Corrosion and Hydrogen Pickup Behaviour of Zr Alloys

Volume II

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Mr Peter Rudling, President of ANT International

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1 Summary

The Volume II contains information on the out-of-reactor corrosion, the Zr alloy development for BWR/RBMK, PWR/VVER, and Pressurized Heavy Water Reactors (PHWR), the variation in performance characteristics, the effect of water chemistry, the current understanding of corrosion, and the corrosion modelling.

In the early 1950ies, the US Naval Nuclear Propulsion Program under Admiral Rickover settled on Zirconium as the fuel cladding material to be used in the submarine Nautilus water cooled reactor core.

Pure Zr has a high corrosion resistance in oxygen but exhibits a high break away corrosion in water and steam, very likely due to the effect of hydrogen on the oxide grain shape formed at the metal/oxide (M/O) interface. Thus, alloying elements that improve the corrosion were researched in the USA, and have ultimately led to the Zircaloy-2 alloy, that was developed in 1952 and initially applied for the Nautilus reactor, and since 1960 also as a new material for BWR fuel rod cladding and structural components. Initially the cladding and components were manufactured from stainless steel, which exhibited stress corrosion cracking problems. In 1959 Zircaloy-4 alloy which contains no Ni but a somewhat higher Fe content and reveals much lower hydrogen pick up (HPU) was developed in the USA. In the early 1960ies Zircaloy-4 was selected as a material for submarine reactor cores, for PWR claddings, and for the Canadian pressure tube reactors (CANDU).

In the late 1950ies extensive investigations were performed also in Russia to find commercial Zr alloys suitable for continuous operation in water and steam at high temperatures. In the 1960ies the Russians selected Zr1Nb (E110), Zr2.5Nb (E125) and later Zr1Nb1.2Sn (E635) as materials for the cladding, pressure tubes, and structural components of their pressurized (VVER) and pressure tube (RBMK) reactors.

The early Zr alloy developments were performed by out-of-reactor corrosion tests in water and steam. These tests showed, that the Zr alloy corrosion always exhibits initially a decreasing oxide thickness (Sox) growth rate, with increasing time (t), Sox=constant·tⁿ, with an exponent n of 0.3-0.5. After an oxide thickness of 1-5 μ m, a corrosion transition occurs, leading either to a very fast break away corrosion or a short increase of the corrosion rate, that again decreases afterwards with time resulting in a cyclic corrosion behaviour. Some alloys, e.g. Zr alloys with Sn content of >1.2%, exhibit a change to a somewhat faster linearly increasing corrosion that occurs after a short initial low corrosion period. In high pressure (>70 bar) steam at 450-550 °C Zircaloy samples often exhibit a localized (nodular) corrosion, which depends in particular, on the Fe content and the size of the secondary phase particles (SPP) in the metallic matrix.

The large number of performed out of pile tests showed that uniform corrosion in hydrogenated water becomes low, if (1st) the Fe+Cr is >0.4% which reduces the hydrogen content in the oxide at the metal/oxide (M/O) interface by bridging the oxygenated metal zone with $Zr(FeCr)_2$ secondary phase particles (SPP) and increasing the hydrogen migration from the oxide to the water, or (2nd) if <0.5% Nb is added to the alloy, which reduces the electrical conductivity of the oxide and the potential gradient in the oxide layer, that drives H⁺ from the oxide/water (O/W) interface (where sub-stoichiometric Zroxide is formed by water reaction), to the M/O interface. Sn reduces the sensitivity against impurities, probably by increasing the tendency to form a new dense barrier layer after each break down of the dense oxide barrier layer (rate transition).

Corrosion tests performed in environments with additions of Boric acid and LiOH or KOH acids show that the corrosion increases when a pH value rises above 9.7. The corrosion increase in acidic environment depends on the content of the acid, which affects the penetration potential of the outer porous layer of the oxide.

Corrosion of Zr alloys in water/steam with oxygen is characterised by a significantly reduced HPUF, a significant decrease of the tendency to breakaway oxidation and nodular corrosion in ZrSnFeCrNi alloys, whereas in case of ZrNb alloys a significant increase of the corrosion is observed due to a barrier layer damage induced by delayed oxidation of ZrNb SPPs.

The in-reactor corrosion in oxygenated coolant (BWRs and RBMKs), is very different to the out-ofreactor corrosion behaviour, thus the later developments were based primarily on in rector tests in oxygenated water (e.g, in BWRs or in oxygenated loops). Up to the year 2000 Zircaloy-2 appeared to be a very good material, only later it was noticed that the hydrogen pickup becomes extremely high at elevated burnup, due to the Ni content in the alloy. Thus, new materials were selected based on in reactor corrosion tests with alternative Zr alloys, as already reported in Volume I. In Volume II the basic aspects of the in-reactor corrosion in oxygenated water and the mechanistic aspects of this phenomenon are described.

In PWRs and other reactor types with hydrogenated coolant, it was noted in the early years (<1970) that the in reactor corrosion is similar to out-of-reactor behaviour, but later results at higher burnup and exposure time showed significant variations, that in most cases did not correlate to out-of-reactor tests. Thus, also for PWRs the later developments were based in most cases on in reactor tests (e.g. in PWRs or in hydrogenated loops). In Volume I the new alternative Zr alloys and many results of the development programs are described. In this Volume II the detailed aspects with all important information and the mechanistic examinations are described for the new improved corrosion resistant Zr-alloys (e.g. ZIRLO, Optimized ZIRLO, Duplex-ELS, and M5) developed by Westinghouse, Siemens, and Framatome in the 1980ies, as well, the later developments in Japan, Korea and China, which often did not result in a real optimum, as they were based mainly or to a large extend on out-of-reactor corrosion tests, , are described. In Japan the SR MDA (Zr0.8Sn0.5Nb0.2Fe0.1Cr) and NDA (Zr1Sn0.1Nb0.4FeCr) alloys were developed based on out of pile tests and were qualified in PWRs, showing only a slight improvement in corrosion compared toto Zry-4, i.e., a similar corrosion resistance as ZIRLO (but a significantly lower creep strength). Nevertheless, they were implemented and applied for reloads since 2004.

For a validation of the conclusions from the observed test results many examinations of the mechanism of Zr corrosion were performed. These examinations clearly showed, that the structure of the grain, formed in the oxide layer, plays an important role. Zr alloys with high corrosion resistance exhibit long and broad columnar grains, with a particulate texture, that minimizes the induced compressive stress by the mechanism of ~50% volume increase due to oxidation of Zr to ZrO₂. A particular aspect, which is however very little discussed in the literature, is that pure Zr exhibits a very high corrosion resistance in oxygen and air but experiences a breakaway to a very high corrosion in water and steam, after a relatively short oxidation period, what indicates that hydrogen, which is known to affect the surface energy of the oxide grains, can have a large effect on corrosion. The very significant effect of SPP density and size is probably due to the fact that most SPPs exhibit a delayed oxidation due to reduction of the hydrogen content in the oxide at the metal/oxide (M/O) interface by bridging the hydrogen diffusion barrier layer at the M/O interface. The compressive stress in the oxide plays an important role for the initiation of transition, at least in case of Zr-alloys with $\geq 0.5\%$ Sn. In other Zr alloys other mechanisms appear to be important for the transition.

A reasonable corrosion modelling is very important for PWRs, where, the operation temperature history and maximum exposure time increases significantly. Different models have been reported. Some do not appear to be very good predicting models. At least in case of one model, predictions of the oxide profiles for fuel rod cladding of alternative alloys with very low corrosion and a hydride rim formation, agree reasonably well with the observations.

2 Introduction

Zirconium alloys are being applied as fuel rod cladding materials and structural components of fuel assemblies in the core of water-cooled reactors. In the early 1950ies Zicaloy-2 and -4 were developed, which were used for water cooled reactors since the late 1950ies. The Zirconium alloys have a hexagonal crystal structure, which build up a strong texture during fabrication in the α -temperature range. A high burnup and power density, governing the corrosion attack, is a very important factor. Thus, extensive Zr alloy development programs are ongoing worldwide since the late 1980ies. Initially most developments were based on out reactor corrosion and mechanical tests. Later it was noticed that for in reactor conditions, special phenomena affect the corrosion behaviour, such as corrosion as consequence of irradiation, irradiation hardening, in reactor creep due to irradiation damage, and irradiation growth as a consequence of the alloy texture. Thus, more and more of the development work was performed by in reactor tests. Corrosion was always a very important aspect for the alloy development. Consequently, large programs were initiated in order to understand the corrosion mechanism.

The corrosion behaviour depends on material and the corrosion environment. During exposure of Zr alloys in an oxidative environment, such as oxygen, air, carbon-dioxide, water or steam, an oxide film forms on the outer surface. In reactor a large effect of oxidation potential on corrosion and hydriding of the Zr alloy component exist. This potential is affected by the impact of the radiolysis, resulting in oxidative radiolysis products, that may be supressed by addition of hydrogen or NH₃. Only in BWRs where a generated hydrogen is moved to the steam formed in the core, the oxidative species remain in the water, resulting in a rather high oxidation potential.

Volume I gives an overview of reactor coolant chemistry in the primary circuit, describes the different fuel designs and materials used in the fuel assemblies, covers the different types of irradiation in a reactor and how it impacts structural materials and water (radiolysis). As well, Volume I provides description of corrosion and HPU performance of Zr alloys, gives a description of CRUD formation, transport to fuel, deposition, activation and transport to system surfaces, covers AOA, and summarises various reported cases of fuel performance issues related to coolant chemistry.

In this Volume II a more detailed description of the

- Early Zr alloy development,
- Out-of-reactor corrosion,
- General in Reactor Corrosion and Hydrogen Pickup behaviour
- Corrosion in BWR/RBMK
- Corrosion in PWR/VVER
- Corrosion in Pressurized Heavy Water Reactors
- Sensitivity against alloying impurities
- Allowable extend of corrosion
- and Corrosion modelling and prediction

is provided.

Despite more than 50 years of research, the development of new alloys for still higher burnup and power density is still being performed. The state of knowledge on such developments will be presented.

3 Early Zr Alloy Development

During 1946 and 1947, several groups of scientists were investigating metals for use in submarine nuclear propulsion plants. Zirconium was one such metal. Stainless steel, aluminium, and beryllium were the other. The most promising plant design was the pressurized water reactor, needing a structural metal, that would withstand corrosion at high temperatures in an environment of intense radiation, and has a low neutron absorption. Initially zirconium did not appear promising, as it was not produced in large quantities and showed rather high neutron absorption. Later, it was discovered that **natural zirconium contains about 2% hafnium, which is responsible for the high neutron absorption**. After separation of hafnium from zirconium it was observed that zirconium, in its pure form, absorbs only a few neutrons. These early promises led Admiral Rickover to decide that zirconium should be used as core structural material for the Mark I PWR in the Idaho prototype and for the Mark II reactor, Nautilus, being built for the nuclear submarine in 1947. But the engineering problems were immense. The first selected fabrication process of Zr metal was the crystal-bar process (also called the Van Arkel DeBoer Process) producing a high-purity zirconium. This process was expensive, but nevertheless it was used for the first core of the Mark I reactor, starting operation in 1953 [Rickover, 1975].

Zirconium and its alloys are highly reactive metals in oxygen containing atmospheres, and consequently always have at least a thin oxide film on their surfaces.

At intermediate temperatures, 200-370 °C, the oxide will grow by the diffusion of oxygen from the outer oxide/water (0/W) interface through the oxide, forming a new ZrO_2 at the inner metal/oxide (M/O) interface.

For the description of the corrosion behaviour during out of pile tests, the weight gain in mg/dm^2 or the average uniform oxide thickness in μm is drawn versus the test time. For conversion of weight gain to oxide thickness the following equation can be used:

Equation 3-1: Oxide thickness (μ m) = Weight gain (mg/dm²)/14.7

The first studies on the oxidation of Zr were performed in air (Figure 3-1) and oxygen at different rather high temperatures, to get a fast information, by extrapolating the deduced temperature dependency on the corrosion behaviour interesting for the long-time behaviour in water cooled reactors operating at <350 °C. These tests showed a parabolic or cubic kinetics and that a breakaway transition only occurred at rather large oxide thickness (>20 μ m) at least in case of Iodide-origin Zr. Thus, in the early days, no breakaway oxidation was expected to occur at the low oxide thickness, although the onset of the breakaway oxidation occurred somewhat earlier in the case of Arc-melted sponge-base Zr. Examinations of the oxide structure after the breakaway showed that the transition occurrence was very localized and was induced by cracks in the oxide, e.g. [Cox, 1970].



Figure 3-1: Corrosion behaviour of lodide Zr in air [Cox, 1970].

However, extended corrosion tests of Zr in hot water and steam at 260-720 °C revealed that the material exhibit very variable properties. Tests results observed in 260 °C (500 °F), 288 °C (550 °F), 316 °C (600 °F), and 360 °C (680 °F) water and 400 °C (480 °F), 100 bar steam are shown in Figure 3-2. Some ingots exhibited black adherent oxide films, which remained adherent for a considerable time (up to 300 d in 360 °C water), whereas others exhibited extensive spallation after short exposure times (≤ 10 - respectively ≤ 100 days at 360 °C (at oxide weight gains of >10-30 mg/cm², >0.7-2 µm)).



Figure 3-2: Corrosion of arc-melted crystal bar Zr in oxygen at 300-650 °C and water at 360 °C. The three branches of the water curve correspond to the behaviour of different grades of zirconium [Cox, 1976].

Later tests revealed that the impurity content of nitrogen, carbon, and other elements has a large effect on the early onset of the breakaway oxidation (Figure 3-3). Obviously, the hydrogen, together with certain impurities in the water/team dramatically reduces the corrosion resistance.





A Zr alloy development program was initiated in the 1950 by out-of-reactor corrosion tests in water and steam, that were at first performed in the USA.

3.1 Early Zr alloy development in the USA

Zirconium, considered as a potential material for the core components in water-cooled and moderated nuclear reactor core, had to exhibit **a good corrosion resistance**, adequate strength properties, and high thermal conductivity. A program was started to check the corrosion resistance of zirconium. The first Zr material available in large quantities, after the development of a low-cost production method, was the so-called Kroll process material. Extended corrosion tests in hot water and steam at 250-400 °C revealed that the material exhibit very variable properties. Some ingots showed black adherent oxide films, other ingots, at \geq 360 °C, exhibited white oxides and extensive spallation after very short exposure time. Figure 3-2 summarizes the weight gain information of arc melted and rolled crystal bar zirconium samples, from 300 different specimens from different ingots. It was noted that none of the specimens showed a rapid corrosion rate increase after 8, 100 or 200 days, with a weight gain of 10, 25, or 35 mg/dm² (an oxide thickness of 0.7, 1.7 or 2.3 µm). In 400 °C steam tests this breakdown of the adherent oxide layer was only seen at high pressure (150 bar) steam, but not at low pressure (1 bar) steam or in O₂ [Thomas, 1954].

The analysis of the data showed that the impurity content of the Zr coupons had a very large effect on corrosion in 360 °C water. The major reason for these differences in the breakaway oxide thickness was found to be the high sensitivity of unalloyed Zr to impurities, such as N, C, Si, etc. [Kass, 1962]. The effect of N is shown in Figure 3-3.

The **main objective in the development of zirconium alloys was to find alloying elements to reduce the corrosion sensitivity to certain impurities.** It was found that Sn reduced the corrosion enhancement effect of N in Zr. The amount of Sn necessary to restore corrosion resistance depends on the N content. Based upon a series of small ingot crystal bar of Zr-Sn-N alloys it was found, that alloys with:

- 200 ppm N needed 0.5%Sn,
- 300 ppm N, 1% Sn, and
- 600 ppm N, 2% Sn

to restore the corrosion performance.

The **first zirconium alloy was defined as Zircaloy-1, having 2.5% Sn**. Corrosion tests, performed in the early 1952 showed, however, that Zircaloy-1 had an increasing corrosion rate at longer times (Figure 3-4). Consequently, an urgent search for a new alloy, with an improved corrosion resistance, was started.



Figure 3-4: Effect of Sn on the corrosion resistance of arc melted sponge base Zr alloys containing 60 ppm N. [Thomas, 1954].

Bettis studied the effect of other alloying elements on corrosion performance. Included was one ingot in which a small amount of stainless steel had been accidentally added. This ingot indicated a beneficial effect of Fe, Cr, and Ni, contained in stainless steel, on corrosion and was the basis for the **definition of Zircaloy-2 (Zry-2, see Table 3-1) in August 1952, which was selected for the Nautilus reactor, starting operation in 1954** [Rickover, 1975], and somewhat later for fuel rod cladding and structural components of BWR fuel assemblies and for the CANDU pressure tubes. Zry-2 **is still used for commercial BWR reactors** up to the present time, with only minor modifications.

