the same coupons using CNPGAA corroborate the previous observations (see Figure 3-14).

3.4.3. Binary alloys: Zr-0.5Cu sheet

The effect of copper has been investigated using binary Zr-Cu alloys. The weight gain is presented on Figure 3-15.

![Figure 3-15: Weight gain for 16 archived samples of Zr-0.5Cu sheet (red lozenges mean archived samples and red numbers corresponds to samples presented in Figure 3-16) in 360°C water](image-url)

In this alloy system also sister samples show wide behavior variation, although less than in pure Zr. Some samples are still protective while others have undergone the breakaway. The n
value for Zr-0.5Cu is equal to 0.17, which is close to that in “pure” Zr or Zircaloy-4 [125]. Some of these samples have been run through VHE to investigate their hydrogen pick-up behavior. Their weight gains and hydrogen pick-up are presented in Figure 3-16.

Figure 3-16: Weight gain and hydrogen pick-up fraction of 7 Zr-0.5Cu sheets archived samples chosen for hydrogen pick-up investigation (numbers are related to Figure 3-15)

On Figure 3-16, some of the archived samples (#2, #3 and #4, indicated by red arrows) have undergone early breakaway. These samples show higher hydrogen pick-up in general. However not all of them show the same hydrogen pick-up fraction after breakaway, such that their hydrogen pick-up fraction varies between 40 and 60%. The samples that are still protective have a higher pick-up fraction (around 23%) than Zircaloy-4 (around 15% in the post transition regime). No significant change is seen in the hydrogen pick-up fractions with exposure time as long as the oxide is protective.
3.4.4. Binary alloys: Zr-Cr sheets

Samples with two different mass fractions of chromium have been investigated in this research: 0.5Cr and 1.0Cr. The weight gains for Zr-0.5Cr samples are shown in Figure 3-17.

![Figure 3-17](image)

Figure 3-17: Weight gain for 16 archived samples of Zr-0.5Cr sheets (red lozenges account for archived samples and red numbers corresponds to samples presented in Figure 3-18) in 360°C water.

One can notice again that although the addition of chromium delays the breakaway compared to pure zirconium it does not promote protective oxide growth. After approximately 30 days for Zr-0.5Cr the coupons lose their protective behavior. It was not possible to determine the $n$ value for Zr-0.5Cr alloy because of its non-protective behavior from the beginning of the corrosion test. The hydrogen pick-up fractions of seven archived samples are presented in Figure 3-19 and 3-21.
The addition of chromium in Zr-0.5Cr appears to decrease the hydrogen pick-up fraction even after breakaway as compared to Zircaloy-4. The sample that is still protective (sample #3) shows a hydrogen pick-up fraction close to 10%. Even the two coupons (1 and 2) that have undergone an early breakaway do not show a significant increase in their hydrogen pick-up fraction. The SEM images of these samples are presented in Figures 3-19 and 3-20.

Figure 3-18: Weight gain and hydrogen pick-up fraction of three Zr-0.5Cr sheets archived samples chosen for hydrogen pick-up investigation (red numbers are related to Figure 3-17)
Although showing unstable oxide growth from the onset of corrosion, the oxide layers formed in Zr-0.5Cr did not show the dendrite-type structures seen at the oxide metal interface in “pure” Zr samples nor did they show macroscopic spallation of the oxide. This means that the oxide growth has, to some extent, been stabilized by the presence of Cr, although not enough to prevent corrosion weight gain breakaway. Thus, oxide growth in this sample is more or less

Figure 3-19: SEM cross-section micrographs in backscattered mode of Zr-0.5Cr sample#1 corroded in 360°C for 14 days a) 4000x and b) 8000x [14]

Figure 3-20: SEM cross-section micrographs in backscattered mode of Zr-0.5Cr sample#2 corroded in 360°C for 21 days
stable, although non-protective. This is reflected in the steady linear increase of corrosion weight gain with time (see Figure 3-17). Extensive cracking is observed in the Zr-0.5Cr oxide of samples #1 and #2, consistent with the high weight gain exhibited by this alloy. The metal/oxide interface shows some undulations, or sections of the oxide front that have advanced further into the metal, or less, but the differences are small, when compared to those seen in the “pure” Zr samples. In the sample #2 oxide micrograph (Figure 3-20), veins are visible perpendicular to the oxide, going from the oxide/water to oxide/metal interface. These oxide veins are totally free of cracks. It seems that the distribution of veins is not homogeneous throughout the oxide. Indeed, more veins are seen close to the oxide/water interface and, as they go deeper in the oxide, the veins gathered to form a single major one. Then, these major veins appear to be correlated to a slower oxidation of the oxide at the oxide/metal interface. These effects were not visible in “pure” zirconium. The veins are likely caused by the cracking pattern undulation.

The hydrogen pick-up fraction of Zr-0.5Cr remains low (~10%) even after the breakaway. Comparing these results to pure zirconium sponge, it appears that the increase in hydrogen pick-up is not due to the breakaway in itself but is either related to the presence of cracked dendrites (see Figure 3-6) or to the spallation of the oxide observed in ”pure” Zr. The chromium has then two effects on hydrogen pick-up fraction:

- 0.5%Cr reduces the hydrogen pick-up fraction in the pre-breakaway regime to close to 10%, and

- 0.5%Cr prevents the formation of dendrites or spallation of the oxide at breakaway, thus avoiding a dramatic increase of hydrogen pick-up fraction.

The weight gains for Zr-1.0Cr samples are shown in Figure 3-21.
In the case of Zr-1.0Cr, it seems that the range of variation of different samples is smaller than in Zr-0.5Cr. After approximately 60 days for Zr-1.0Cr (and 30 days for Zr-0.5Cr), the coupons lose their protectiveness. Thus, it seems that the addition of chromium from 0.5% to 1.0% delays a bit the onset of breakaway. The $n$ value for Zr-1.0Cr is equal to 0.21, similar to that of “pure” Zr or Zircaloy-4 [125].
Figure 3-22: Weight gain and hydrogen pick-up fraction of four Zr-1.0Cr sheet archived samples chosen for hydrogen pick-up investigation

Figure 3-22, shows the corrosion weight gain and hydrogen pick-up fraction for four Zr-1.0Cr samples. The hydrogen pick-up fraction for the two samples in the pre-breakaway regime is approximately 10%, suggesting that the addition of chromium reduces the hydrogen pick-up fraction in the pre-breakaway regime. The beneficial effect of the chromium (at this low concentration level) on $f_H$ is confirmed by Klepfer et al. [68]. No difference in the pre-breakaway regime is seen between 0.5%Cr and 1.0%Cr, $f_H$ remaining equal to approximately 10%. However, in the post-breakaway regime, the $f_H$ of Zr-1.0Cr seems to increase to a value higher than 20%. SEM images of the oxide cross sections are presented in Figure 3-23.
Figure 3-23: SEM cross-section micrographs in backscattered mode of Zr-1.0Cr, sample #3 corroded in 360°C water for 55 days (weight gain = 41.9mg/dm²): A) 4000x, B) 11300x

Figure 3-23 shows post-breakaway oxide, with lateral cracking and exhibits an undulated or serrated metal/oxide interface. The roughness of the interface seems more significant compared to other breakaway oxides such as Zr-0.5Cr, but does not show the same type of dendrite-like structures associated with the unstable oxide growth found on “pure” Zr samples. A small portion of the oxide near the oxide/metal interface, maybe about 1µm thick, is also crack-free. However, this time, the hydrogen pick-up fraction increases to 20% after the breakaway. To highlight this difference between the two alloys, the hydrogen content is plotted as a function of the weight gain for the two alloys in Figure 3-24.
At comparable weight gains (close to 50mg/dm$^2$), Zr-1.0Cr picks up more hydrogen (~20%) compared to Zr-0.5Cr (~10%). At higher weight gains, it is possible that the two alloys behave in the same manner such that $f_H$ decreases at higher weight gain. The solubility limit of chromium being low, it is possible that ZrCr$_2$ precipitates play a role. Zr-1.0Cr contains a higher density of precipitates [16] and if ZrCr$_2$ precipitates are supposed to be a window for hydrogen ingress into the oxide [103], this could explain the differences in $f_H$ observed between Zr-0.5Cr and Zr-1.0Cr.

Figure 3-24: Hydrogen content (mg/dm$^2$) of Zr-0.5Cr and Zr-1.0Cr as a function of weight gain (mg/dm$^2$)
### 3.4.5. Binary alloys: Zr-Nb

Several niobium alloys have been investigated: Zr-0.2Nb sheet, Zr-0.4Nb sheet, Zr-1.5Nb sheet, Zr-2.5Nb sheet and Zr-2.5Nb tube. The tube is a quenched alloy whereas the sheets have been aged and are fully recrystallized. The weight gain results are presented in Figure 3-25.

![Figure 3-25: Weight gain of different niobium alloys (red lozenges mean archived samples) corroded in 360°C water](image)

The corrosion kinetics vary with the weight percent of niobium, especially in the region where the Nb percentage is <0.4% (where Nb is in solid solution). Since below 0.4% Nb is in solid solution, the influence is that the amount of niobium as a solid solution element (as opposed to a precipitate) affects the corrosion kinetics (increases). However beyond the solubility limit little effect of niobium concentration on corrosion kinetics is observed. It appears that the tube...
shape slightly increases the oxidation kinetics, relative to that of sheet. The $n$ value for the different Nb contents is shown on Table 3-3.

Table 3-3: $n$ value for different Nb contents in Zr-Nb alloys [14]

<table>
<thead>
<tr>
<th>Alloys</th>
<th>$n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr-0.2Nb</td>
<td>0.43</td>
</tr>
<tr>
<td>Zr-0.4Nb</td>
<td>0.52</td>
</tr>
<tr>
<td>Zr-1.5Nb</td>
<td>0.44</td>
</tr>
<tr>
<td>Zr-2.5Nb (RX)</td>
<td>0.40</td>
</tr>
</tbody>
</table>

From Table 3-3, we can conclude that, for Zr-Nb alloys, in general $n$ is closer to parabolic than in Zircaloy-4. If we looked at the variations of $n$ more precisely, $n$ increases as long as we increase the amount of Nb in solid solution, reaching parabolic behavior at the solubility limit. Once we reached the solubility limit, $n$ starts decreasing but stays higher compared to “pure” Zr or Zircaloy-4. The hydrogen pick-up fraction of Zr-2.5Nb tube as function of exposure time has been carefully measured at 15 day time intervals on sister samples, as shown in Figure 3-26.