Table 3-1: Chemical composition of Zircaloy-2.

Alloying Element	Weight (%)
Tin	1.20 to 1.70
Iron	0.07 to 0.20
Chromium	0.05 to 0.15
Nickel	0.03 to 0.08
Note: The sum Fe+Cr+Ni must be at 0.18 to 0.38%	
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Furthermore, the max. impurity limits were specified as: Al (75 ppm), B (0.5 ppm), Cd (0.5 ppm), C (270 ppm), Co (20 ppm), Cu (50 ppm), Hf (200 ppm), H (20 ppm), Mn (50 ppm), N (80 ppm), Si (200 ppm), Ti (50 ppm), W (100 ppm) and U (3.5 ppm).

Later corrosion tests confirmed the selected composition for Zry-2. Figure 3-5a shows the effect of small amounts of Fe-, Cr-, and Ni-additions to Zircaloy-1, with 2.5%Sn on the corrosion weight gain in:

- (1st) 400 °C/103 bar steam after 53 d,
- (2nd) in 360 °C water after 168 d, and
- (3rd) in 315 °C water after 252 days.

Addition of 0.2% of Ni, Fe, and Cr reduces the corrosion significantly. Ni and Fe have similar effect on weight gain, whereas Cr was less beneficial at least at \geq 360 °C. Figure 3-5b shows similar tests for ternary alloys with 1.8% Sn revealing a similar effect of Ni, Fe, and Cr. However, the corrosion rate of the alloys with a Sn content of 1.8% was significantly lower than the corrosion rate of ZrSnFeCrNi alloys with Sn content of 2.5%. The tests performed in the 1950ies indicated that there is an optimum total Fe+Cr+Ni content of 0.2-0.35%, as Figure 3-6 shows.



Figure 3-5: Effect of Fe, Ni, and Cr additions to arc melted sponge with a Sn content of (a) 2.5% and (b) 1.8%, [Kass, 1962].



Figure 3-6: Effect of total Fe Ni and Cr content on corrosion of Zry-2 [Kass, 1962].

The most important property of Zry-2 is the corrosion resistance. The long-time corrosion tests with Zry-2 showed, that after an initial corrosion period with a corrosion rate decreasing with time, a

transition to a new rate law, with an approximately constant corrosion rate (Figure 3-7), was established. The transition in the corrosion rate kinetics in 360 °C water occurred after 100-120 d and in 400 °C steam after ~40 d. Later tests indicated that the rate transition in 316 °C respectively 288 °C water occurs only after 600 respectively 1800 d [Kass, 1962].



Figure 3-7: Weight gain versus time curves for corrosion of Zry-2 [Kass, 1962].

In 1953 a new development program was undertaken to develop new Zr alloys, having a superior corrosion, compared to Zry-2. This program has led to three new alloys:

Zircaloy-3A: 0.25% Sn + 0.25% Fe Zircaloy-3B: 0.5% Sn + 0.4% Fe Zircaloy-3C: 0.5% Sn 0.2% Fe + 0.2% Ni

Figure 3-8 reveals the corrosion behaviour of the Zircaloy-3 alloys (specimen furnace cooled from 775 °C) in 400 °C/103 bar steam [Kass, 1962]. The post transition rate of all three alloys in 400 °C steam is considerably lower than that of Zry-2. The lowest corrosion was observed for Zr alloy-3A. The Zr alloy-3 alloys exhibited a much lower strength than Zry-2. Thus, the Zr alloy-3 alloys were never used for commercial fuel rods. Only once, Zr alloy-3A was tested via PWR pathfinder fuel rods with a full-size cladding and a Duplex cladding in the late 1980ies in a Siemens PWR [Seibold & Garzarolli, 2002] they exhibited a rather low corrosion (see section 5.3).



Figure 3-8: Corrosion of Zry-2 and -3 in 400 °C/103 bar steam [Kass, 1962].

Hydrogen pickup (HPU) by the cladding during aqueous **corrosion has been found to be a potential limit for Zry-2**. The oxide layer formation on Zr alloys during corrosion in water results in the formation of hydrogen (Zr+2H2O -> ZrO₂+2H⁺). It was observed already in 1953 that Zr, Zr alloy-1 and Zry-2 absorb a certain amount of the hydrogen during corrosion. Small quantities of hydrogen exert an embrittling effect, but experience showed that the amount of hydrogen absorbed was small. Later tests demonstrated that hydrogen pick up fraction (HPUF) of Zr alloys is enhanced when Ni is present in the alloy (Figure 3-9).



Figure 3-9: HPUF of several binary Zr-alloys in 343 °C degassed water after 575 d, [Berri et al., 1961].

Consequently, the Zry-2 composition was re-evaluated mainly considering the HPUF and a new alloy Zircaloy-4, containing no Ni but a somewhat higher Fe content, was specified in 1959 (Table 3-2). Corrosion tests with Zry-4, a Ni-free Zry-2, and Zry-4 in 316 °C and 360 °C water and 400 °C steam showed similar weight gain versus time behaviour for all three alloys. The HPUF varied as follows: Ni-free Zry-2 showed the lowest HPUF, and Zry-4 a lower HPUF, than Zry-2 e.g. [Kass & Kirk, 1962]. Table 3-3 [Kirk, 1959] concluded that the Fe content of Zry-4 should be limited because HPUF of Zry-4 appeared to increase with increasing Fe content, what is probably a consequence of the SPP density, affecting the HPUF.

Table 3-2:	Chemical con	position of Zry-4.

Alloying Element	Weight (%)
Tin	1.20 to 1.70
Iron	0.18 to 0.24
Chromium	0.07 to 0.13
Nickel	max. 0.007
Note: The sum Fe+Cr must be ≥0.28 %	·
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4 Out-of-reactor Corrosion

4.1 Corrosion tests

For the qualification of fabricated Zr products for nuclear services a short time (3 d) corrosion tests in 100 bar 400 °C steam are generally applied, as specified in ASTM Recommended Practice for Aqueous Corrosion of Samples of Zr Alloys (G 2-74) for a reasonable corrosion resistance ($\leq 22 \text{ mg/dm}^2$). The test is only a check, that the overall manufacturing process has not dramatically deteriorated the Zr alloy microstructure or local composition to such a large extent that it results in an oxide weight gain value > 22 mg/dm^2 , what may result in an extremely increased corrosion in reactor. However, this test does not give any information on the normal in-reactor corrosion performance of the particular lot.

For the development of Zr-alloys for fuel rod cladding long time corrosion tests in 300-370 °C water and 400-600 °C steam have been used. Most water and steam corrosion tests were performed according the ASTM specification G2/G2M, defining the water/steam conditions, the sample surface condition (pickling), and the number of specimens.

- For water tests, both static and refreshed tests have been employed. Static tests are usually carried out in stainless steel autoclaves. Refreshed tests are conducted with refreshed water, in circulating loops constructed usually by stainless steel, comprising a pump, heaters, a test section containing the specimen, and suitable controls and instrumentation. Circulating loops have the advantage that coolant composition remains more constant than that in static tests. Unless additions to the test water are desired, usually a resistivity of 500,000 ohm/cm, and a pH of 6 to 8, and a low gas content are specified. Thus, a degassing of the test water by boiling is used to reduce the oxygen content to <0.05 ppm, as well as to keep low nitrogen level (except in most reported tests in Russia). Specimens are weighed before and after exposure, usually after certain day-, week-, or month-intervals to estimate the weight change via the exposure time (e.g. in mg/dm²).
- Steam tests are usually done in the same equipment as described above for static water tests, in some cases also in refreshed steam tests. The specimens are loaded into the autoclave using water of the purity as described above. The autoclave and its load of samples are then gradually heated and excess water or steam is bled until the desired temperature and pressure are attained. Most steam tests have been performed at 400 °C and 100 bar (1500 psi). It should be pointed out here, that the pressure and the gas content, particularly nitrogen and the hydrogen formed by the corrosion of the Zr-alloy coupons, are important variables in the steam test.

However, the ranking of different alloys in these tests often does not correlate with the in-reactor corrosion performance. The best material in an out-of-reactor corrosion test could even be the worst in reactor and vice versa. Thus, these types of long-time corrosion tests should **not be the basis for the final Zr alloy selection for reactors**, but only for variants tested in reactor for the selection of the final composition and condition of a good advanced alloy.

4.2 Type of corrosion and mechanistic aspects

The corrosion rate of the Zr alloy depends on:

- the temperature (usually tests at ≥250 to ≤550 °C, are used in out-of-reactor studies),
- the environment (which can be oxygen, CO₂, pressurized water or steam or supercritical water).For tests in water and steam the oxygen content, hydrogen content and potential additions of boric acid, LiOH, H₂S, etc. are an important parameter. For PWR most important type are tests in O₂ free or hydrogenated water and steam and tests in water with Li and B additions,
- the alloying (Sn, Nb, Fe, Cr, V, etc.) and the impurity (C, Si, etc.) content of the material,
- the material condition, which is governed by process steps, the quenching rates, the distribution of the alloying elements, the intermediate annealing temperatures, the final cold work and the

final annealing (size and distribution of second phase precipitates (SPP) as well as dislocation density, yield strength, creep strength, and grain size).

The <u>type of corrosion</u>, which may be (1st) <u>low and uniform</u> (see section 4.3), (2nd) <u>late increased</u> (see section 4.4), (3rd) <u>a breakaway corrosion</u> (see section 4.4), or (4th) <u>nodular</u> (see section 4.4), vary with temperature, system pressure, and impurities in the corrosion environment. Furthermore, the effect of alloying elements and microstructure on corrosion rate and kind is different in different corrosion environments.

For description of the uniform corrosion (the most observed type of corrosion in water, steam and in water cooled reactors), the weight gain in mg/dm^2 or the average uniform oxide thickness in μm is used. For conversion the following equation can be used:

Equation 4-1: Oxide thickness (μ m) = Weight gain (mg/dm²)/14.7

In case of nodular corrosion (which is observed in BWRs and can be also formed in high pressure steam at 450-550 °C steam), or shadow corrosion (which only occurs in reactor in oxygenated coolant), the local peak oxide thickness and the relative surface extend of the locally thick oxide, respectively the nodule density are important parameters.

The *initial oxide* formed on corrosion resistant Zr-alloys is black (sub-stoichiometric) and consists of a barrier layer. The corrosion rate decreases with increasing barrier layer thickness. The initial corrosion rate follows a power law:

Equation 4-2:

 $S_{ox} = const x t^n$

with S_{ox} = the oxide thickness, const = rate constant, t = the exposure time, and n = the time exponent. The corrosion behaviour depends on the material and the corrosion environment.

<u>The water chemistry condition can have a large effect on the initial corrosion behavior of all Zr</u> <u>alloys.</u>

The corrosion of unalloyed Zr in oxygen indicates an almost ideal behaviour, a continuously decreasing rate law ($n \approx 0.3$), with no evidence of any oxide breakdown up to 20 µm, as pointed out in Figure 3-1. Only at very high temperatures, >600 °C a transition to an increased corrosion was observed for unalloyed Zr in O₂ and air. However, the corrosion behaviour of unalloyed Zr in degassed water and steam shows a breakdown of the protective oxide film at oxide film thickness of 0.7-2 µm (Figure 3-2) and a dramatic corrosion increase afterwards (called *breakaway corrosion*) [Lustman & Kerze, 1955].

Thus, Zr-alloys with a reasonable corrosion resistance in water and steam were developed, e.g. Zircaloy-2 (Zr1.5Sn0.14Fe0.1Cr0.05Ni) and Zircaloy-4 (Zr1.5Sn0.2Fe0.1Cr) in the USA, see Section 3.1. Furthermore, E110 (Zr1Nb) was developed in Russia (see Section 3.2), and later additional alloys by the reactor suppliers (see Volume I and section 5 to 7 of Volume II).

In Zircaloy type and Nb containing Zr alloys *the protective regime of the <u>uniform oxide layer persists</u> in water and steam <u>until the transition occurs</u>, at ~2–5 \mum oxide thickness. The oxide film is initially thin, uniform, and black (due to its sub-stoichiometry by the diffusion connection to the underlaying metal). At the transition lateral cracks are formed at the metal/oxide (M(O) interface, starting at some local positions, and making the colour somewhat more grey (Figure 4-1) as a consequence of the reduced sub-stoichiometry of the outer oxide.*



Figure 4-1: Appearance of corroded Zircaloy-4 tube exposed to high-pressure water containing 70 ppm LiOH at 350 °C for 140 days [Beie et al., 1994].

After the transition the corrosion rate increases, *and a new barrier layer is formed*, reducing the **corrosion again similar as during initial oxide formation** (with similar power law characteristics as during the first transition), *resulting in a <u>cyclic behaviour</u>*, with a low to moderate average corrosion rate. This type of oxide layer contains periodic layers with interjacent mini cracks.

TEM examinations indicate that initially fine tetragonal oxide grains are formed, that modify after some time to larger columnar monoclinic oxide grains, and become cracked or porous at the transition, resulting again in the formation of fine equiaxed tetragonal grains, that modifies to columnar monoclinic, etc.

In case of alloys with a high Sn and a moderate Fe content after several transitions a 2nd transition to a somewhat increased average corrosion is often observed (Figure 4-3).

With increasing thickness, the uniform oxide layer becomes more and more white (the colour of stoichiometric ZrO₂).

Sn was found to reduce the sensitivity of Zr alloys against impurities, and to increase the uniform corrosion at concentrations of $\geq 0.5\%$, whereas the transition metals (TM = Fe, Cr, and Ni) and Nb generate an improvement of the average corrosion rate.

In low pressure steam, the corrosion is not cyclic post transition, as indicated by Figure 4-2d.

In case of corrosion tests with poorly behaving Zr alloys or in water with aggressive impurities, e.g. a high Li content, the corrosion shows **after the first transition a very high increase of the corrosion rate** (Figure 4-2b), i.e. a corrosion **breakaway** with a high or very high corrosion rate increase is noted. The onset of the high corrosion starts after an initial corrosion of 0.2-2 μm.

In case of Zr-type alloys, which have a moderate corrosion as consequence of Fe-, Cr-, or Ni-addition forming *Zr-TM second phase precipitates (SPP)*, the corrosion follows a rather low cyclic corrosion rate (Figure 4-2a). However, *Zr-type alloys produced at low temperatures (with very fine SPPs) show in oxygen free water or steam a breakaway occurring somewhat later* with a large increase of the corrosion rate (Figure 4-2c). Obviously, the oxide layer formed on Zr-type alloy with very fine SPP after the breakaway (large corrosion increase) is not any more reasonably protective.



Figure 4-2: Principle corrosion behaviour of different materials in different environments.





The <u>time exponent n value, governing pre-transition corrosion rate</u>, is different for different alloys, different material conditions, and different water chemistries. It should be 0.5, if oxidation is governed only by normal O-ion diffusion. In Zr alloys, the n-value is between 0.2 and 0.6, indicating that the oxidation rate is not only governed by normal O-ion diffusion through the oxide barrier layer but also by other parameter, e.g. the electron migration (electronic resistance). Figure 4-4 shows that the n value of Zry-4 in 350 °C water (blue circles) and in 400 °C high pressure steam (red

squares) is similar. However, pickled samples (red squares) have generally a somewhat lower n value (0.29) than electro-polished (red triangles) with an n of 0.35, probably due to the initially higher corrosion rate, as a consequence of the fluoride contamination from pickling with a F containing solution.

In 1 bar oxygen at 400 °C the n value of Zry-4 (green datapoints) was significantly higher (0.5), indicating that in this environment the corrosion is only governed by O-diffusion, what is certainly questionable, because pure Zr oxidized in oxygen shows a much lower n-value, as will be shown later, indicating that the low electronic conductivity also contributes to the corrosion rate. *Furthermore, in* 400 °C O₂ no obvious repeated transition occurs (Figure 4-4). TEM examinations of this post transition oxide layer formed in O₂ after 36 d showed at one position equated tetragonal oxides above an inner amorphous layer and columnar monoclinic formed on another position of the same sample, *indicating* that transition occurs in O₂ locally leading to an almost constant corrosion, and not as in 400 °C steam a transition on the whole sample after repeated time periods leading to a cyclic corrosion [Garzarolli et al., 1991]. In case of 400 °C steam and 350-360 °C water tests a 1st rate transition occurs at an oxide thickness of ~2 µm (Figure 4-4).



Figure 4-4: Corrosion behaviour of a Zry-4 strip samples from a certain ingot in 350 °C, water, 400 °C high pressure steam and in 1 bar oxygen at 400 °C. Data from [Garzarolli et al., 2001a].