The pick-up fraction is low compared to Zircaloy-4 at equivalent exposure time and is approximately equal to 6%. However, the exposure time is comparatively low and we cannot address the effect of transition on $f_H$ in this particular alloy. The beneficial effect of niobium alloying in the pre-transition regime is evident.

To compare the different niobium alloys, the hydrogen content is plotted as a function of weight gain in Figure 3-27.
Figure 3-26: Pick-up fraction and weight gain as function of exposure time for Zr-2.5Nb tube corroded in 360°C water (red lozenges mean archived samples)

Figure 3-27: Hydrogen content as function of weight gain for different niobium alloys
Figure 3-27 shows that the hydrogen uptake is lower for the β quenched alloy, as compared to the fully recrystallized sheet alloys. It is rather difficult to determine if this observation is an effect of niobium content, metallurgical state or exposure time since the archived samples do not have the same weight gains. However, a of hydrogen uptake (Figure 3-27) in the niobium β quenched alloys was also reported by Choo et al. [78] and by McDougall et al. [88]. Indeed, after a quench from the β phase (~1000°C), a martensitic-type structure develops, the β phase having transformed to the close-packed hexagonal martensitic α’ phase. This martensitic phase is known to be supersaturated in niobium [18, 127]. The most stable oxidation state of Nb in the matrix oxide of the Zr-Nb binary alloy is known to be Nb⁵⁺ [52]. As the aliovalent cation is substituted for Zr⁴⁺ in the oxide structure, the concentration of quasi-free electrons in the matrix oxide is increased. Indeed, in the case of ZrO₂ doped with Nb₂O₅, the Nb₂Zr centers can be compensated with electrons (the point in the notation means that the Nb⁵⁺ ion has an extra positive charge compared to the relative oxide cation Zr⁴⁺). Since the role of the compensating electronic defect is to balance the abnormal charge of the impurity center, they will have opposite charges, so that there is the possibility of electrostatic attraction. If the electron is strongly bound to the Nb₂Zr center, it will not be available to contribute to the electron conductivity of the doped zirconia. However, Nb²Zr centers are essentially all ionized at room temperature and the free electron concentration is approximately equal to the Nb²Zr concentration in solid solution [128]. The dissolution of Nb₂O₅ in ZrO₂ is given by Equation 44.

$$2\text{Nb}_2\text{O}_5 \overset{4\text{ZrO}_2}{\longrightarrow} 4\text{Nb}^\ast_{2\text{Zr}} + 8\text{O}_0 + \text{O}_2 + 4\text{e}^\prime$$ (44)

In the case of donor impurities such as Nb⁵⁺, the positively charged impurity centers can be compensated by interstitial oxygen, Zr vacancies, or electrons. Interstitial anions are often unlikely and Zr vacancies are highly charged. However, the conduction band, which is derived
from the empty Zr 3d states, should be quite receptive to electrons, and they are a reasonable choice for the compensating defect.

The greater availability of electrons would result in an increased rate of cathodic reaction at the oxide/water interface and hence a predominance of the evolution of hydrogen gas (Equation 8) over hydrogen absorption through the oxide and into the metal. As the electron concentration increases, the hydrogen absorption relative to the total reduced hydrogen (hydrogen pick-up fraction) decreases. Compared to recrystallized alloys (such as the sheet alloys), the Nb content in solid solution is higher due to the supersaturation induced by the β quench.

Considering the lower Nb content in the α-Zr matrix induced by the aging treatment (the solubility limit being close to 0.4 wt% at 360°C), the higher hydrogen pick-up fraction of aged alloys relative to the quenched alloys could also be explained based upon the aliovalent effects of Nb. However, the hydrogen pick-up fraction of these alloys should be compared at the same weight gain to draw any conclusions.

3.4.6. Ternary alloys: Zr-Fe-Cr sheets

Four different compositions of the alloys Zr-Fe-Cr: Zr-0.2Fe-0.1Cr (L), Zr-0.2Fe-0.1Cr (H), Zr-0.4Fe-0.2Cr (L), Zr-0.4Fe-0.2Cr (H) were studied. The (L) and (H) represent two different processes of hot rolling and vacuum annealing temperatures: (L) =580°C and (H) =720°C. In Zr-Fe-Cr alloys, changes in corrosion behavior has been associated with the size of the second phase precipitates (Zr(Cr, Fe)₂) and the alloying element volume fraction have an impact on corrosion resistance [96]. The (H) alloys have larger precipitates (diameter ≈ 110nm) than (L) alloys (diameter ≈ 40nm) [14]. The weight gains as a function of exposure time of these four alloys are illustrated in Figures 3-28, 3-29, 3-30, 3-31:
Figure 3-28: Weight gain for 16 archived samples of Zr-0.2Fe-0.1Cr (L) sheets (red lozenges account for archived samples and red numbers corresponds to samples presented in Figure 3-32) in 360°C water

Figure 3-29: Weight gain for 16 archived samples of Zr-0.2Fe-0.1Cr (H) sheets (red lozenges account for archived samples and red numbers corresponds to samples presented in Figure 3-33) in 360°C water
The $n$ value for these alloys is constant and equal to 0.21 [14]. As explained in Chapter 2, for a constant Fe/Cr ratio = 2 (similar to the ratios found in the Zircaloy-4), the two different types of alloys in this series were processed at 580°C and 720°C. The precipitate size is different for each processing temperature. The volume fraction of precipitates increases as the Fe and Cr content increases. The plot of weight gain, shown in Figure 3-28 for Zr-0.2Fe-0.1Cr (L), shows a marked increase in corrosion rate after 200 days of exposure, indicating a loss of protective
character in the oxide layer. The plot of the weight gain for Zr-0.2Fe-0.1Cr (H), in Figure 3-29, shows a slight increase in corrosion rate between 300 and 400 days, suggesting the upcoming onset of a transition or breakaway. The plots for Zr-0.4Fe-0.2Cr (L) and Zr-0.4Fe-0.2Cr (H) (Figures 3-30 and 3-31) show consistently low weight gains and corrosion rates up to the full length of the exposure time. Little variability of the corrosion behavior among sister samples is seen in ZrFeCr alloys.

Comparing Figures 3-28, 3-29, 3-30 and 3-31 it seems that initially (<150 days), the corrosion rates for all four alloys were essentially the same. Zr-0.2Fe-0.1Cr (L) (low alloying content and low processing temperature) exhibited an acceleration of corrosion around 200 days, and alloy Zr-0.2Fe-0.1Cr (H) showed signs of the same after 300 days. Such behavior suggests that the higher alloying element content (0.6% in Zr-0.4Fe-0.2Cr versus 0.3% in Zr-0.2Fe-0.1Cr), which resulted in a higher precipitate volume fraction, had a positive impact on the oxide protectiveness.

This could indicate a anodic protection role of the SPP’s, as previously proposed by Barberis et al. [129]. Thus Zr-0.2Fe-0.1Cr (L) has the lowest corrosion resistance and Zr-0.4Fe-0.2Cr (H) the highest. The comparison of Zr-0.4Fe-0.2Cr (L) and Zr-0.4Fe-0.2Cr (H) shows little effect of precipitate size (or processing temperature) on oxide protectiveness; however, in alloys Zr-0.2Fe-0.1Cr (L) and Zr-0.2Fe-0.1Cr (H), a higher processing temperature was found to be beneficial.

The effect of precipitate size is more clearly seen in the low alloying content samples, in which the breakaway happens earlier for small precipitate sizes.

The total hydrogen pick-up fraction of these alloys is presented in Figure 3-32, 3-33, 3-34 and 3-35.
Figure 3-32: Total hydrogen pick-up fraction and weight gain of Zr-0.2Fe-0.1Cr (L) as a function of exposure time.

Figure 3-33: Total hydrogen pick-up fraction and weight gain of Zr-0.2Fe-0.1Cr (H) as a function of exposure time.
Figure 3-34: Total hydrogen pick-up fraction and weight gain of Zr-0.4Fe-0.2Cr (L) as a function of exposure time

Figure 3-35: Total hydrogen pick-up fraction and weight gain of Zr-0.4Fe-0.2Cr (H) as a function of exposure time
These alloys having different oxidation kinetics, their hydrogen content was plotted as a function of weight gain in Figure 3-36:

Figure 3-36: Hydrogen content (mg/dm$^2$) as a function of weight gains for Zr-Fe-Cr alloys

All these alloys show similar evolution of $f_H$. At the start of the corrosion reaction, $f_H$ is approximately 20% until at a weight gain approximately equal to 21 mg/dm$^2$ (or 1.4 µm oxide thickness). Then, the total hydrogen pick-up fraction drops to values close to 10%. The alloys do
not seem to pick-up more hydrogen until they reach a weight gain close to the breakaway value.

This value varies among the different alloys. The values of weight gains and oxide thickness at breakaway are presented in Table 3-4.

Table 3-4: Weight gain and critical oxide thickness for protective behavior for Zr-Fe-Cr alloys

<table>
<thead>
<tr>
<th>Alloys</th>
<th>Exposure time (days)</th>
<th>Weight gain (mg/dm²)</th>
<th>Oxide thickness (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr-0.2Fe-0.1Cr (L)</td>
<td>190</td>
<td>32.5</td>
<td>2</td>
</tr>
<tr>
<td>Zr-0.2Fe-0.1Cr (H)</td>
<td>240</td>
<td>38</td>
<td>2.6</td>
</tr>
<tr>
<td>Zr-0.4Fe-0.2Cr (L)</td>
<td>465</td>
<td>&gt;51</td>
<td>&gt;3.4</td>
</tr>
<tr>
<td>Zr-0.4Fe-0.2Cr (H)</td>
<td>493</td>
<td>&gt;48</td>
<td>&gt;3.2</td>
</tr>
</tbody>
</table>

Compared to Table 3-2, it seems that adding 1.3Sn to Zr-0.2Fe-0.1Cr reduces the transition time (if we suppose that the breakaway of Zr-0.2Fe-0.1Cr (H) and the transition of Zr-1.3Sn-0.2Fe-0.1Cr (H) are comparable). In these experiments, Sn is associated with the occurrence of the oxide transition (loss of protectiveness followed by recovery), since no transition was seen on samples without Sn. Takeda [44] and Barberis [130] suspected that Sn would play a role by either stabilizing the tetragonal ZrO₂ layer close to the oxide/metal interface (acting as a barrier to oxygen diffusion) or by changing the electrical properties of the oxide layer and thus the electrical conductivity.