In corrosion-resistant zirconium alloys, e.g. with >0.3% Fe+Cr or $\ge 0.5\%Nb$, during corrosion in pressurized water and high-pressure steam a first rate-transition occurs at a thickness of about 2-5 μ m (27-70 mg/dm²). At the transition the former barrier layer becomes permeable for H₂O and a new barrier layer is formed. The barrier layer thickness at the transition and its quality govern the average corrosion rate (see Section 4.3).

<u>Certainly, it is not evident, that a cyclic transition always occurs</u> at moderate corrosion rates. In low-pressure steam, and oxygen the corrosion rate appears to remain constant after the transition (Figure 4-2d). Surprisingly, the average post transition corrosion rate in low-pressure steam is often similar as that in high-pressure steam at the same temperature. The not cyclic behaviour indicates that, in such cases the corrosion rate after transition is governed either (1st) by the H₂O molecules migration through the outer porous oxide layer, or (2nd) by repeated transitions, which do not occur on the whole sample at the same time but locally at different times, as was already pointed out for Zry-4 samples exposed in oxygen at 400 °C (Figure 4-4). *The mostly discussed characteristic corrosion rate of Zr alloys is the average post-transition corrosion rate after the 1st transition.* The average post-transition corrosion rate (ds/dt) exhibits an exponential temperature dependence. For the post transition corrosion rate the following equation is used:

Equation 4-3: $ds/dt = C \cdot exp(-Q/RT)$

where C = constant, Q = activation temperature, R = gas constant, and T = temperature. The temperature dependency Q/R for uniform corrosion reported in different publications is reported to be between 10.000-16.000 K.

The time to the 1st transition depends not only on the Zr material composition and condition but also on the surface treatment. Whereas ground and polished as well as electro-polished samples show a similar time to transition for the 1st and the later transitions, pickled samples exhibit generally longer time (and a slightly larger oxide thickness up to the 1st transition, than ground or electro-polished samples [Garzarolli et al., 1985a].

As already pointed out, the corrosion behaviour depends on the material and the corrosion environment. After formation of a certain oxide thickness either a breakaway and drastic corrosion rate increase occurs (at 0.2-2 μ m) or a rate transition (at 2-5 μ m), where the corrasion increases for a short time and decreases afterwards again resulting in a *uniform cyclic corrosion with a relativly low average rate, if the transition thickness is high*, or a more moderate rate, if the transition thickness is rather low (see section 4.3).

The Zr alloy corrosion processes in water is illustrated in Figure 4-5. The new ZrO₂ at the M/O interface forms by migration of oxide ions from the sub-stoichiometric oxide layer into the metal, increasing the oxygen content of the Zr metal at the M/O interface, till the O content exceeds the solubility limit, and ZrO₂ is formed by the reaction: $Zr+2O^{2-} \rightarrow ZrO^{2+}4e^{-}$. The oxidation rate increases with decreasing sub-stoichiometry at the M/O interface, governed by the oxide barrier layer thickness.

The **electrons have to move through the dense barrier layer to the W/O interface** to reduce the electronic potential in the oxide at the M/O interface, what builds up a significant electronic potential gradient in the barrier layer, due to the low electronic conductivity in the outer part of the oxide layer.

The water molecules at the still sub-stoichiometric oxide/water (O/W) interface dissociate $(H_2O \rightarrow O^{2-}+2H^+)$. The oxygen ions from the water will fill up oxygen ion vacancies (VO^{2+}) in the outer surface of the oxide layer, at the O/W interface, which will increase the local oxidation potential, leading to diffusion of O ions to the much more sub-stoichiometric M/O interface. Since oxygen ion vacancies exhibit a faster diffusion than the O-ions, the transport of oxygen to the M/O interface, that governs the oxide thickness growth rate, proceeds mostly via O-vacancy diffusion from the M/O to the O/W interface.

The electrons formed by the oxidation reaction of Zr at the M/O interface reduce the electronic potential and must diffuse to the O/W interface and there may react with the H⁺ ions and form hydrogen gas (2e⁻⁺ 2H⁺ \rightarrow H₂) or migrate into the water. The electric resistance of the oxide is low in the innermost heavy sub-stoichiometric zone close to the M/O interface, but increases usually significantly in the remaining outer, less sub-stoichiometric part of the dense barrier layer, e.g. [Bei et al., 1994]. The increase of the electric resistance with increasing oxide layer thickness will increase the electric potential difference between M/O and O/W interface (electric potential difference in Figure 4-5). The electric resistance depends on the alloying elements dissolved in the oxide. If the electric resistance is high, as in most cases, it will also influence the time dependency exponent (n) of corrosion rate to $n\approx 1/3$. Only, if the electric resistance is low, the corrosion rate is only governed by the oxygen vacancy diffusion and n becomes $\approx 1/2$.

The **hydrogen ions** from H₂O formed at the O/W interface by filling up the oxide vacancy at the O/W interface **will either recombine to H₂ and go into the water, or migrate as H⁺ ions to the M/O interface,** depending on **the driving force, which is very likely the electric potential gradient over the dense oxide layer, that forms by the electron migration from the M/O interface to the O/W interface.** The fraction of hydrogen produced by the corrosion reaction, which goes into the metal, is usually called the **hydrogen pickup fraction (HPUF)**. The HPUF increases (1st) with increasing electric

resistance, (2nd) with increasing thickness of dense oxide barrier layer (increasing potential gradient), (3rd) via metallic Zr/FeCr₂ SPP bridging the O saturated metallic zone with reduced H solubility at the M/O interface, (4th) with decreasing corrosion rate as consequence of the potential gradient, due to the increased time for H⁺ migration, although the increasing thickness of the oxide saturated interlayer very likely reduces the migration of H ions from the oxide to the metal, and (5th) decreasing driving force (potential gradient) in the outer porous layer for H⁺ migration to the flowing outer coolant. A high NiO content in PWR with Ni-base SG tubes transforms in the porous part of the oxide back to Ni due to the radiolysis induced potential reduction, The Ni layer at the O/W interface , reduces somewhat the surface potential and consequently the HPUF, as pointed out in Volume I and in this Volume in Section 4.8.



Figure 4-5: Zr alloy corrosion reaction processes.

The early tests on oxidation of unalloyed Zr in oxygen suggested an almost ideal behaviour up to 600 °C. It showed a decreasing corrosion rate (CR) with increasing corrosion time (t) at a constant temperature following a cubic law (CR=constant·t^{1/3}), governed by 0-ion diffusion from the O/W to the O/M interface and the electron migration from the O/M to the O/W interface governed by the low electric conductivity of the oxide, what is different to the oxidation of Zry-4 in 1 bar oxygen, where n was found to be ~0.5. In early days it was thought that that pure Zr would not undergo oxide breakdown at a temperature <600 °C. Only at \geq 600 °C a transition was observed, connected with cracks formed in the oxide e.g. [Cox, 1976]. Contrary to the behaviour of pure Zr in O₂, air, and CO₂, in high temperature aqueous environments, unalloyed Zr showed, that after formation of a low oxide layer thickness (0.5-3 µm), a breakaway to a white non adherent oxide, and a very large increase of the corrosion rate (Figure 3-2).

The reason for the difference in corrosion behaviour of Zr in water and steam and in oxygen, CO₂ and air, is very likely the H⁺ migration from the oxide/water (W/O) interface to the metal/oxide (M/O) interface, leading to a significant H⁺ concentration in the oxide at the M/O interface, probably because the migration of the H⁺ ions at the M/O interface from the oxide into the Zr metal is restricted, by an interlayer with a reduced H solubility, the O-enriched Zr layer at the M/O interface, causing a relative high H content in the oxide at the M/O interface. This increased H⁺ content may lead to a significant change of the oxide crystallization on the M/O interface. *The quality of the barrier layer depends mainly on the oxide structure*. ZrO₂ is normally up to 1170 °C monoclinic, between 1170 and 2370 °C tetragonal and above 2370 °C cubic. The monoclinic oxide has, however, a high surface energy and can consequently exist only at a relatively large grain sizes, at >30 nm. Annealing tests of amorphous ZrO₂ samples, revealed that at first very fine metastable tetragonal oxide crystals form [Gravie, 1965].

Consequently, *the fine oxide grains formed first at the M/O-interface are mostly tetragonal*. Moisture and **OH**⁺, **H**⁺, **however, reduces the oxide surface energy and shifts the critical grain size for monoclinic ZrO**₂ **to a much finer size** [Murase & Kato, 1980]. Furthermore, a high compressive stress (>2500 MPa) can stabilize the tetragonal crystal structure [Arashi & Ishigame, 1982]. Other mechanism that can stabilize tetragonal, or even amorphous ZrO₂ are the sub-stoichiometry at the M/O interface [Iltis et al., 1994] and certain alloying elements, e.g. Sn [Frankel et al., 2015].

Analysis of the oxide structure of corrosion resistant Zr alloys has shown, that, in many cases, the initial oxide formed at the M/O interface has a fine grain size, is equiaxed, and mostly tetragonal and transforms after some distance to larger columnar monoclinic grains e.g. (Figure 4-6).



Figure 4-6: Oxide film of the E110 alloy parallel to the growth direction [Shevyakov et al., 2013].

The initially formed ZrO_{2-x} layer, respectively the oxide formed at the transition at the M/O interface is probably amorphous but transforms fast to small (5-10 nm) equiaxed tetragonal grains with a somewhat random orientation. A high compressive stress is formed in the oxide layer as consequence of the volume increase. It depends on the texture of the oxide grains. Oxide grains with proper orientation, with a small lateral expansion (low compressive stress), grow and transform above a certain size to monoclinic columnar grains $Zr/(002)_t/(020)_m$, e.g. [Motta et al., 2008]. Only very few small tetragonal grains remain. Thus, an initial tetragonal oxide may be important for an optimized oxide grain shape and low compressive stresses. But a thick tetragonal oxide interlayer may also have a negative effect.

TEM examination of the oxide layer (after a usually very slow cooling from the corrosion temperature in a furnace, which may affect the structure) show, that many columnar monoclinic grains grow up to the M/O interface e.g. [Beie et al., 1994], somewhat after transition, when the corrosion becomes low, and that the content of tetragonal grains at the M/O interface in corrosion resistant Zr alloys significantly decreases (e.g. Figure 4-7). Obviously, **the initial formed oxide grains formed at the transition are**

mainly equiaxed, whereas the oxide formed some time afterwards is preferentially columnar with proper orientation, resulting in small oxidation induced lateral expansion and a relatively low compressive stress, as will be shown with more details in Volume III.



Figure 4-7: Monoclinic crystal grains (grey grains) and tetragonal grains (coloured grains with different orientation) from TEM cross-sectional of Zry-4 sample with a pre-transition oxide layer of 2.1 µm (350 °C water for 106 d) [Garner et. al., 2014].

During the development of Zr alloys with a high corrosion resistance, it was observed that in case of Zr-(Sn) alloys, additions of transition elements (TM), Fe+Cr(+Ni), increase the corrosion resistance significantly above a certain concentration (>0.3%) e.g. [Kass, 1962]. The very low solubility of the transition metals (Fe, Cr, Ni, etc) in Zr leads to the formation of Zr-(FeCrNi) secondary phase precipitates (SPP). The SPP size depends on the fabrication temperature and the SPP composition. Most of the SPP types have a delayed oxidation, compared with Zr, and remain metallic at the M/O interface, and reduce the corrosion extremely, if their size, density, volume fraction is above a critical value, as Figure 4-8 shows, for Zry-4 with 0.2% Fe and 0.1% Cr. The volume fraction of the SPP and their size depends on the time (t) and temperature (T) of the previous heat treatment steps, what can be applied for the calculation of the ΣA-parameter =(t*exp(-40.000/T). The corrosion rate is lowest and the HPUF highest at a ΣA-parameter of 1·10⁻¹⁸ to 1·10⁻⁷ h, where the SPP volume fraction becomes >80% and the SPP size >70 nm up to <150 nm, whereas at <1·10⁻¹⁹ h, where the fraction of the precipitated SPP is <10% [Motta et al., 2002] and the SPP size <30 nm the corrosion

increases and the HPUF decreases significantly, probably due to the decreasing SPP size and volume fraction, resulting in an increased H⁺ content in the oxide at the O/M interface affecting the oxide crystallisation. At a Σ A-parameter of >1·10⁻¹⁷, where the SPP size becomes much larger, but the SPP density decreases significantly, the corrosion increases and the HPUF decreases again somewhat. The optimum heat treatment depends also on (1st) the SPP type, (2nd) the total TM content, and (3rd) the type of TM elements. Ni and Fe result in rather large SPP, whereas Cr and V in rather small SPP. *The beneficial effect of SPP with a certain size on corrosion resistance is very likely due to their bridging of the O saturated interlayer formed in the metal at the M/O interface, being an additional path for the H migration to the metal, increasing the HPUF, and reducing the H⁺ content in the oxide at the M/O interface, what improves the oxide crystallisation. There are some indications that the O solubility in Zr is reduced at very high O contents in Zr [Moalem & Olander, 1991 and Miyake et al., 1999].*





Thus, a low corrosion and high HPUF is in ZrSnTM alloys only observed, if a certain density of *SPPs with a delayed oxidation* exist. SPPs with a delayed oxidation, as the Zr(FeCr)₂ Laves phase, remain metallic in the inner half of the barrier layer [Pecheur et al., 1994] and can bridge the O-enriched interlayer. Other Zr rich SPPs as Zr₂(FeNi) oxidize at the M/O interface [Proff et al., 2013], but the Fe and Ni fraction remain metallic. Furthermore, Ni and Fe may concentrate on some metal grain boundaries close to the M/O interface [Sundell et al., 2012] (at the interlayer with increased O content), what also may decrease the H⁺ content in the oxide at the M/O interface by bridging the O-enriched interlayer.

The H⁺ content in the oxide at the M/O interface depends also on the electric conductivity of the outer oxide (barrier) layer and the electrochemical potential at the O/W interface. *Alloying elements, which increase the electric conductivity of the oxide significantly, as Nb, consequently reduce the HPUF* and the SPP size effect on HPUF, what agrees with the observations e.g. [Yao et al., 2011] *and leads to a very low general corrosion*.

Another aspect affecting the HPUF are the metallic SPP remaining metallic through the whole barrier layer, if they remain large enough to bridge the barrier layer (Cu) or if they can precipitate in the O enriched metal at the O/M interface on grain boundaries (Ni).

<u>The growth rate of the dense oxide barrier layer</u> decreases significantly with increasing thickness up to a certain thickness (oxide transition thickness), where the major part of this layer becomes porous, probably by cracks. *Afterwards, either*

(1st) a breakaway with a very much increased corrosion rate occurs or

(2nd) in case of corrosion resistant Zr alloys a new barrier layer is formed, resulting in a cyclic corrosion.

In case of corrosion resistant Zr alloys, analysis of the oxide structure often showed that the initial oxide formed at the M/O interface has a fine grain size, is equiaxed, and mostly tetragonal and transforms after some distance to larger columnar monoclinic grains. TEM examinations of the oxide layers with slow or fast post transition corrosion indicated, that the most important aspect for the development of an optimized microstructure is (1st) the grain nucleation and growth process to columnar grains, and (2nd) the alloying effect on the growth behaviour of the columnar grains.

<u>The oxide layer formed after breakaway or after a local significant increase of nodular corrosion</u> is generally equiaxed and monoclinic e.g. [Garzarolli et al., 1991 and Warr et al, 1991], very likely as consequence of a high local H⁺ content at the M/O interface creating fine monoclinic grains instead of fine tetragonal grains. Probably, columnar monoclinic grains form via growth of tetragonal grains with an optimum crystal orientation, resulting in a low compressive stress, whereas fine initial monoclinic grains only grow in size, forming many intergranular cracks, due to the higher compressive stress and the less crack resistant structure, therefore reducing the thickness of the inner dense barrier layer significantly as will be shown in more detail in section 3, 4.3 and 4.8.

Zr-alloy developments have, furthermore, shown that <u>*Sn additions reduce the sensitivity against*</u> <u>*metal impurities*</u> (e.g. N and C, etc.) and coolant impurities (O₂ and LiOH etc.), probably by reducing the tendency to form fine monoclinic grains at the M/O interface. Acc. [Frankel et al., 2015] Sn stabilizes the tetragonal oxide, and reduces the oxide grain size probably by the increased metallic Sn content at the grain boundaries. The **increased tendency to form fine tetragonal grains may also reduce the likelihood of the H⁺ induced formation of fine equiaxed monoclinic oxide grains** at the M/O interface, which destroy the protectivity of the oxide layer. **However, Sn increases the uniform corrosion, especially at >0.5%** [Kass, 1962], probably due to the decreasing grain size of the oxide layer affecting the diffusion and the time to transition.