Before breakaway, f_H increases again to value higher than 20%. Unfortunately, all the alloys did not reach the breakaway before the corrosion tests were stopped. From the results of Zr-0.2Fe-0.1Cr (L) alloy appear to show that after breakaway, f_H has a value of 25%. This effect of breakaway on f_H was also observed on Zr-Cr binary alloys. Although some scatter in f_H is observed near breakaway, it is clear that f_H increases before breakaway. The hydrogen pick-up fraction (and thus the hydrogen concentration) is seen to increase close to but before the breakaway (between 40 and 50 mg/dm² or between 2.7µm and 3.4 µm oxide thickness), as previously seen on Zircaloy-4. However, according to the weight gain curves (Figs 3-30 and 3-
31) the samples are not at the transition yet. Thus, the hydrogen pick-up fraction increase occurs

before the weight gain transition.

There are only three different ways to increase the hydrogen content in a sample:

1) $f_H$ increases, which means that for the same degree of oxidation, more hydrogen is
picked up. This is characterized by a constant oxidation rate but an increase in $f_H$.

2) The oxidation rate increases which means that there is more oxidation reaction although
$f_H$ is constant. Thus more hydrogen is picked-up by the metal. This is characterized by a
constant $f_H$ but an increase in oxidation rate, or

3) Additional sources of hydrogen become available in addition to the oxidation of the
zirconium alloy sample.

From the different figures presented here, for ZrFeCr alloys that have not gone into
breakaway, we are in the Case 1) where the oxidation rate is constant between 40mg/dm$^2$ and
50mg/dm$^2$ but the hydrogen concentration increases. Thus, it is $f_H$ that increases (see Figure 3-
36). After breakaway the hydrogen pick-up fraction in Zr-0.2Fe-0.1Cr (L) alloy stays constant at
25% but the corrosion rate increases, and we are in Case 2).

From Figure 3-36, it is not easy to characterize the hydrogen pick-up fraction as function
of precipitate size or volume fraction. It seems that as the precipitates sizes decrease, the
$f_H$ increase just before the transition is more significant. The volume fraction apparently does not
play a major role in hydrogen pick-up, since Zr-0.2Fe-0.1Cr (H) and Zr-0.4Fe-0.2Cr (H) show
similar hydrogen pick-up behavior. The effect of precipitate size and precipitate volume fraction
on corrosion behavior and hydrogen pick-up fraction is summarized in Table 3-5.
In conclusion, larger Zr(Cr,Fe)$_2$ precipitates somehow cause the increase in hydrogen pick-up fraction before breakaway to be less significant. In a future work, it will be interesting to see if these effects are also seen in Zircaloy-4 based alloys.

It is known that the intermetallic precipitates present in Zr alloys are more noble than the zirconium matrix and enter the oxide as metallic phases [129, 131]. The aliovalent effect of iron cation in solid solution could explain why bigger Zr(Cr,Fe)$_2$ precipitates decrease the magnitude of the increase of hydrogen pick-up fraction. Indeed, in the case of an acceptor impurity (such as iron), oxygen vacancies are the most probable compensating defect induced by the lower positive charge of iron cation (see equation 45 in the case of Fe$^{3+}$). Indeed the acceptor content can be charge compensated by Zr interstitials, oxygen vacancies or holes. Since the valence band is not receptive to holes, it is more likely that one of the ionic defects is preferred. The Schottky defect being the intrinsic ionic defect in ZrO$_2$, oxygen vacancies are expected to be produced to counter balance acceptor aliovalent cations.

$$\text{Fe}_2\text{O}_3 + 2\text{ZrO}_2 \rightarrow 2\text{Fe}_{2zr} + 3\text{O}_\text{O} + V_{O}^\ast$$

(45)

The notation Fe$'_{Zr}$ designates an iron ion (Fe$^{3+}$) at the oxide cation position which has an excess negative charge compare to the cation of the oxide (Zr$^{4+}$). So in the impurity-controlled ionic region, charge neutrality does not imply electrons but anion vacancies. Since the anion vacancy concentration is fixed by the iron cation content, the electron concentration decreases closer to the water/oxide interface where the oxygen activity is higher. Thus, less hydrogen can recombine with electrons and more hydrogen will be picked-up. Bigger precipitates are supposed to oxidize

<table>
<thead>
<tr>
<th>Corrosion Behavior</th>
<th>Precipitate size</th>
<th>Precipitate volume fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen pick-up fraction</td>
<td>significant</td>
<td>negligible</td>
</tr>
</tbody>
</table>

Table 3-5: Effect of Zr(Cr,Fe)$_2$ precipitate size and Zr(Cr,Fe)$_2$ precipitate volume fraction on corrosion behavior and hydrogen pick-up fraction for ZrFeCr alloys.
further away from the oxide/metal interface than smaller ones [107], so the effect of iron on hydrogen pick-up could be less pronounced for alloys with bigger precipitates. However, the decrease in pick-up fraction after 21 mg/dm\(^2\) could not be explained by this model. This model considers the effect of Fe in solid solution and not in precipitates. The solubility limit of iron plus chromium in the \(\alpha\text{Zr}\) matrix has been reported to be 180 wt.ppm according to the phase diagram (see Chapter 1). However, the Fe concentration in Zircaloy-4 in solid solution has been measured using synchrotron radiation microprobe X-Ray fluorescence and is equal to 290 wt.ppm (0.029Fe\%)[132]. The high concentration of Fe in the matrix compared to the TSS in the pure metal could be attributed to the possibility that the alloys are not fully in equilibrium or that the alloy TSS is higher than in the pure metal. Thus more iron in solid solution could be available to affect the electrical conductivity of the oxide.