It **is certainly interesting**, that in case of Zr alloys with a good corrosion resistance in water and steam, **the corrosion is cyclic and that the transition occurs on the whole sample** at almost the same time, and that the first local porosity formation do not lead to local oxidation variations, but leads to an oxide structure change on the whole sample.

It is also interesting that in case of Zry-4 oxidation in oxygen, no cyclic corrosion appears, as already pointed out. Here, at some local position fine equiaxed oxide grains, crystallizing from a quasi-amorphous oxide layer were grown up to the M/O interface, whereas at other positions of the same sample columnar grains were seen (Figure 4-9). Obviously, the repeated transitions of the oxide grain formation mode does not occur in oxygen at certain time/oxide-thickness intervals, as in water and steam, but at different time and local positions. This indicates, that the modification of the grain formation mode from columnar monoclinic to fine equiaxed Zr-oxide grains is initiated by different mechanism in H_2O and in O_2 . Probably, the transition in H_2O is also affected by an increase of the H^+ content at the M/O interface with increasing dense oxide (barrier) layer, affecting the crystallization mode at a certain barrier thickness, whereas in 0_2 the local change of the crystallization mode is probably only driven by high local stresses, which depend on local corrosion variations (interface undulations) resulting in local oxide cracks and a high local oxide growth rate or by the fact that the migration speed of O_2 molecules through the outer porous oxide is lower at low pressure and may result in significant local variations. The post transition corrosion in low (~1bar) pressure steam is not cyclic, indicating that the low and locally varying speed of the oxidative molecules may be an important aspect.





Different types of corrosion (cyclic uniform corrosion, breakaway corrosion, late increased corrosion, nodular corrosion) can appear, that will be described in sections 4.3 and 4.4. The corrosion behaviour in oxygenated water is different to that in oxygen free (degassed), respectively hydrogenated water, as section 4.3 and 4.7 shows. The effect of boric acid and alkaline additions is discussed in section 4.7.4 and the potential effect of coolant impurities in section 4.7.5.

4.3 Uniform corrosion

The long-term corrosion behaviour of different Zr alloys in degassed and hydrogenated 350 °C water and degassed 400 °C 105 bar steam is quite different for different alloys, as obvious from Figure 4-10. **In 350 °C water** (Figure 4-10a), the ZrSnFeCr and ZrNb alloys show a **cyclic corrosion behaviour (repeated transitions)** with weight gain intervals of 25-70 mg/dm² (equivalent to an oxide layer thickness of 1.7-4.6 μm) and exposure time intervals of 100 to 900 d.

Besides the normal uniform corrosion often a late increased corrosion can arise. In case of the ZrSnFeCr alloys Zry-4 lots with high Sn and low Fe or high Cr, black and blue curves in Figure 4-10a, a late increased corrosion rate was observed in 350 °C water after a total exposure time of >1100 respectively >1350 d, what will be discussed in more detail in section 4.4. In the normal uniform post-transition corrosion range in 350 °C water the corrosion rate decreases with decreasing Sn content, but the lowest corrosion is observed for the ZrNb alloys with optimized microstructure.

Similar long-time tests were reported by [Sabol et al., 1989 and 1994] for different Zry-4 materials, ZIRLO, and Zr2.5Nb in 316° and 360 °C water, as well as in 400 °C and 427 °C high pressure steam (Figure 4-11). In the 316 °C and 360 °C water tests the corrosion resistance was observed to be highest for Zr2.5Nb, high for ZIRLO, and lowest for Zry-4.



Figure 4-10: Corrosion behaviour of different Zr alloys in 350 °C water (purged with argon gas, evacuated and an over-pressured in case of 0.25 bar hydrogen and 5 bar argon, resulting in <10 ppb oxygen and 2 ppm hydrogen in the water) and 400 °C steam with an unrestricted specimen load [Sell, 2012].

In 400 °C/100 bar high pressure steam tests, reported by [Sell, 2012] only Nb containing alloys had generally a linear post transition corrosion behaviour, whereas the ZrSnFeCr alloys showed an extensive reduction of the corrosion rate with increasing exposure time to unusually low value (Figure 4-10b), significantly increasing with increasing Sn content. The test reported by [Sell, 2012] had a very short time intervals between the cooling and weight gain measurements and a slow cooling after each 12d interval, and a very high, unrestricted, specimen load, creating a high H₂ content during the steam corrosion and also a very extensive oxygen evacuation before reach restart, what may affect the corrosion environment. In difference, the data reported by [Sabol et al., 1994], showed, in case of the two Zry-4 lots in 400 °C steam corrosion data, a normal linear behaviour after the 1st transition at about 40 mg/dm^2 and in case of conventional Zry-4 a late increased corrosion after >550 d (~450 mg/dm³). \sim 30 μ m), but in case of the 427 °C steam Zry-4 data, a reduction of the late corrosion rate occurs after >100 d (at \sim 200 mg/dm²) and a late increased corrosion in case of all 3 Zry-4 variants after >about 300 d (400-500 mg/dm²), as Figure 4-11 shows. The reason for the different corrosion behaviour in different \sim 105 bar steam tests is not known. Eventually, it can relate to the fact that the autoclave tests performed by [Sabol et al., 1989 and 1994], were consistent with the ASTM practice and had a restricted specimen load and consequently less hydrogen content in the steam and eventually also a less effective degassing. Figure 4-12 compares the corrosion behaviour of 3 different Zry-4 lots in 360 °C water, 400 °C steam and 427 °C steam. It is interesting that improved Zry-4 in 360 °C water and 400 °C steam has about the same corrosion behaviour and that β -quenched Zry-4 is somewhat better than conventional Zry-4 at 400 °C but not at 427 °C.

It is certainly also interesting that the Nb containing Zr alloys (Zr2.5Nb, Zr1Nb, and ZIRLO (Zr1Sn1Nb0.1Fe) showed lower corrosion compared to Zry-4 in 316-360 °C water (Figure 4-10a and Figure 4-12b), but somewhat higher corrosion in 400-427 °C steam (Figure 4-11c and d). The relatively high corrosion rate of ZIRLO at \geq 400 °C is possibly a consequence of the significant decreased $\alpha/(\alpha+\beta)$ transition temperature from ~800 to ~600 °C by the alloying Nb content.



Figure 4-11: Autoclave corrosion test with ZIRLO, Zry-4 and Zr2.5Nb in 316 and 360 °C water and 400 and 427 °C steam [Sabol et al., 1989 and Sabol et al., 1994].



Figure 4-12: Autoclave corrosion results for different Zry-4 variants in 360 °C water, 400 °C steam, and 427 °C steam [Sabol et al., 1994].

A comparison of the weight gain versus time results, of different Zr alloys during corrosion at 350-360 °C indicates that the average corrosion correlates to the time respectively to the weight gain at transition. The average corrosion rate is low if the time to transition is long and respectively the weight is high, and vice versus.

To describe the corrosion behaviour accurately, several important data have to be deduced from the corrosion graphics, such as:

- the pre-transition characteristics (the exponent n and the constant a),
- the time to the 1st rate transition and the oxide layer thickness or the weight gain at the transition,
- the average corrosion after the 1st rate transition and
- the average late corrosion that may arise after long corrosion times in case of ZrSnFeCr alloys with a high Sn content and a low Fe content or a fine SPP size.

As pointed out previously for Zr alloys in the **pre-transition** range, the oxide thickness (Sox) growth via exposure time (t) was found to proceeds via a power law:

Sox=const.tn

with the **exponent n**, which is 0.2 for ZrFeCr and ZrCu, 0.3 for Zircaloy-type alloys and-0.4-0.5 for ZrNb alloys [Motta et al., 2008], followed by a transition after a certain oxide thickness ($2-5 \mu m$) and a power law on a cyclic basis.

A detailed analysis of the corrosion data in 350 °C hydrogenated water, is shown in Figure 4-13, revealing that the n value is 0.33 for Zr1.5Sn0.3FeCr, and 0.31 for the more corrosion resistant Zr0.5Sn0.3FeCr but much higher in case of Zr1Nb (0.39) and specifically for Zr2.5Nb (0.53) samples. The figure, furthermore, shows that the weight gain at transition is 34-36 mg/dm² (2.3-2.5 μm) in case of the ZrSnFeCr alloys and 56 respectively 75 mg/dm² (3.1 respectively 5.1 μm) in case of Zr1Nb and Zr2.5Nb.



Figure 4-13: ZrSn0.3FeCr and Zr2.5Nb cladding lot samples tested in 350 °C hydrogenated water [data from Figure 4-10].

A large program for the evaluation of the reason of the large variation in the corrosion performance was implemented during the extensive studies performed by dissertations at the Department of Mechanical and Nuclear Engineering at Pennsylvania State University, advised by Arthur T. Motta., e.g. [Motta et al., 2008], evaluating a large number of model Zr alloys by corrosion tests in 360 °C pure water, 500 °C steam, and 500 °C supercritical water. *The model alloys were chosen to highlight the role of alloy additions on the corrosion process*. Oxides formed on the model alloys were examined to identify oxide features that were characteristic of stable oxide growth (protective layers) or breakaway growth (nonprotective oxide). Detailed study of corrosion kinetics with many data points and characterizing of the structure of the oxide layers with advanced techniques were performed to relate oxide structure to corrosion kinetics and oxide stability.

In Table 4-1 characterisation data from several corrosion tests in water at 360-370 °C, normalized to 360 °C are shown, reported by [Broy et al., 2000; Sell 2014; and Garzarolli et al., 1991], based on ground + polished or electro-polished samples, and by [Motta et al., 2007; Yilmazbayhan et al., 2003; Couet et al., 2015], based on pickled samples.

The n values are in most cases below the parabolic value (0.5), as a consequence of the space charge, that develops in the barrier layer due to electron migration, formed by the oxide formation $Zr+2O^2 \rightarrow ZrO_2 + 4e^2$, from the M/O interface to the O/W-interface.

A change in the corrosion rate due to a loss of protectiveness occurs after formation of a uniform oxide of >1-5 μ m due to either an oxide transition to a new oxide, that recovers its protective character again or to a breakaway oxidation, where the oxide remains non-protective. The two processes arise from different degradation mechanisms. In case of the breakaway oxidation the formation of the monoclinic oxide structure becomes equiaxed, not stress reduced texture, creating a high compressive stress in the oxide layer , according to our understanding, due to a high H content at the O/M interface transition, affecting the oxide structure due to a significant reduction of the surface energy of the monoclinic oxide, whereas in case of the low cyclic corrosion, similar as in case of the initial pretransition corrosion, after the transition new fine tetragonal oxide is formed, which grows in case of the crystals with an optimum crystal orientation (inducing very little stress) to columnar monoclinic grains, resulting again in a protective oxide. As mentioned before, the rat -transition occurs, during cyclic corrosion, at an oxide thickness growth values of about 2-5 μ m, followed by repeated power law dependent corrosion cycles in pressurized water and high-pressure steam on corrosion-resistant zirconium alloys, e.g. alloys with >0.2% Fe or ≥0.5%Nb.

The <u>time to the 1st rate transition</u> is short (5-60 d) for Zr-Fe(Cr,V,Cu) alloys, if the Fe content is low, but becomes large (>500 d), if the Fe content is high (e.g. 0.4%), probably as a consequence of the Zr-FeCrV SPP, with delayed oxidation, bridging the M/O interface, reducing the local H content and increasing the thickness of columnar grains and optimizing their texture. The weight gain at the

transition increases with increasing time to transition (Figure 4-14), depending on material type. The lowest weigh gain at transition is observed in Zr alloys with 0-0.2% Fe. Zr alloy with 0.5-1.5% Cu+Mo additions have a higher weight gain at transition and the highest weight gain and longest transition time have ZrFeCr alloys with ≥ 0.4 Fe. The scatter-band for the Zr-Sn-FeCrV alloys is also at medium position. The time to the 1st transition decreases with increasing Sn content from ~ 230 days at 0.25-0.5% to ~ 100 days at 1.6% Sn, connected to a weight gain decrease at the transition from 40-50 to 25-35 mg/dm² (Table 4-1). The scatter in data may have different reasons, one is certainly the surface treatment (pickled, ground and polished, or electro-polished). In any case, the trend for Zircaloy type alloys is similar to the one reported by [Garzarolli et al., 1985a]. In case of the Zr-Nb alloys, the time to the 1st transition and the weight gain at the transition, depends at >0.4% Nb on the condition. If the condition is optimized, the time to the 1st transition is between 200 and 500 days and the weight gain at the transition is 49 to 70 mg/dm². ZrSnNbFe alloys have a lower time to the 1st transition (~ 120 days) than optimized Zr-Nb alloys, and a weight gain at the transition which corresponds to not optimized Zr-Nb alloys (49 to 20 mg/dm²)

Table 4-1: Corrosion behaviour of Zr alloys in 360 °C water, 400 °C steam, 500 °C supercritical water, and oxygen.

Material	Process	Corr.test	Pre tra	insition	Tr-time	Trnns-W.Gain	PT-corr.r.	(ma/dm²d) Start of la	e corr	HPUF	Reference
	temp.	temp. (°C)	Const. a	a Expon.r	n (d)	(mg/dm²/µm)	early	late	, time (d)	WG	(%)	
	°Ċ	/	350 & 37	′0°C data ∖	were no	ormalized to 360°(C by appliv	ation of a C	R value of	14200	ĸ	
Sponge Zr	580	360/water	8.5	0.2	3-60	Breakaway >0.8	-1.3 µm				~13	Couet 2011
Crystal Bar Zr	580	360/water	6.6	0.24	60	Breakaway >1.2	um	~10				Yilmazbayhan et al. 2005
Pure Zr	580	360/water		0.2	14	Breakaway >1.5	um				18	Couet et al. 2014a
Zr0.5Cu	580	360/water	13.6	0.17	230	Breakaway					~30	Cuet et al. 2014a
Zr1Cu	580	360/water	15.1	0.17	>270							Yilmazbayhan et al. 2005
Zr0.5-1Cu0.5Mo	580	360/water	13.8	0.18	130	Breakaway >3 m	m	> 10				Motta et al. 2008
Zr0.5Cr	580	360/water	non prote	ctive	5	Breakaway		12				Motta et al. 2009
Zr0.5Cr0.2Fe	650	360/water	11.8	17	55	Breakaway >1.5	μm	3				Motta et al. 2009
Zr1Cr0.2Fe	650	360/water	11.6	0.19	180	Breakaway >2 µ	ım	0.8	300	80		Motta et al. 2009
Zr0.2Fe0.1Cr (H)	720	360/water	10.2	0.2								Yilmazbayhan et al. 2005
Zr0.2Fe0.1Cr (L)	580	360/water	10.2	0.2	200	33	0.37					Yilmazbayhan et al. 2005
Zr0.4Fe0.2Cr (L)	580	360/water	9.8	0.21	>470	>48					~30	Couetet al. 2014
Zr0.4Fe0.2Cr (H)	720	360/water	9.4	0.22	>470	>46					~16	Couet et al. 2014
Zr0.2Sn		360/water	9.3	0.29	40	31						Yilmazbayhan et al. 2005
Zr1.2Sn		360/water	10.6	0.27	60	38						Yilmazbayhan et al. 2005
Zr0.5Sn0.2Fe0.1Cr	750°C/CW/PR	350/water	7.4	0.28	147	30	0.22	0.29	956	214	22	Sell 2012
Zr1Sn0.16Fe0.1Cr	RX. A=1E-17	370/water	6.5	0.35	156	38	0.31	1.15	298	104		Broy et al. 2000
Zr1Sn0.21Fe0.2Cr	RX. A=1E-17	370/water	7.6	0.31	213	40	0.25	1.15	369	97		Broy et al. 2000
Zr1Sn0.4Fe0.2Cr	RX. A=1E-17	370/water	9.5	0.29	227	46	0.20					Broy et al. 2000
Zr1Sn0.55Fe0.2Cr	RX. A=1E-17	370/water	6.8	0.37	233	51	0.17					Broy et al. 2000
Zr1.1Sn0.2Fe0.1Cr	750°C/CW/PR	350/water	7.7	0.3	94	30	0.31	0.44	739	235	24	Sell 2012
Zr1.5Sn0.2Fe0.1Cr sheet	650-700	360/water	8.6	0.32	106	38						Cuet et al. 2014
Zry-4 sheet		360/water			80	31	0.33				~24	Cuet et al. 2014
Zry-4 tube		360/water			140	36	0.25				~23	Cuet et al. 2014
1.5Sn Zry-4		360/water			28	23	0.5	0.71	560	320		Yilmazbayhan et al. 2005
1.7Sn Zry-4	750°C/CW/PR	350/water	6.3	0.31	120	28	0.35	0.67	739	264		Sell 2012
Zr0.2Nb		360/water	6.4	0.43	210	34						Yilmazbayhan et al. 2005
Zr0.4Nb		360/water	5	0.52	210	55	0.24					Yilmazbayhan et al. 2005
Zr0.4Nb		360/water		0.49								Couet et al. 2015
Zr0.5Nb, tube	580/CW/SR	360/water			150	Breack away						Sabol et al. 1989
Zr1Nb		360/water	5.9	0.45	240	72						Yilmazbayhan et al. 2005
Zr1Nb, tube	570°C/CW/SR	350/water	6.5	0.37	244	50	0.14					Sell 2012
Zr1Nb	720°C	360/water	6.2	0.47	75	47	0.55					Couet et al. 2015
Zr1.5Nb		360/water	5.8	0.44								Yilmazbayhan et al. 2005
Zr2.5Nb, tube		350/water	6.9	0.37	488	68	0.12				12	Sell 2012
Zr2.5Nb, tube	580	360/water	7.3	0.36	175	47	0.23				11	Couetetal. 2014
Zr2.5Nb, tube		360/water			112	36	0.21					Yilmazbayhan et al. 2004
Zr2.5Nb0.5Cu	580	360/water	3.8	0.47	200	46	0.22				~35	Couet et al. 2014
Zr2.5Nb0.5Cu		360/water			112	36	0.18					Yilmazbayhan et al. 2004
Zr2.5Nb		360/water	6.5	0.4	120	39						Yilmazbayhan et al. 2005
Zr0.4Sn0.2Nb		360/water	5.9	0.43	210	32						Yilmazbayhan et al. 2005
Zr0.4Sn0.4Nb		360/water	7.1	0.39	120	38						Yilmazbayhan et al. 2005
Zr1Nb1Sn0.1Fe sheet	580	360/water	6.2	0.41	105	42	0.34				~18	Couetet al. 2014
Zr1Nb1Sn0.1Fe tube		360/water	7.4	0.37	130	45	0.25				17	Couet et al. 2014
Zr1Nb1Sn0.1Fe tube	580/CW/SR	360/water			84	34.8	0.33					Yilmazbayhan et al. 2004
Zr1.1Sn0.2Fe0.1Cr	750°C/CW/PR	400/steam		0.29	48	43	~0.2				19	Sell 2012
Zry-4, pickled		400/steam		0.29	84	39	0.45					Garzarolli et al. 1991
Zry-4, pickled		400/steam		0.35	54	34	0.45					Garzarolli et al. 1991
Zr1.7Sn0.2Fe0.1Cr	750°C/CW/PR	400/steam		0.3	24	34	~0.4					Sell 2012
Zr1Nb, tube	570°C/CW/SR	400/steam		0.39	271	93	~0.2					Sell 2012
Zr2.5Nb, tube		400/steam		0.34	415	95	~0.2				19	Sell 2012
Zr0.4Fe0.2Cr		500°C/SCW		0.33	>150							Motta et al. 2009
Zr1Cr0.2Fe		500°C/SCW		0.34	60	160	3					Motta et al. 2009
ZrNb		500°C/SCW		0.67								Motta et al. 2009
Zry-4, electropolished		400°C/O2		0.5	20	31	1.8					Garzarolli et al. 1991



Figure 4-14: Weight gain at transition for different Zr alloys in 360 °C water. Data from Table 4-1.

As already pointed out, the mostly diagnostic value for the corrosion behaviour of a certain Zr alloy is the *average post transition corrosion rate*. This rate depends on (1st) the exponential n value of the barrier layer growth behaviour (cyclic pre-transition) and (2nd) the time and the layer thickness between the repeated transitions. The average corrosion rate after the 1st transition appears to be related to the time to the 1st transition (Figure 4-15), although there might be somewhat different correlations for Zr-FeCr alloys, ZrSnFeCr alloys, and ZrNb(Fe) alloys.



Figure 4-15: Post transition corrosion rate versus the time to the 1st transition for different Zr alloys in 360 °C water. Data from Table 4-1.
5 General on in Reactor Corrosion and Hydrogen Pickup

5.1 Characteristics of different reactors

A detailed description of the different reactor types, their fuel assembly designs, and in reactor corrosion behaviour is given in the Volume I of this report. The most important characteristics for the corrosion behaviour are the temperature (Table 5-1). The peak temperature of the fuel rod cladding depends on the heat flux and the system pressure, which is ~155 bar in PWRs, ~100 bar in CANDU PHWRs, and 70 bar in BWRs. Consequently, the peak temperature on the outer side of the cladding extends up to ~350 °C in modern PWRs, up to ~330 °C in CANDU PHWRs, and up ~300 °C in BWRs.

Reactor Type	Coolant entrance temp. (°C)	Coolant outlet temp.(°C)	System pressure (bar)	Max. FR heat flux (W/cm²)	Max cladding temp. (°C)	
CANDU	250-260	285-312	100			
RBMK	270	284	67			
BWR	220-275	286	70	110-135	310	
PWR	285-293	316-327	156	116-148	350	
VVER 440/1000	270/290	298-320	125/165	156/128	325/350	
ANT International 2020						

Table 5-1:	Operation temperatures in different reactor types.
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Furthermore, **the water chemistry is different** in PWRs and CANDU PHWRs, where the steam, used for the turbine electrical production, is produced in a steam generator, and the coolant keeps the system pressure and the temperature increases in the core from ~290 °C to ~320 °C in PWRs and from ~250 to ~285 °C in CANDU PHWRs. To minimize the oxygen content in the water formed in the core by radiolysis 2-4 ppm (25-50 cc/kg) H₂ is added in PWRs. However, a complete suppression of the radiolysis in the core is not possible. Thus, the radiolytic formed H₂O₂ content in the coolant (Figure 5-1), and the electrochemical potential in the core is significantly higher than out reactor (Figure 5-2), even at a very high hydrogen content in the water.



Figure 5-1: Modelling calculations: Influence of H₂ on H₂O₂ and O₂ concentrations in the PWR core under power operation conditions, after [Henshaw et al., 1998].



Figure 5-2: In-pile measured and calculated stainless steel ECP in the PWR plant and INCA loop in Studsvik Data from [Christensen et al., 2000] and [Lundgren, 2004].

A particular aspect in case of PWRs, where the maximum allowed power is controlled by in core measurements (e.g. Siemens PWRs and modern PWRs), is a FRs exposure to so high heat flux, that a significant void fraction is formed at the upper end of the FR (Figure 5-3). In case of a significant void fraction some H can be stripped off from the water to the steam bubbles dropping down the hydrogen content in remaining water (Figure 5-4). [Garbett et al., 1998] concluded that the hydrogen content remains high enough to keep the radiolysis moderate. However, the concentration of H_2 in the surrounding of the steam bubbles becomes somewhat lower resulting in a local higher O_2 content than

the average equilibrium values in the coolant water, as shown in Figure 5-5. Oxygen is also taken up by the bubble increasing its O_2 content, consequently. The radiolytically formed oxygen also concentrates in the void bubbles and may lead to high local oxygen induced corrosion close or in the plenum area, if the cladding is sensitive on oxygen in the coolant, as ZrNb alloys are.



Figure 5-3: Calculated Void Fraction for Siemens Konvoi and Vorkonvoi PWRs.



Figure 5-4: Effect of sub-cooled nucleate boiling on dissolved hydrogen concentrations in the water according to calculations of [Garbett et al., 1998 and Zmintko et al., 1999].



a) H₂ concentration profiles



b) 0₂ concentration profiles

Figure 5-5: H₂ and O₂ concentration profiles at different times around 10 µm bubbles, at a bulk water H₂ content of 40 cc cm³/kg. [Dickinson et al., 1992].

Most Zr alloys are not sensitive against a moderate oxygen content in the water, but ZrNb are very sensitive. During tests with experimental fuel rods, performed under WWER conditions in the MIR reactor under surface boiling and an oxygen content in the water of 20 ppb, a steep increase of corrosion (nodular type) was observed at >110 W/cm² due to a critical void/oxygen content in case of E110 (Zr1Nb) claddings, whereas the less oxygen sensitive alloy E635 (Zr1.2Sn1Nb0.35Fe) did not reveal any corrosion acceleration, only the moderate temperature induced increase



Figure 5-6: Steep increase of E110 corrosion at >110 W/cm² due to boiling/void formation under WWER conditions [Konkov et al., 1999].

In several Siemens PWRs an void induced increased corrosion has been observed on the hottest FRs with M5 (Zr1Nb) cladding, e.g. [Schmidt & Hoffmann, 2007].



a) Normal oxide thickness at peak temperature

b) increased corrosion

Figure 5-7: Normal peak corrosion behaviour of M5 in PWRs (a) and increased corrosion at the upper FR end in KKP in 2005 (b) [Schmidt & Hoffmann, 2007].

Another species, which suppress the radiolytic formation of O_2 and H_2O_2 is ammonia. Radiolysis forms ammonia in the coolant, if the N content in the water is high, respectively decomposes ammonia, if the NH₃ content is high via the equation:

Equation 5-1: $2NH_3 \leftrightarrow N_2 + 3H_2$

A steady state level of 1.75 ppm NH₃ corresponds to a H₂ content of 25 cc/kg and a N₂ content of 35 cc/kg [Solomon, 1977]. In WWERs hydrogen is kept between 2.6 and 5.3 ppm (30-60 cc/kg) and the NH₃ content is typically >5 ppm (6-30 ppm) [Yurmanov et al., 1997]. Also, in western type PWRs some NH₃ is often seen, if the cover gas in the Volume Control Tank (VCT) consists mostly of nitrogen or excess hydrazine is used during start up. Once the ion resins have reached NH₃ equilibrium NH₃ concentrations can reach values up to 2 ppm in the coolant.

PWRs contain boric acid for reactivity control. The concentration is reduced with time during a fuel cycle, usually being near zero at the end of cycle. The initial boron concentration is 900 to 1800 ppm and is reduced rapidly over the first few days of the cycle and afterwards approximately linearly at ~ 3 ppm/d. Some PWRs use B¹⁰ enriched boric acid. These plants operate with lower total B concentrations. Because acidic coolant conditions result in an increased attack of the circuit materials LiOH, or for Russian WWERs KOH, is added to render the coolant slightly alkaline. LiOH, however can affect corrosion of the Zr alloy cladding as was reported in Section 4.6.4. For long time, the optimum pH at 300 °C was 6.9, the initial Li content at ≤ 2.2 ppm and decreased over the cycle to ~ 0.5 ppm. In the last decades the optimum pH increased up to 7.1-7.4 and the maximum initial Li content increased up to 3.5-5 ppm. In Figure 5-8 the different operational regimes for Li and B are shown.



Figure 5-8: Different operational regimes for Li and B.

In the late 1990ies it was started to inject Zn (5-15 or 25-50 ppb) to the coolant of PWRs with the goal to lower the shut-down dose rate and to reduce the corrosion of system materials.

The Fe content in the coolant, resulting from corrosion of structural components, is not so different among the different reactor types under optimized coolant conditions. The total Fe content is normally low in Siemens PWRs (0.5-3 ppb) low in WWERs is (0.2-3 ppb) and low in plants with Inconel SG tubes (1-10 ppb) [Dickinson et al., 2002]. However it can happen that half of Fe and Ni exists in dissolved form. The corrosion products deposit to a large fraction on fuel rods as CRUD. Highest CRUD loads are generally formed in the upper third of the core, at the peak temperature position of the fuel rods, especially if they experience subcooled boiling. If the corrosion products contain mostly Fe, the CRUD has low density and consists of relatively loose particles. If, however, the content of bivalent metals (Ni and Zn) in the coolant is high the CRUD can become quite dense and may contain boiling chimneys. The fuel rod behaviour is only very little affected by a loose CRUD, but can be significantly affected by a dense CRUD, due to due to higher surface temperatures, increasing the local corrosion rate and due to concentration of boric acid, lithium hydroxide, and other solutes within the CRUD causing axial offset anomalies (AOA) of the power profile. AOA occurred in some cases in high duty PWR cores with Inconel (high Ni) steam generator tubes with Ni rich deposits. An important parameter for these occurrences is that B increases the soluble Fe and Ni content significantly [Cubitt et al., 2004].

Besides the CRUD induced effects on Zr alloy fuel rod cladding corrosion, certain impurities in the coolant can cause an increased Zr-alloy corrosion above a critical concentration. Besides the impurities that increase the Zr alloy corrosion out of pile, such as F and Cl, certain impurities may increase the

corrosion as a consequence of radiolytic effects. A particular impurity is sulphur, which may result especially from defects of clean-up systems. In a hydrogenated environment H₂SO₄, which does not have a mayor negative effect on Zr alloy corrosion, will be changed by radiolysis to H₂S, which can increase the Zr-alloy corrosion significantly. Another species is carbon. According [Bibilashvily et al., 1992 and 1994]; C containing species from ion-exchange resin filter failures or decontaminations caused in VVERs local fuel rod failures by superheating due to an increased hydraulic resistance via insulating CRUD. Often nodular corrosion was observed under C-deposits probably caused by the microenvironment formed under the C-deposits.

The **Boiling Water Power Reactors** (Open Cycle), operates at a system pressure of 70 bars. The reactor core is contained in a pressure vessel through which condensate supplied by a feed water pump is circulated and allowed to boil. The coolant enters the core with a temperature 272 to 278 °C and leaves the core as steam-water mixture with a temperature of 286 °C. Steam is separated from the coolant within the pressure vessel, flows to the turbine, and then to the condenser which is built either from brass, SS, or Ti tubes, what affects significantly the metal impurity content of the coolant. The condensate is degassed in the condenser and cleaned in a filter demineralizer or mixed-bed filter. Afterwards heating occurs in low pressure pre-heaters to about 140 °C and further on in high pressure pre-heaters to about 220 °C. In modern plants, the so-called forward-pumped plants, some fraction of the condensate is returned uncleaned to the feed water line after the low-pressure pre-heaters. Under normal water chemistry (NWC) conditions nothing is added to the coolant. Corrosion products from the feed water line, the turbine (particularly in the case of forward pumped plants), and the condenser, depending on the efficiency of the condensate cleanup system, are entering the reactor. Since 1986 Zn injection to feed water (FW) of BWRs is performed (5-10 ppb). This water chemistry (DZO) is based on the observed dose rate increase after replacement of the brass condenser by SS or Ti, which was traced back to the reduction of the reactor water Zn content.

BWRs are normally open cycle reactors with direct connections between the reactor and turbine in the steam system, the condenser and the reactor in the feedwater system. If nothing is added, an oxygen content of 125-500 ppb is measured in the reactor coolant in the water sample line before the reactor cleanup system, and 20-30 ppm in the steam. This oxygen is formed by radiolysis in the water phase within the core due to stripping off of the hydrogen. In early closed cycle BWRs the oxygen in the reactor coolant had reached equilibrium values of 1000 to 2000 ppb. As calculations indicate the oxygen content between the fuel rods may be even less than in the rector water, before the reactor clean up system, however, short living radical species, especially H_2O_2 , may reach quite high concentrations within the fuel. These oxidizing radicals decompose after leaving the core to O_2 increasing the oxygen content of the reactor coolant in a short time. At the position of the reactor sampling line before the reactor cleanup system the H_2O_2 concentration is usually very low. The corrosion potential in a water with 300 ppb oxygen would be out-of-pile at 0 to 0.1 V SHE. Within the core of BWRs with NWC even higher values have been found (0.1 to 0.3 V, SHE), what reflects the high red/ox potential of the H_2O_2 , [Indig, 1989].

Since the late 1980ies several BWRs were operated under hydrogen water chemistry (HWC), where hydrogen is added (1-2 ppm to feed water) for the most part of operation, to reduce the risk of inter granular stress corrosion cracking (ISCC) in structural materials of the water circuit (stainless steels and Inconel). HWC was not effective in some BWRs and has a big disadvantage to significantly increase the activity of the steam.

Since the late 1990ies several BWRs have applied noble metal chemistry application (NMCA). For NMCA a few kilograms of Pt and Rh are added during a reactor shut down (with the goal to be plated out over the whole system surface) and a small amount of hydrogen (0.15-0.30 ppm) is injected during the most of operation time. NMCA is believed to be more efficient to mitigate ISCC and needs less hydrogen addition. It increases the steam activity less than HWC. In mid 2000s the noble metal application method was changed to online noble chemistry (OLNC), where small quantities of Pt (<1µg/cm² of active fuel rod surface) are injected to the reactor coolant over 10-14 days with the plant at full power. Under HWC the profile of the radiolytic species changes with increasing H₂ addition between the fuel rods especially in the lower part and in the water bypass between the channels respectively within water rods over the whole length. As obvious in the case of boiling channels, H₂ addition cannot suppress radiolytic formation of oxidizing radicals due to the fact that all H₂ is stripped off to the steam. Electrochemical measurements in BWRs under HWC have shown a significant reduction of the corrosion potential only

in the bypass channel whereas in the boiling channel a significant reduction was only seen in the lower part [Indig, 1989].