### 3.4.7. Ternary alloys: Zr-Nb-Cu

The hydrogen pick-up fraction in Zr-2.5Nb-0.5Cu tube has been investigated. The weight gain of Zr-2.5Nb-0.5Cu quenched tube is plotted in Figure 3-37 along with Zr-2.5Nb quenched tube and Zr-0.5Cu recrystallized sheet.
From Figure 3-37, it seems that the addition of copper into Zr-2.5Nb decreases the oxidation rate. Also, at first sight, it seems that niobium has little effect on the oxidation kinetics. However, one should not forget that the Zr-Cu sister samples do not behave equally (Figure 3-15) and the weight gain curve presented here is for the samples that have not undergone an early breakaway. These discrepancies among samples have not been noticed in Zr-2.5Nb-0.5Cu (and in Zr-2.5Nb), which could mean that niobium addition homogenized the corrosion kinetics among the samples. In order to compare their hydrogen pick-up fractions, their hydrogen contents (in mg/dm²) as a function of their weight gains were plotted in Figure 3-38.

Figure 3-37: Weight gain for Zr-2.5Nb tube, Zr-0.5Cu sheet and Zr-2.5Nb-0.5Cu tube (red lozenges mean archived samples) in 360°C water.
The beneficial effect of niobium on hydrogen pick-up fraction is easily observed in Figure 3-38 when comparing Zr-0.5Cu to Zr-2.5Nb-0.5Cu tube. Once again the aliovalent effect of Nb cation in solid solution of the matrix oxide could explain the lower hydrogen pick-up of Zr-Nb and Zr-Nb-Cu alloys. Zr-2.5Nb tube appears to pick-up less hydrogen than Zr-2.5Nb-0.5Cu tube. This could be due again to the aliovalent cation effect copper. The copper sub-cation would behave the same way as the iron sub-cation in solid solution. Thus, the addition of copper results in a decrease in electron concentration and a consequent higher hydrogen pick-up. It is possible that the different sub-cations present in Zr-Nb-Cu, Nb^{5+} (donor) and Cu^{2+} (acceptor), will compensate each other. This is why it is observed that $f_H^{Zr-2.5Nb} < f_H^{Zr-2.5Nb-0.5Cu} < f_H^{Zr-0.5Cu}$.
3.4.8. Quaternary alloys: Zr-Nb-Sn-Fe alloys (ZIRLO based)

Finally, various ZIRLO-based alloys were studied ZIRLO (Zr-1.0Nb-1.0Sn-0.1Fe) sheet and tube, Zr-1.0Nb-0.4Sn-0.4Fe sheet, Zr-1.0Nb-1.0Sn-0.1Fe sheet and Zr-1.0Nb-0.6Sn-0.4Fe sheet. The weight gains of the archived samples are plotted in Figure 3-39.

![Weight gain as a function of exposure time of Zr-Nb-Sn-Fe alloys (red lozenges mean archived samples)](image)

The weight gain transition values of the different ZIRLO based alloys are presented in Table 3-6.

Zr-1.0Nb-0.6Sn-0.4Fe and Zr-1.0Nb-1.0Sn-0.1Fe sheets follow exactly the same weight gain kinetics (transition around 25 mg/dm²). Zr-1.0Nb-0.4Sn-0.4Fe sheet has undergone a later transition (at approximately 30 mg/dm²). ZIRLO sheet (Zr-1.0Nb-1.0Sn-0.1Fe) has also
undergone a later transition (at approximately 35 mg/dm²). Finally, ZIRLO tube (Zr-1.0Nb-1.0Sn-0.1Fe) has undergone the latest transition (around 45 mg/dm²).

Table 3-6: Weight gain and critical oxide thickness for protective behavior for Zr-Nb-Sn-Fe alloys

<table>
<thead>
<tr>
<th>Alloys</th>
<th>Exposure time (days)</th>
<th>Weight gain (mg/dm²)</th>
<th>Oxide thickness (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZIRLO sheet</td>
<td>94</td>
<td>38.5</td>
<td>2.6</td>
</tr>
<tr>
<td>ZIRLO tube</td>
<td>120</td>
<td>45</td>
<td>2.4</td>
</tr>
<tr>
<td>Zr-1.0Nb-1.0Sn-0.1Fe</td>
<td>45</td>
<td>25</td>
<td>1.6</td>
</tr>
<tr>
<td>Zr-1.0Nb-0.4Sn-0.4Fe</td>
<td>75</td>
<td>30.5</td>
<td>2.1</td>
</tr>
<tr>
<td>Zr-1.0Nb-0.6Sn-0.4Fe</td>
<td>45</td>
<td>25.5</td>
<td>1.7</td>
</tr>
</tbody>
</table>