The Pt and Rh added under NMCA respectively the Pt added under ONMC deposit not only on the structural SS components, but with preference also on the fuel rods. If these metals would precipitate locally on a Zircaloy-2 surface a large HPU might occur locally. In late 2001 to 2003 in the US Browns Ferry BF-2 and BF-3 reactors FR failures occurred in the second respectively third FA irradiation cycle in the cycle after introduction of the NMCA. A hot cell post-irradiation examination (PIE) program on fuel rods from BF-2 showed numerous heavily hydrided regions at the upper elevations (>2.3 m) of the defective rods (Figure 5-9). To clarify whether the heavily hydrided regions were formed after the defect or were the primary reason of the defects, sound rods with heavy corrosion were also carefully examined. In one of the three examined intact fuel rods excessive nodular corrosion, spallation, and local hydriding were seen at the axial position were the failures were observed in defective fuel rods, near 2.4 m and above, indicating that the primary failure cause was associated with tight cracks in heavily hydrided regions. In the others intact fuel rods only oxide spallations but no localized hydriding were found [Lutz et al., 2015]. Furthermore, high Li levels were observed by SIMS line scans on the oxide surface of failed BF-2 rods, lower Li level in sound BF-2 rods with lower corrosion and even lower Li surface contents in a sound rod from another plant. Sulphate, chloride, Ca values were also higher at BF-2 FRs relative to a FR from other plants. According to the authors, these findings indicate that environmental effects might be responsible for the enhanced corrosion. It was assumed that hydrogen will become locally concentrated at positions with large oxide spallations due to the temperature differences caused by the rather high heat flux, similar as it was observed in PWR fuel. The authors believe that different coolant impurities created high corrosion and HPU and caused the formation of massive hydride layers and oxide spallation that led to defects.

Fuel rod failures due to the formation of large localized hydride blisters have been observed in PWR fuel rods operating at \geq 70 W/cm² at oxide layers of >140-160 µm and average H contents of \geq 1000 ppm [Garzarolli & Stehle, 1987]. Only under such extreme condition, hydride blister, formed by temperature gradient induced redistribution, have been seen that exceed a significant fraction of the cladding wall. Thus, the root cause proposed by [Lutz et al., 2015] for the BF-2 failures needs very likely some other aggravating conditions. One aspect is, that deposition of Pt and Rh on the fuel rod surface during the 1st NMCA treatment performed during the outage before the cycle started, 9-7 months after the start up, might increase the HPU, due to a pickup of catalytic hydrogen. A severely accelerated HPU however, could only occur if the protective character of the oxide layer would be locally disturbed. Very likely, NMCA is not responsible for the observed enhanced corrosion, because in BF-3 a sibling rod of the failed three cycles burned rods, discharged after one cycle, without being exposed to NMCA water chemistry, already exhibited substantial accelerated corrosion at both the 1-2 m and 2.5-3 m elevations. However, once accelerated corrosion has occurred, the tendency of oxide spalling during cooling down after the shutdown, may eventually open up locally a metallic surface, where noble metals could deposit during the NMCA treatment. At such positions hydride blisters would be formed. Such a phenomenon would not occur under OLNC, the technique which is mostly applied today.



Figure 5-9: Etched cladding cross-section from failed BF-2 reload 10 at 2398 mm showing cracks within massive hydride localization near primary failure location [Lutz et al., 2015].

BWR type nodular corrosion depends significantly on water chemistry (O-content and probably N-, Na-, Cr^{6+} -content, Fe/(Ni+Zn)-ratio). [Shimada et al., 1997] reported on corrosion performance of Zr-alloys in a simulated BWR environment in the Halden BWR corrosion test loop. The mini-autoclave tests showed that nodular corrosion could be formed especially around the onset of boiling region in the fuel rod. The nodular corrosion increased with oxygen additions (250 -> 750 ppb) and Zn(NO₃)₂ addition (250 ppb), whereas 250 ppb Cu(NO₃)₂ and 750 ppb CuSO₄ suppressed nodular corrosion. A strong correlation between the Cr⁶⁺ content and nodular corrosion were also found in an evaluation of water chemistry effects on in-BWR Zr corrosion by AREVA (Figure 5-10).





High concentrations of sodium-hydroxide can result even in fuel cladding corrosion defects, if released from the demineralizer resins in larger concentrations [Kobayashi et al., 1997]. The release rate depends on cleanup system, operation temperature, resin treatment, and type of resin.

The **Russian BRMK** reactors use graphite as moderator and light water as coolant to produce steam and can be considered from chemical viewpoint, as similar with the typical light water BWR. However, they have a lower power rating and neutron flux.

The **Canadian pressurised heavy water reactors (CANDU reactors)**, unlike light water pressure vessel reactors, has a core that comprises of hundreds of small (100 mm) diameter pressure tubes containing natural uranium fuel. The pressure tubes through which the pressurized heavy water flows, are separated from each other by a low pressure/low temperature heavy water moderator contained in a cylindrical tank. The CANDU system contains also steam generators, a pressurizer and cooling pumps. The later plants have primary coolant boiling in the reactor core with steam qualities up to 4% at the fuel channel outlet. The necessary content of H₂ respectively NH₃ to supress O₂ and H₂O₂ in heavy water reactors is significantly lower than for light water reactors. Heavy water is more stable than light water to radiation and γ -ray cause more efficient recombination of D₂ + D₂O₂ than H₂ + H₂O₂ [Hart et al., 1956]. Test in NRX reactor showed that oxidative radiolysis products can be supressed by deuterium addition of 0.5 cc/kg [Elliot & Stuart, 2008], which is a much lower value than that relevant for light water reactors. A deuterium concentration of 3 to 10 cc/kg (0.3-1 ppm H equivalent) is used to reduce dissolved oxygen to acceptable low values. In the CANDU reactors there is no soluble poison (boron) present in the D₂O. Alkalinity is achieved by addition of lithium hydroxide. A lithium value of about 1

ppm is added to raise the room temperature pD value to 10.3 - 10.8. In case of the CANDU reactor the component with the most critical corrosion aspect is the pressure tube, operating only at a temperature of 250-305 °C, but for several decades. For the early pressure tubes Zircaloy-2 was used, which showed a quite high corrosion after 10 years of operation and was changed to Zr2.5Nb in the 1970ies.

As far as the $\underline{O_2}$ and $\underline{H_2}$ gases are considered, the basic effect is the influence of these gases on the **corrosion potential of Zr alloy in high temperature water**. These gases govern the electrons, oxide vacancies, protons, and oxide ions at the barrier layer surface. [Rishel et al., 2008] studied the effect of the environment on the electrochemical potential in reactor (in a loop in the Halden reactor) of different preoxidized (in air at 565 °C to 25-30 µm) RX Zircaloy-4 samples with platinum as a reference. The corrosion potential of the oxidized Zircaloy-4 samples as well as the potential gradient over the oxide layer was measured at different temperatures in water under pH control with LiOH with:

- a hydrogen overpressure of 25-50 cc/kg (5 ppm H₂),
- without hydrogen or oxygen additions,
- with 400 ppb oxygen and
- with 5000 ppb oxygen

Figure 5-11 shows the measured electrochemical potentials for different gas contents and temperatures under a fast neutron flux of 0.5-2.5·10¹³ (n/cm²·s). The corrosion potential in mV versus the standard hydrogen electrode (SHE) is very low (between -800 and -1000 mV, SHE), if hydrogen is added (see left part of red dashed curve in Figure 5-11), and decrease somewhat with increasing temperature. These values are significantly lower than the reported by [Christensen et al., 2000] (corrosion potential is about -0.4 V SHE versus Pt) measured in 290 °C water with 1600 ppm B, 2 ppm Li, and a hydrogen content of 16 cc/kg. The difference may be due to some extend due to pH, but other factors nay also contribute.

If the oxygen content is considerable, the corrosion potential increases significantly but much less than the potential that would be expected at the outer side of the oxide layer respectively a thin dense oxide layer, that should be at +50 to 170 mV (see green curve in Figure 5-11). The potential gradient over the oxide is a small negative value (-10 to -60 mV) in hydrogenated water but becomes large (-320 to -720 mV) in oxygenated water. This is different to out-of-reactor results, which show only a small negative potential gradient over the oxide layer under all conditions, e.g. [Garzarolli et al., 1982]. The reason for the large negative potential difference over the oxide in reactor is according [Rishel et al., 2008] that the corrosion hydrogen reacts in the outer porous part with oxygen from the coolant by radiolysis and reduces its content at the outer surface of the barrier layer. The pore size and the pore volume in the air formed oxide is certainly much larger than in oxide layers formed in water. Thus, the radiolysis effect and the potential drop over the oxide layer in oxygenated water should be even much larger in oxide layers formed in reactor with oxygenated coolant. This is certainly an important aspect also for the hydrogen pickup of Zircaloy-2 at high burnups, as will be discussed later.

6 Corrosion in BWR/RBMK

6.1 General

6.1.1 Early observations

There are two **different types of reactors operating under oxygenated coolant conditions**:

- The Boiling Water Reactor (BWR), developed originally by GE, operating at a system pressure of 70 bars, with a reactor core contained in a pressure vessel through which H₂O condensate, supplied by a feed pump, is circulated by pumps and allowed to boil. The coolant enters the core with a temperature 272-278 °C and leaves the core as steam water mixture (~14% mass content) with a temperature of 286 °C. The average fast neuron flux in the core is 4-7·10¹³ n/cm²s (>1MeV). The maximum fuel rod surface temperature is 285-305 °C. The O₂ content in water coolant is normally between 200 and 400 ppb.
- The RBMK developed by the Russians is a boiling pressure tube reactor with graphite moderator, operating with H₂O coolant entering with 270 °C and 67 bar in the pressure tubes containing fuel assembly, forming 284 °C steam with a mass content of ~14%. In difference to the BWR the average fast neuron flux in the core is only $2 \cdot 10^{13}$ n/cm²s (>1MeV). The maximum fuel rod surface temperature is ~290 °C. The O₂ content in the water coolant is only <20 ppb.
- Many tests in oxygenated coolant were performed in the test reactor HBWR (Halden Boiling Water reactor) for safety-focussed research into materials, fuel burnup, and fuel behaviour in prolonged operating. The (HBWR) was a natural circulation boiling reactor. The maximum power was 25 MW (thermal), and the water temperature 240 °C, corresponding to the operating pressure of 33.3 bar.

Zircalopy-2 has been originally selected for BWR fuel rod cladding, whereas for the RBMK E110, a Zr1Nb alloy, was applied. For structural components of BWRs Zry-4 and Zry-2 have been used and for the pressure tubes of RBMK E125, a Zr2.5Nb alloy. For the HBWR FR cladding mainly Zry-2 was used.

RBMKs operate at a rather low neutron flux of 1-2·10¹³ n/cm²s (>1MeV). For RBMKs **Zr1Nb (E110)** are used for the fuel rod claddings and **Zr2.5Nb (E125)** for the pressure tubes. [Markov et al., 2010] reported on PIE of eight RBMK-1000 fuel assemblies. PIE showed that a very large oxide film thickness forms on RBMK fuel rods with E110 cladding on the outer surface (Figure 6-1) especially at positions under stainless steel spacer grids. *This PIE result clearly reveals that a Zr1Nb alloy (without any Sn) is very sensitive to in reactor corrosion in oxygenated water*.





Zr1.3Sn1Nb0.35Fe (E635) was tested as a potential alternate FR cladding.

Zr1Nb and Zr2.5Nb are sensitive against oxygen in the coolant and form a very thick nodular oxide especially on positions close to stainless steel spacers, as obvious from Figure 6-2. Zr1.3Sn1Nb0.35Fe exhibits a much lower corrosion in RBMKs.





In case of Zr1Nb cladding, nodule nucleation starts in RBMK at <130d, [Biblilashvili et al., 1996] and in case of Zr2.5Nb pressure tubes, after <400 days (< $7 \cdot 10^{20}$ n/cm²), [Kovyrshin et al., 1999]. Zr2.5Nb seems to show an even larger nodular corrosion tendency compared to that of E110. After 800d (~ $1.5 \cdot 10^{21}$ n/cm², >1MeV) nodules with a diameter of 1-2 mm and a depth of up to 100 µm, exist [Kovyrshin et al., 1999] (Figure 6-3).



Figure 6-3: Nodular corrosion of Zr2.5Nb in RBMK-1000, [Kovyrshin et al., 1999].

According [Bibilashvily et al., 1996/1998], oxide thickness measurements of fuel rods in RBMK-1000 reactor Leningrad (Table 6-1) showed a uniform dark-coloured 10-20 µm thick oxide film on the Zr1Nb cladding and also nodular corrosion, drastically increased under spacer grids (SG) in spite of the rather low neutron flux (~1.3·10¹³ n/cm²s, >1MeV). The uniform corrosion of Zr1Nb and of ZrNb1Sn0.35Fe (tested as potential alternative for future cladding and pressure tubes) was rather low due to the rather low temperature, but drastically increased (ca 3 × higher than Zry-2 in BWR, 10 × higher than Zry-4 out of pile or Zr1Nb out of pile in 0 free water, but similar as Zr1Nb out of pile in oxygen containing water (see Figure 5-46). Also, the nodular corrosion and shadow corrosion of Zr1Nb mas very high, similar as the extreme values observed in BWR with Zry-2. The shadow corrosion of ZrNb1Sn0.35Fe, was significantly lower.

Table 6-1:	Corrosion behaviour of fuel rod claddings operated in RBMK-1000 (Leningrad) [Bibilashvili et al.,
	1996/1998].

Cladding Material	Expos. Time (d)	Burnup (MWd/kgU)	Unif. oxide thickness (µm)	Max. nodular oxide thickness (μm) betw. SG / at SG	H-content (ppm) betw. SG / at SG
Zr1Nb	160	1.3	10-20	40 / 150	30-60 /
Zr1Nb	1100	9.9	10-20	60 / 180	100 /
Zr1Nb	1210	19.3	15-20	130 / 380	110 / 150
Zr1Nb1Sn0.4Fe	1060	11.4	10-20	0/0	75 /
Zr1Nb1Sn0.4Fe	1210	19.3	15-20	0 / 100	175 / 175
		·	·	·	ANT International 2020

[Amaev et al., 1971] showed the extent of the sensitivity of Zr1Nb (E110) Zr2.5Nb (E125), Zr2.5Nb0.5Cu, Zr1Sn0.5Fe, Zr0.7Fe0.7Ni, and Zr1Sn1Nb0.5Fe (E635) to oxygen in water in the absence of irradiation (Table 6-2). **Obviously the Zr1-2.5Nb alloys and Zr2.5Nb0.5Cu are very sensitive against oxygen in water/steam at >1 ppb. Irradiation has no effect on theses alloys, but it has a significant effect in case of Nb free alloys Zr1Sn0.5Fe and especially in case of Zr0.7Fe0.7Ni. In case of Zr0.7Fe0.7Ni the hydrogen pickup during corrosion under irradiation was much higher (1160 ppm) than out-of-reactor similar to the behaviour for the other alloys in reactor and out-ofreactor (46-89 ppm). This extreme HPU of Zr0.7Fe0.7Ni in reactor is very likely connected with the fact, that once an outer porous oxide film has formed, the O is fully consumed by the hydrogen (corrosion product) via radiolytic reactions. Consequently, the corrosion potential at the outer side of the dense barrier layer becomes so low, that the Ni remains fully metallic and can lead to a metallic bridging of the barrier layer for H ions and to an extreme HPU, what also degrades the corrosion resistance.**

Allov	Condition	Without irradiation				3E13 n/cm ² .s
		static	static	22% steam	22% steam	22% steam
O ₂ content:		<0.1 ppb	~0.5 ppb	~3 ppb	~6 ppb	~15 ppb
Zr1Nb	580 °C/5h 700 °C/0.5h	~20	25	57 62	159 160	176 225
Zr2.5Nb	500 °C/5h 580 °C/5h 700 °C/0.5h 450 °C/24h	23	27	78 80 122 279	135 108 190 50- 300	91 86 53
Zr2.5Nb0.5Cu	500 °C/5h 500 °C/24h	38	48	116 41	85 65	62 53
Zr1Sn0.5Fe	750 °C/1.5h		~20		37	102
Zr0.7Fe0.7Ni	500 °C/8h 600 °C/1h 750 °C/1.5h		20		25 31 17	600 600 610
Zr1Sn1Nb0.5Fe	550 °C/3h 750 °C/1.5h		~20		38 44	44 46
ANT International 202						ANT International 2020

Table 6-2:	Effect of Oxygen in the water/steam on corrosion weight gain after 3500 h of Zr alloys in NBU-Loop
	(280 °C) and autoclaves (300 °C), [Amaev et al., 1971].

For boiling water reactor (BWR) fuel rod (FR) claddings Zry-2 was originally selected, whereas for structural components of BWRs, Zry-4 and Zry-2 have been applied. Due to the relatively low operation temperature, the normal uniform corrosion rate of Zry-2/4 is rather low. The uniform oxide thickness is <20 μ m, and the corrosion hydrogen pickup (HPU) has historically been rather low (typically <100 ppm) even at high burnups.

As the early examinations showed, in BWR the uniform corrosion rate of Zry-2 FR cladding is enhanced compared to that for out-of-reactor tests, already from the beginning of irradiation (Figure 5-43, Figure 5-46, and Figure 5-47 in Section 5.4.1, and Figure 6-4). Interesting is that the uniform corrosion does not increase significantly with increasing neuron flux as Figure 5-46 shows. Figure 5-46 and Figure 6-4 show furthermore, that **binary ZrNb alloys (Zr1Nb and Zr2.5Nb) exhibit a much higher corrosion increase** compared to the out of pile corrosion of these alloys in 0 free water. In 0 containing water the ZrNb alloys exhibit also a very high corrosion in out-of-reactor tests, even higher than in BWR. This heavily increased corrosion of ZrNb alloys is very likely due to a very large volume increase induced by the delayed oxidation of the dissolved Nb atoms and the β -Nb SPPs. Under irradiation, the Nb content of the large SPPs decreases and the dissolved Nb content in the Zr matrix decreases as a consequence of the formation of very fine Nb containing SPPs because of the much lower than the typical value during the fabrication heat treatment, solubility of Nb at operation temperature.



Figure 6-4: Corrosion of Zircaloy and Zr2.5Nb in BWR and out-of-pile in water [Garzarolli et al., 1996a].

A similar irradiation increased corrosion of Zry-2 was also observed with coupons and FR claddings in the HBWR at 240 °C at a very low fast neutron flux of 7.10⁹ n/cm²-s and 3.10¹² n/cm²-s (much lower than in BWR). The increased corrosion in water in HBWR (Figure 6-5) shows similar oxide thickness growth behaviour than observed in BWR (Figure 5-46) with an increase of the factor of 2.5 to 8, compared with the corrosion behaviour without irradiation. The time exponential slope n is with ~ 0.6 significantly higher than out-of-reactor value of ~ 0.2 . The rather low out-of-reactor slope, which usually should be ~ 0.33 , is probably a consequence of a rather high initial corrosion due to the Fluorine contamination during the pickling step of manufacturing. In any case the corrosion of Zry-2 in water, in HBWR at 240 °C, operating with heavy water, is similar as in BWR at 280 °C in spite of the much lower neutron flux ($0.7-3\cdot10^{12}$ in HBWR versus ~ $5\cdot10^{13}$ in BWR) what indicates that the irradiation effect is not governed by the fast neutron flux but more likely by γ – irradiation. The increased exponential slope in water in HBWR indicates that a mayor effect of the irradiation is an increased diffusion of oxygen ions into the dense barrier layer. It is also worth mentioning, that corrosion in steam is increased only slightly much less than the corrosion in water. Probably, in case of pickled samples, a thicker outer porous layer is formed, that reduces the corrosion potential by radiolytic reactions with corrosion hydrogen.



Figure 6-5: Corrosion of Zry-2 in different environments (water, steam, different neutron flux, different O2 content) in HBWR at 240 °C, Data from [Lund & Videm, 1971].

Early examinations on the corrosion behaviour of BWR Zircaloy-2 fuel rod cladding were reported by [Garzarolli et al., 1971] for several BWRs, with exposure times of 650 – 2400 days, under a fast flux of $3-5\cdot10^{13}$ n/cm²s, and different oxygen contents of ~0.15 (for most BWRs) and ~1.8 ppm (in the early closed cycle BWRs VAK). They observed that for up to 650-1000 days, in most cases a rather thin and uniform oxide thickness was obtained (Figure 6-6b) as well as nodular corrosion in some cases. An extremely thick oxide layer (up to 250 µm, a nodular corrosion where the nodules have grown together) was observed on a 1st core fuel, , exposed for up to 2500 days, which was later explained by the very large size of the SPPs (which could be even seen in light microscopic examinations) of these tubes, produced by annealing sequences in the β -, (α + β), and α -range, without any β -quenching. All estimated weight gain- and hydrogen pickup-data from the three first German BWRs VAK, KRB-1 and KWL are plotted in Figure 6-7 together with early literature data from the US BWRs, VBWR, DNPS-1, and BRP-1. It demonstrates that all the fuel rods show a similar corrosion behaviour in spite of different water chemistries and heat fluxes, except for the 1st core of VAK, which exhibited a significantly higher corrosion and SPP size. The HPU was always rather low, as Figure 6-7b shows, indicating a HPUF of 3-7%.





- a) Very thick oxide on VAK 1st core rod
- b) Rather thin oxide on VAK 1st reload



c) Nodular corrosion on KRB-1 rod

Figure 6-6: Unusual oxide layer characteristics on Zircaloy-2 BWR fuel rods [Garzarolli et al., 1971].



Figure 6-7: Estimated Zircaloy-2 fuel rod cladding corrosion as function of exposure time [Garzarolli et al., 1971; Garzarolli & Manzel, 1977].

Later information on the in BWR corrosion behaviour of FR cladding, fabricated by annealing in the α -range after a previous β -quenching, showed a much lower peak oxide thickness, but significant variations between different BWRs, cycles, and material lots (Figure 6-8).



Figure 6-8: Uniform (lower curve) and nodular corrosion (two upper curves) of BWR Zry-2 fuel rods irradiated during 1965-1980. [Garzarolli & Stehle, 1987].

Nodule nucleation occurs usually after 10 to 20 days for Zircaloy-2 and after 30-100 days for Zircaloy-4, [Garzarolli & Sell, 2006].

The axial thickness profile of fuel rod nodular corrosion mostly follows the rod burn-up profile (Figure 6-9), although sometimes a pronounced nodular corrosion peak is observed in the bottom part of the rod, where boiling starts and where CRUD deposition becomes significant, or at some other axial position, [Garzarolli & Holzer, 1992]. This axial profile of nodular corrosion indicates that burnup (fast fluence) has a large effect on nodular corrosion, much larger than observed for uniform corrosion. Often sharp transitions in nodule density is seen at positions where heat flux changes abruptly, e.g. at positions of enrichment changes and where pellet-to-pellet gaps exist. In high-power rods higher nodular corrosion was seen in the low power area (e.g. lower blanket) whereas in low power rods higher nodular corrosion behaviour it is recommended to plot the peak nodular oxide thickness versus the average bundle burnup or the fast neutron fluence. The nodule number density stays in general constant and no new nodules are formed with time after the first nodules have nucleated. In extreme cases the nodules can grow together, coalesce, on the material surface and form a thick uniform nodular oxide. Nodular oxide layer thickness values of >100 µm can be reached after long exposure times.



Figure 6-9: Oxide thickness and relative burnup profile of a five-cycle fuel rod [Garzarolli & Holzer, 1992].

The cladding surface treatment has changed over the years. Initially the cladding was pickled and pre-filmed, later it was belt grounded or electropolished (in Europe). According [Rudling et al., 1992], the effect of the surface treatment varied depending on the SPP size. Belt-ground and electropolished materials have superior corrosion performance compared to pre-filmed surface, in case of LK0 cladding (Figure 6-10a), fabricated with an intermediate annealing at 675 °C, that has an average SPP size of 140 nm, and a certain tendency to nodular corrosion. No significant differences in corrosion resistance was observed in case of LK1 cladding (Figure 6-10b), fabricated with an intermediate annealing at 565 °C and a SPP size of 110 nm, which has a much lower tendency to nodular corrosion. LK2 cladding, having a very fine SPP size (45 nm) exhibits no nodular corrosion and no surface treatment effect at moderate burnup but a late increased corrosion especially in case pre-filmed cladding (Figure 6-10c). Obviously, the pr-filming reduces the time to the rate transition, where a significant outer porous oxide thickness establishes, that changes the corrosion environment.



a) Oxide thickness of LK0 cladding



b) Oxide thickness of LK1 cladding





Figure 6-10: Rod average oxide thickness versus assembly burnup for LK0 (a), LK1 (b) and LK2 (2) Zircaloy-2 claddings with different surface treatment. These rods were irradiated in the same BWR. [Rudling et al., 1992].

In the early seventies it became clear that the so-called "pellet cladding interaction" (PCI) defects were responsible for a significant fraction of the fuel rod failures, which were relatively high at that

time. The PCI defects were caused mainly by local power increases associated with control rod manoeuvres. Different concepts were examined to improve the resistance of the cladding against PCI. A soft inner layer (Zr liner tubing) was tested by [Armijo et al., 1994]. The high PCI resistance of the Zr liner tubing was confirmed through special power ramp tests in test reactors with BWR-preirradiated fuel rods, and in a broad test program in Quad Cities reactors between 1977-1984. **The Zr liner concept was finally selected for the most BWRs in the US and Europe since 1984.**

6.1.2 **Optimization of nodular corrosion**

A high degree of nodular corrosion was often observed at low burnups [Nelson, 1962; Garzarolli et al., 1971; Garzarolli & Manzel, 1977; Cheng & Adamson, 1987]. For many years the nodular corrosion did not result in any fuel rod failures, although the observed corrosion extent was ranging to complete surface coverage and a nodular oxide thickness up to 250 μ m (Figure 6-6a and Figure 6-7). <u>However</u>, **a low resistance to nodular corrosion has been identified as an important contributor to a type of fuel failure termed CRUD-induced localized corrosion (CILC), which was first observed in 1978 [Marlowe et al., 1985]. The failure (Figure 6-11) occurred at burnups of 15-20 MWd/kgU in particular in (U, Gd)O₂ fuel rods. Heavy CRUD deposited preferentially between oxide nodules promoting delamination by the growing nodular oxide, while locally increasing the thermal resistance.**



Figure 6-11: Nodular corrosion on BWR fuel cladding and Cu rich CRUD deposits above and in-between nodules and near through wall CILC pit [Marlowe et al., 1985].

GE (*GNF* today) concluded that the fabrication process for Zircaloy cladding has to be modified to avoid nodular corrosion and studied the sensitivity and reproducibility of nodular corrosion formed in high-temperature/high-pressure steam tests for Zircaloy as a function of temperature, pressure, test duration, and other variables. A test involving a pre-filming step at 410 °C/102 bars for 8 h and a nodule sensitivity step at 510 °C/102 bars for 16 h was applied for calibration to the in-reactor corrosion performance using samples pre-tested in BWR and irradiated plenum samples removed from fuel rods (Figure 6-12).

7 Corrosion in PWR/VVER

7.1 General

7.1.1 Early observations

A detailed description of the pressurized reactors, reactor and fuel assembly design as well as their coolant conditions, such as water chemistry, system pressure, coolant inlet and outlet temperature, and coolant velocity is presented in Volume I. Here in Volume II only a short summary of the most important data is presented.

There are two different types of pressurized water reactors operating under hydrogenated coolant light water conditions:

- The Pressurized Water Reactor (PWR) developed originally by Westinghouse, operates at a system pressure of 155-158 bar, at a coolant inlet temperature of 279-294 °C and an average core outlet temperature of 313-329 °C. The max FR cladding outside temperature is 320-350 °C, depending on the power rating (average: 80-125 kW/m) and the coolant flow rate (3-6 m/s). In PWRs 1.5-4 ppm (17-50 cc/kg) H₂ is added to keep the oxygen content low (<5 ppb), 0-2200 ppm Boron (as H₃BO₃) for reactivity control and 0.2-6 ppm LiOH for pH control, as was shown in Figure 5-13 in Section 5.1. The average fast neutron fluence in the core is 6-9·10¹³ n/cm²·s.
- The Russian 440/1000/1200 MW VVER operates at a system pressure of 125/157/162 bar, at a coolant inlet temperature of 267/290/298 °C and an average core outlet temperature of 298/320/330 °C. The max FR cladding outside temperature is 335/352/354 °C, depending on the power rating (average: 83/108 kW/m), the coolant flow rate (3.5/6 m/s), the max steam content (0/5/11.6%). In VVERs 2.6-5.3 ppm (30-60 cc/kg) H₂ is added to keep the oxygen content low (<10 ppb), 0-1500 ppm Boron (as H₃BO₃) for reactivity control and 2-20 ppm potassium as KOH + 0.05-0.5 ppm LiOH for pH control. The average fast neutron fluence in the core is 5-7·10¹³ n/cm²·s.

7.1.1.1 Zr-materials for VVWR

The VVER development in Russia started with the Zr alloy development in the late 1950ies e.g. [Ambartsumyan et al., 1958]. The first VVER demo plant with a electric power output of 210 MW was built in 1964. The first commercial PWR in Russia was the VVER-440. The commercial operation of VVER-440 started in 1971. This reactor has hexagonal fuel assemblies, containing 126 E110 (Zr1Nb) fuel rods with an active length of 2420 mm and a diameter of 9.1 mm (cladding wall thickness 0.65 mm), 10 spacer grids, and a central water tube serving to axially fix the spacer grids. In 1980 the first more advanced VVER-1000 started operation and in 2006 the VVER-1200 was introduced. **For the VVER-1000**, 312 E110 fuel rods with an active length of 3530 mm and the same diameter and wall thickness, as applied for VVER 440, were selected for the FR cladding. The examinations, performed before the selection of E110 are described in Volume I. For spacer grids, guide tubes (GT), central tube (CT) and frame angles material of VVER-1000s, originally stainless steel was used and since 1994 E110, and since 1997 E635, a Zr1.2Sn1Nb0.35Fe alloys were introduced. The cell wall thickness of spacer grids is 0.25 mm.

The cladding was produced (forging, β -quenching, extrusion, cold rolling with intermediate and final annealing) as a homogeneous structure, consisting of a fully recrystallized α -Zr matrix, with a grain size of 4-5 µm, with fine β -Nb SPPs. The ingot was fabricated via a blend of electrolytic zirconium powder and iodide zirconium bars, as well as recycled zirconium products. Material produced via this process results in an increased corrosion at high (LOCA) temperatures. Since 2005, a change to Zr sponge as E110 alloy basis started for fuel rod cladding [Markelov et al., 2011]. As a consequence of this fabrication change the impurity content in the E110 alloy has changed. Especially the Fe and O content has increased from 100 respectively 400 ppm to 450-1200 respectively 800-1200 ppm (E110M). The material E110M has a significant higher creep strength [Markelov et al., 2011], what is important for the higher burnups. The material condition of VVER E110 cladding was in different to the CWSR Zry-4 PWR

cladding, as it was recrystallized from the very beginning [Markelov et al., 2008]. Most of VVER corrosion data available today are from cladding produced by the early fabrication process.

Pickling was used as final surface treatment step for the VVER fuel rod cladding. Only in the last years the surface treatment has been changed to belt polishing.

The corrosion of E110 FR cladding in VVER coolant, which does not contain oxygen (<0.05 ppb) is extremely low, and the oxide increase with increasing temperature (along FR height) is almost zero, what is totally different to experimentally tested FRs with other Zr-alloys (e.g. E635, with a lower impurity sensitivity and a higher creep strength), as Figure 7-1 shows. The oxide profile of E635 was more like that observed in PWR FRs with Zry-4 cladding.

Figure 7-2 and Figure 7-3 show the oxide profile and the maximum oxide thickness in VVER 1000 after a burnup of 45 and 70 MWd/kgU and the 2013 database on peak oxide thickness (at axial elevation \sim 3000 mm) versus burnup. The peak oxide thickness formed in VVER-1000 under normal corrosion behaviour is only 3-13 µm, what is \sim 3 times lower than observed on Zr1Nb (e.g. M5) in PWRs.



Figure 7-1: Distribution of oxide film along the FR claddings made of E635 and E110 alloys after operation within 3 fuel cycles [Smirnov et al., 2006]



Figure 7-2: Typical oxide film profile of VVER E110 FR after a burnup of 45 MWd/kgU (2) and 70 MWd/kgU (1) [Pavlov, 2013].



Figure 7-3: Max oxide thickness, estimated by EC or metallography of WWER E110 FR versus burnup [Pavlov, 2013].