The hydrogen pick-up of ZIRLO sheet is presented in Figures 3-40 (sheet) and 3-41 (tube).
In Figures 3-40 and 3-41, it is again observed that $f_H$ increases before the weight gain transition. For the ZIRLO sheet alloy (Figure 3-40), $f_H$ increases from 5% to more than 10% at approximately 32 mg/dm$^2$. At the transition the hydrogen pick-up fraction does not evolve and remains constant. Since a similar effect has been noticed on Zircaloy-4 and ZrFeCr alloys, it seems unlikely that this increase is related to the oxidation of precipitates. The ZIRLO tube hydrogen pick-up fraction behaves the same way as ZIRLO sheet (see Figure 3-41), although, as we have observed, the weight gain transition was delayed for the tube shape (120 days compared to 94 days for sheet samples). However, as in the case for Zircaloy-4, $f_H$ increase is observed at the same weight gain (between 30 mg/dm$^2$ and 35 mg/dm$^2$) for both tube and sheet samples. This

Figure 3-41: Total hydrogen pick-up and weight gain of ZIRLO tube (red lozenges mean archived samples)
is another observation that leads to assume that this increase in $f_H$ may not be related to the weight gain transition.

This particular increase is well observed on Figure 3-42, where the instantaneous pick-up fraction of ZIRLO sheet and tubes are plotted along with their weight gains.
Figure 3-42: Weight gain (red=ZIRLO sheet and blue=ZIRLO tube) and instantaneous pick-up fraction using a 15 day-step (red lozenges mean archived samples)
The increase in hydrogen pick-up fraction is very well localized, occurring before the weight gain transition at 70 days of exposure at a weight gain of approximately 34 mg/dm$^2$. The sheet and tube shapes show the same evolution of $f^i_H$, although their weight gain transitions do not happen at the same exposure time.

However, these variations could be due to spreading of the results induced by the use of sister samples. Few measurements have been done using CNPGAA due to a premature shut down of the beam line, but CNPGAA results confirm the behavior observed on ZIRLO samples (see Figure 3-43).

Figure 3-43: Instantaneous pick-up fraction using ZIRLO sheet, comparison between sister samples and two CNPGAA coupons (red lozenges mean archived samples)
The instantaneous pick-up fraction of ZLS1 and ZLS2 coupons (blue and red “x”) were determined every 30 days using CNPGAA and we compared it to the sister samples instantaneous pick-up fraction (green). In conclusion, from Figure 3-43, the hydrogen pick-up fraction increase is not an artifact due to the use of sister samples.

### 3.5. Summary of the results

The results presented in this chapter are summarized in the following:

Cold Neutron Prompt Gamma Activation Analysis technique is a non-destructive technique, which can accurately and precisely detect low level of hydrogen concentration in various zirconium alloys (as low as 5 wt.ppm). The experimental error is approximately equal to ±1 wt.ppm, lower than usual destructive techniques such as Vacuum Hot Extraction. The examination of the evolution of hydrogen content among the different samples allows us to conclude that CNPGAA measurement does not alter the corrosion process and hydriding of zirconium samples. This makes CNPGAA one of the most powerful non-destructive techniques to detect hydrogen in zirconium alloys.

The addition of copper increases $f_H$, either in binary alloys (Zr-0.5Cu) or in ternary alloys such as Zr-0.5Nb-0.5Cu (compared to Zr-2.5Nb). It is possible that copper, as an acceptor impurity, would decrease the equilibrium concentration of electrons in the oxide scale (see equation 45 in the case of iron). Thus, fewer electrons would be available for the cathodic reaction at the oxide/water interface leading to a possible diffusion of protons in the oxide layer increasing $f_H$.

The addition of Nb (in binary Zr-Nb alloys) decreases $f_H$ compared to Zircaloy-4 (at least in the pre-transition regime). At the difference of Cu, Nb is a donor impurity so that it increases the concentration of electrons in the oxide (see equation 44). Thus, more electrons are available at
the oxide/water interface to recombine with protons formed by the dissociation of water molecules. This process will result in a smaller $f_H$ observed in Zr-Nb alloys. This effect of donor impurities is confirmed by the fact that a Zr-2.5Nb β-quenched alloy, with a possible super saturation of Nb in solid solution, shows a lower $f_H$ compared to fully recrystallized Zr-2.5Nb alloy. Considering the lower Nb content in the α-Zr matrix induced by the annealing treatment (the solubility limit being close to 0.4wt%), the higher $f_H$ of aged alloys relative to the quenched alloys could also be explained based upon the aliovalent effects of Nb.

In the pre-transition regime, $f_H$ of Zircaloy-4 and ZIRLO alloys are approximately equal to 5% and are constant. Zircaloy-4 and ZIRLO alloys do not seem to pick-up more hydrogen until they reach a weight gain close to the weight gain transition value. The total hydrogen pick-up fraction $f_H$ seems to increase close but before the alloy weight gain transition. This effect is more visible if we consider the instantaneous hydrogen pick-up fraction $f_H^I$. A peak in $f_H^I$ appears at 75 days of exposure, before the alloy transitions. Both ZIRLO and Zircaloy-4 alloys show an increase in $f_H^I$ at the same weight gain (between 30 mg/dm² and 35 mg/dm²), for an exposure time of 75 days. Thus, this sudden increase in $f_H^I$ is independent on the type of precipitates present in the alloy (since Zircaloy-4 and ZIRLO present different type of precipitates) and also on the weight gain transition since ZIRLO and Zircaloy-4 alloys do not go into transition at the same exposure time. After the first transition, $f_H^{ZIRLO}$ (~11%) is inferior to $f_H^{Zircaloy-4}$ (~15%). After this pre-transition increase, $f_H^{Zircaloy-4}$ remains constant (~15%) even after further transitions.

The ZrFeCr alloys also show an increase of $f_H$ before the breakaway. This particular increase happens at weight gain between 30 mg/dm² and 35 mg/dm², which makes it similar to the ones observed in Zircaloy-4 and ZIRLO alloys. This increase is more significant for alloys with smaller precipitate size. The precipitate volume fraction has a negligible effect on $f_H$. This
trend is opposite to the corrosion behavior, since higher precipitate volume fractions will lead to a better corrosion resistance while the precipitate sizes do not play a significant role on corrosion kinetics. Thus, even if the $f_H$ increase is independent of the type of precipitates, it seems that bigger precipitate size reduces the magnitude of this increase.

Measurements of $f_H$ at early exposure time on ZrFeCr alloys have shown that $f_H$ increases rapidly at the beginning of corrosion to reach values as high as 25% at an oxide thickness close to 1µm. After that, $f_H$ decreases to lower values (~10%). It is possible that precipitates act as a window for hydrogen absorption at small oxide thickness. Precise $f_H$ determinations at early exposure time and TEM examinations of thin oxide layers will be necessary to determine the role of precipitates on this early $f_H$ peak.

It seems that the oxidation kinetics ($n$) and $f_H$ in the pre-transition or pre-breakaway regime are related. Indeed, $n$ is the same for the “pure” Zr and the ZrFeCr alloys ($n \sim 0.21$). Thus, it appears that the presence of second phase particles does not influence the pre-breakaway kinetics. In the same manner, $f_H$ does not vary between “pure” Zr and ZrFeCr alloys (as long as the weight gain is inferior to 30 mg/dm$^2$) and is approximately equal to 15%. It has also been observed that the addition of copper slows down the oxidation kinetics ($n \sim 0.17$) but increases $f_H$ (~23%). On the other hand, it has been reported that the addition of Nb (as soluble element) in “pure” Zr speeds up the kinetics ($n \sim 0.50$), while it reduces $f_H$ (~5%). In conclusion, it appears that addition of elements that slows down the oxidation kinetics (compared to “pure” Zr or ZrFeCr alloys), actually increases $f_H$, while the addition of elements that speeds up the oxidation kinetics, actually decreases $f_H$. In addition it appears that addition of acceptor impurities (as a solute element) are associated with a higher $f_H$ (and to lower oxidation kinetics) and that the addition of donor impurities (as a solute elements) are related to a lower $f_H$ (and to higher oxidation kinetics). It appears that the main link between alloy composition and microstructure with pre-transition (or pre-breakaway) corrosion rate and hydrogen pick-up fraction stems from the
amount of solute in solid solution, and from the valence of this element. The evidence above would appear to indicate that the overall chemistry of the solid solution controls the hydrogen pick-up fraction, such that elements such as Nb reduces the hydrogen uptake of the metal and increases the oxidation kinetics. For the precipitate-forming elements, the amount in solid solution is very small, and the pre-transition hydrogen pick-up fraction and kinetics are likely controlled by impurities in solid solution. Precise determination of oxidation states and concentrations of solute elements across the oxide would evaluate the role of elements in solid solution. A good characterization of the second phase particles across the oxide also seems necessary.

The inverse relationship between oxidation kinetics and hydrogen pick-up fraction (fast oxidation kinetics meaning low hydrogen pick-up fraction) would indicate that vacancy migration adjusts itself to the availability of electrons to allow for charge compensation and thus that electron migration from the oxide/metal interface to the oxide/water interface is the rate-limiting step (at least in the pre-transition regime). If electron migration is the rate-limiting step the theoretical parabolic law deviates to lower kinetics. This model entails a significant accumulation of space charge across the oxide (and so to an increase in the oxide capacitance). It is possible that this accumulation of charge would be the cause to the sudden increase in $f_H^{i}$ in an effect comparable to a semi-conductor dielectric breakdown. Electrical conductivity measurements of the oxide would be necessary to corroborate this model.
Conclusions

Cold Neutron Prompt Gamma Activation Analysis has been benchmarked and used as a non-destructive technique for hydrogen level assessment in zirconium alloys. This study has shown that CNPGGA is one of the most efficient non-destructive technique to precisely determine low level of hydrogen in zirconium alloys. Coupled to usual Vacuum Hot Extraction technique, the hydrogen pick-up fraction evolution of a wide range of zirconium alloys has been evaluated. The hydrogen pick-up fraction significantly varies with exposure time, at least in the pre-transition (or pre-breakaway) regime. A sudden peak in the instantaneous hydrogen pick-up fraction in ZrFeCr, Zircaloy-4 and ZIRLO alloys has been observed at weight gains comprised between 30 mg/dm$^2$ and 35 mg/dm$^2$, which does not seem to be related to the weight gain transition or to the type of precipitates. However, the size of second phase particles appears to have an effect on the magnitude of this increase. The results of this study are consistent with solute elements controlling the pre-transition hydrogen pick-up fraction and kinetics via their effect on electron migration from oxide/metal interface to oxide/water interface. These observations support the hypothesis that electron migration is the rate-limiting step of the zirconium alloys kinetics (at least in the pre-transition regime). Experiments to characterize the solute elements across the oxide (concentration and oxidation state) and to determine the oxide electrical conductivity as function of exposure time are necessary to verify these assumptions.
REFERENCES