The E110 oxide layer thickness values from VVER-440 and VVER-1000 are quite similar (Figure 7-4) and up to ~3 times lower than observed for Zr1Nb in KKG for M5 cladding in a PWR (Figure 7-5a). Figure 7-6 compares the oxide thickness profile on Zr1Nb claddings observed in VVER, under normal PWR condition and under a very high average LHGR (350-250 W/cm) in KKG revealing that the temperature has a significant effect, indicating that Zr1Nb can experience local oxide thickness variations at the peak temperature position under a high LHGR [Seibold & Fuchs, 1998]. The reason for the similar peak oxide thickness observed on FRs in VVER-440 and VVER-1000 is probably that VVER-440 has a lower system pressure (125 instead of 160 bar) and a lower LHGR (in average 129 instead of 167 W/cm), which reduces the surface temperature, as well as significantly lower coolant flow rate (3.0 instead of 6.0 m/s) which increases the cladding surface temperature. The reason of the different corrosion rate of Zr1Nb in VVER and PWR might be connected with different FA design (hexagonal and cubic), and the much larger number density of spacer grids (15 in VVER 1000 and 7-8 in PWR) resulting in lower local peak temperature variations, but may also be connected with the differences in water chemistry.



Figure 7-4: Oxide film thickness on the outer surface of the VVER-440 (□) and VVER-1000 (△) FR claddings [Smirnov et al., 1997].

The HPUF is very low for Zr1Nb FR cladding, but it is likely lower in PWR than in VVER, as Figure 7-5b indicates, revealing that the H content versus exposure is similar in VVER FRs and PWR FRs also the oxide reported thickness is ~3 times higher in PWR than in VVER.



160 140 VVER D M5 in PWRs 120 Hydrogen content (ppm) 100 80 60 40 ٥ 20 0 10 20 30 50 60 70 0 Burnup (MWd/kgU)

- a) Corrosion of E110 in VVERs, Zr1Nb in KKG and M5 in PWRs.
- b) Hydrogen pick up of E110 in VVERs, and of M5 in PWRs.
- Figure 7-5: Normal corrosion behaviour of E110 FR cladding in VVERs, Data from [Solonin et al., 1997; Smirnov et al., 2001; Markov et al., 1999; and Markelov et al., 2005], in comparison with Zr1Nb in KKGg [Garzarolli et al., 2001b] and M5 in PWRs, after [Thomazet et al., 2005].



Figure 7-6: Comparison of the oxide thickness profile of high burnup fuel rods with Zr1Nb claddings in VVER, a normal PWR and in Siemens PWR under an extreme hot power density. Data from [Smirnov et al., 2006; Thomazet et al., 2005; and Seibold & Fuchs, 1998].

The colour of the oxide layer on the VVER FRs with E110 cladding with a very low TM content was reported to be black and uniform. However, above a certain oxide thickness the oxide layer becomes gray-white at the high temperature positions and exhibits cracks and spallations at >45 MWd/kg and oxide thickness >7 μ m (see Figure 7-6a). Zr1Nb and M5 FRs with a higher TM content tested in PWRs exhibited such spallations only after operation under very high power-density (av. LHGR of 350-250 W/cm) and an oxide thickness of >20 μ m. PIE of such Zr1Nb FRs exposed at very high power-density showed pustules in the oxide layer but no locally increased corrosion [Seibold & Fuchs, 1998].

Peaks of oxide layer thickness were observed on E110 FRs at spacer grid positions especially in the lower half of the FR at high burnup (Figure 7-7).





For some time, it was believed that E635 is much superior to E110 as VVER fuel rod cladding material, due to its resistance to irradiation-induced creep, growth and nodular corrosion [Nikulina et al., 1996]. However, the oxide thickness of E635 cladding is much higher than that of E110, increasing significantly with increasing burnup, as [Markelov et al., 2011] reported (Figure 7-8a). HPU material has similar behaviour (Figure 7-8b).



Figure 7-8: Corrosion (a) and hydrogen pickup (b) of E110 and E635 fuel rod cladding in VVER [Markelov et al., 2011].

The structural components of the VVER 1000 FAs are the following: 15 spacer grids (SG), 18 guide tubes (GT) + 1 central tube (CT), 312 fuel rods (FRs), and in particular fuel designs 6 frame angles. In the early times stainless steel was used for most structural components, later E110 and finally E635, having a higher strength than E110. E635 GTs tests showed (Figure 7-9) a very low oxide thickness in the lower part, but a corrosion increase above a certain axial position at an oxide thickness of about 5 μ m. The significant irradiation induced corrosion increase (rate transition) at an oxide thickness of 5 μ m was already observed in several Zr alloys (e.g. Zry-4) containing a significant Sn content, as reported in Section 5.4.1, e.g. Figure 5-48. The distance to the axial corrosion transition decreases with increasing exposure in the case of E635 GTs.



Figure 7-9: Oxide thickness along an E635 alloy guide tube after a 3-year exposure in a VVER-1000 [Sablin et al., 2005].

According [Sablin et al., 2005] the oxide thickness after 3 year exposure was 6 μ m in the case of E110 FR cladding and GTs and ~25 μ m in case of E635 GT, CT, and FR claddings tubes and frame angle. The normal oxide thickness of E110 structural components remains still low (a few μ m) (Table 7-1), up to 6 cycles but E110 spacer grids (SG) experience crevice corrosion attacks (Figure 7-10) with local oxide thickness up to 200 μ m, as it was observed after 5 cycle operation.

Structural E635 components exhibit a higher oxide thickness (up to max \leq 50 µm) after 6 cycles, what is acceptable.

Table 7-1:Summary data on the corrosion state of the Zr-alloy structural FA components [Sablin et al., 2005; Smirnov
et al., 2006; Markelov et al., 2011; and Shevyakov et al., 2013].

Component	Alloy	Oxide thic	kness (µm)	HPU (ppm)		
		3-4 cycles	5-6 cycles	3-4 cycles	5-6 cycles	
FR cladding	E110	2-7	15-16	40-110	30-130	
SG	E110	up to 90	up to 200	30-55	50-70	
GT/CT	E110	2-3	2-3	50-90	30-50	
FR-cladding	E635	10-45	≤80	140		
GT	E635	3-27	5-46	30-200	300	
Angle	E635	1-28 5-48		100	400	
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Figure 7-10: Microstructure of different VVER-400 spacer grids areas after a 5 cycle operation [Smirnov et al., 2006].

[Shishov et al., 2013] reported values on the corrosion behaviour of E635 fuel rods and guide tubes. The HPUF (Figure 7-11) deduced from these data, considering a wall thickness of 0.65 mm for all components, indicate a rather low HPUF which decreases with increasing oxide thickness and temperature. The deduced HPUF appears to be rather low, much lower than that of ZIRLO in PWR, in

spite of the similar alloy composition. Probably, the low HPUF relates to the water chemistry of VVERs (NH₄OH and no Ni).



Figure 7-11: HPUF of E653 in VVER deduced from the data reported by [Shishov et al., 2013].

However, the H-content, especially at relatively thin ($\sim 0.6 \mu m$) frame angle corroding on both sides, is relatively high (400 ppm) and forms in the bending area radial hydrides (Figure 7-12).



Figure 7-12: Hydride morphology in the bending area of the E635 frame angle [Shevyakov et al., 2013].

An observed problem with E110 cladding corrosion, was its high sensitivity against oxygen content in the coolant. The in-reactor corrosion of E110 is significantly increased if the free oxygen radicals induced by radiolysis of the coolant are not suppressed significantly by a high hydrogen content in the

coolant. Tests with experimental fuel rods with E110 cladding exposed in loops with a simulated VVER water chemistry in MR at a very low O content of < 5 ppb showed low corrosion but loop tests in MIR with a moderate O content of < 20 ppb showed significantly higher corrosion and at >20 MWd/kgU in most cases even nodular corrosion (Figure 7-13).



Figure 7-13: Corrosion of E110 test FR claddings in loops under VVER type water chemistry and an O content of <5 ppb (MR) respectively <20 ppb (MIR) [Ritchie, IAEA-TECDOC-966, 1998].

[Sablin et al., 2009] concluded from this and other available information that nodular corrosion occurs under VVER water chemistry, if the oxygen content in the coolant is ≥ 15 ppb.

The analysis of the oxide thickness on individual test FR with E110 and E635 cladding, exposed in a loop in the MIR under VVER conditions, at different axial positions with different heat flux, shown in Figure 5-6 in Section 5.1, indicates that the effect of heat flux on maximum oxide thickness in case of E635 is moderate, probably only due the heat flux induced temperature increase, but in the case of E110 it becomes very large, probably due to the local increase of void and the radiolysis induced oxygen content. The large effect of surface boiling induced void on the Zr1Nb corrosion was already discussed in section 6.1.1 on corrosion in RBMK in Figure 6-2. Thus, in modern PWRs at very high LHGR respectively high void, Zr1Nb can have an increased corrosion at the upper FR position, as was observed in Siemens PWRs with M5 cladding, as described in section 5.1 with Figure 5-7 and can occur in E110 (Zr1Nb).

The high sensitivity of Zr1Nb against O results in a thicker oxide formation at the cladding inner surface, which is in contact with UO_2 (Figure 7-14).





Furthermore, several cases of significantly increased corrosion, were observed for E110 in VVERs which were induced by:

- coolant contamination by carbon containing species from ion-exchange resin,
- increased oxygen in the coolant, and
- galvanic coupling with Ni base alloys and stainless steel.

In Volume I it was reported that severe nodular corrosion was observed (1st) in the late 1960ies / early 1970ies in a VVER 210, operating with an oxygen content of 15 ppb under high alkaline water chemistry conditions (pH 9-10) and (2nd) in a VVER 1000 operating during a period at a slightly higher oxygen content (<20 ppb). Increased nodular corrosion with experimental Zr1Nb and Zr2.5Nb was also observed on experimental fuel rods exposed by Westinghouse in BR3 at an oxygen content of 30-44 ppb [Sabol et al., 1989 and 1997]. Zry-4 and Zr1Sn1Nb0.1Fe did not reveal such a high sensitivity against oxygen as the ZrNb alloys.

Obviously, Sn addition to the alloy, as in the case E635, reduced the sensitivity against increased corrosion, due to locally increased oxygen in the coolant and other impurities, but increase the inreactor corrosion rate at >5 μ m (transition) in hydrogenated O-free environment.

A big advantage of the E110 cladding was the low HPUF observed in VVERs even in cases with increased corrosion.

Westinghouse had delivered FAs with ZIRLO claddings for a VVERs. The reported oxide data from a VVER FRs appears to be lower than the oxide thickness of the majority of PWR FR at a burnup >40 MWd/kgU (Figure 7-15), that is mostly due to the different fuel design, but, [Oliver et al., 2018] concluded that the lower corrosion is primarily due to KOH water chemistry, which results in a lower corrosion, compared to the LiOH water chemistry in PWRs. However, according to the state of knowledge the used LiOH concentration in PWRs is not high enough to cause corrosion to increase.



Figure 7-15: Maximum FR oxide thickness of ZIRLO in PWR and VVER [Oliver et al., 2018].

7.1.2 Zircaloy-4 materials for PWRs

For PWR fuel rod cladding stainless steel initially was used. **In the late 1960ies Zry-4 has been selected**, as pointed out in section 3.1. In the early days, when the burnup was still low (<30 MWd/kgU) and the coolant conditions of the PWRs was still moderate, the corrosion attack of Zry-4 appeared to be very low (peak oxide thickness after 1170 d was <20 μm) e.g. [Dalgaard, 1976].

In the late 1970ies a significant variation of the corrosion behaviour in different reactors was noticed (Figure 7-16). The maximum oxide thickness of US/Westinghouse PWR fuel rods, operating at an average LHGR of 131-216 W/cm published in 1967-1979, are shown in Figure 7-16a and was at a burnup of 30-38 MWd/kgU between 5 and 35 μm. Data from KWU PWRs, operating at an average LHGR of 177-226 W/cm published in 1975-1979, are shown in Figure 7-16b and was at burnups of 36-42 MWd/kgU between 5 and 60 μm in KWU PWRs.



Figure 7-16: Maximum oxide layer thickness of standard fuel rods with Zry-4 cladding in non KWU PWRS (a) and KWU PWRs (b) [Garzarolli et al., 1980].

[Garzarolli & Manzel, 1977] reviewed the fuel rod corrosion data observed during poolside inspections and PIE examinations in PWRs up to 1976. A comparison of the PWR data (axial peak values) with the prediction by the model of [Stehle et al., 1975] considering out-of-reactor corrosion behaviour, the heat flux effect, and the maximum surface temperature at the OD of the oxide layer of 347 °C indicated that the peak oxide thickness agrees well with the predictions (Figure 7-17), confirming the conclusion of [Dalgaard, 1976] that the corrosion in PWR is similar as the out-of-reactor corrosion. Certainly, the real surface temperature at that time was very likely lower, especially at higher burnups as a consequence of the rather low U²³⁵ enrichment applied at that time, resulting in a low heat flux especially at burnups >30 MWd/kgU.



Figure 7-17: Oxide thickness at the hottest position of PWR fuel rods with Zircaloy-4 cladding versus the exposure time [Garzarolli & Manzel, 1977].

Figure 7-18 summarizes the Siemens data on hydrogen pick-up of Zry-4 available up to the middle of the 1980ies (plotted versus the oxide layer thickness) and compares them with the published data from two US plants (Saxton and Oconee). The HPUF of the KWU data was below 10% (2-9%) up to an oxide layer thickness of 100 μ m. Only at oxide layer thickness >100 μ m the HPUF become >10% (11-13%). An average hydrogen concentration of 500 ppm is reached at around an oxide layer thickness of 100 μ m (at a wall thickness of 0.72 mm). The typical hydrogen distribution across the cladding wall at an oxide thickness of \geq 110 μ m showed an increase of the hydride density at the outer surface of fuel rods (Figure 7-19), due to thermal H diffusion, but did not lead to a conclusion, that the hydride distribution might be a limiting phenomenon for the extended burnup [Garzarolli & Stehle, 1986]. The data from Saxton (extending up to an oxide thickness of 25-30 μ m) appeared to be similar to the Siemens data reported in in 1986, but the data from Oconee had a higher HPUF (~15%) over the examined oxide thickness range (20-50 μ m).



Figure 7-18: Hydrogen pick up of Zry-4 cladding in PWRs [Garzarolli & Stehle, 1986].



Figure 7-19: Hydride distribution across the cladding wall of a fuel rod with an oxide thickness of \geq 110 µm [Garzarolli & Stehle, 1986].

In the early days, the PWR oxide layer thickness estimation was performed by metallographic examinations in hot cells and since the late 1970ies, when it became clear that many oxide thickness data from different reactors are needed, mostly by eddy current (EC) measurements in the pool, initially at discrete points along the FR and later on by continuous traces of the oxide layer thickness by axial moving of the EC probe or the FR. A description of this technique and a comparison of the measurements obtained by EC and metallography, showing a good agreement was reported in [Garzarolli et al., 1980].

After 1980, the analysis of the significantly larger data base extending up to a burnup of 40 MWd/kgU, led to the conclusion that the in-PWR corrosion is enhanced in many cases compared with the predictions based on out-of-reactor corrosion [Garzarolli et al., 1982]. A more detailed analysis of the available data (Figure 7-20) clearly indicated that the maximum corrosion of Zry-4 fuel rods depends largely on the core average power, the inlet temperature, the coolant flow, the active length, and the particular power history of the fuel rods.



Figure 7-20: Influence of rod average power on Zircaloy-4 maximum oxide layer thickness for 3 cycle fuel rods of three different KWU PWRs [Garzarolli et al., 1982].

Later, **several in-PWR FR test exposures were performed to high burnup and at a high heat flux.** In the late 1970ies a few highly enriched (4% and 6%) experimental fuel rods were exposed in KWO [Stehle et al., 1982] for two yearly cycles (605 EFPD) at the average heat flux of ~300 W/cm in the first cycle and at 400-460 W/cm (surface heat flux of 120-140 W/cm²) in the 2nd cycle, and showed a dramatic increase in the peak oxide thickness with increasing heat flux, as Figure 7-21 shows. At the peak power also a locally extremely increased corrosion was observed, that may limit the allowable burnup, what will be discussed in Section 10.


Figure 7-21: Oxide layer thickness on experimental high enriched fuel rods exposed in the PWR KWO for two yearly cycles at different in some cases extreme surface heat flux values [Garzarolli et al., 1979a].

Long-time isothermal tests in hydrogenated coolant (PWRs and ATR-loops) under a high neutron flux at 310-360 °C showed that normal corrosion of Zry-4 in PWR initially follows a corrosion behaviour similar to that observed in out-of-pile tests, but exhibits, after the in-PWR transition (3-7 μ m), an increase of the corrosion rate by the factor of F, which is about 4 in case of Zry-4 (Figure 7-22b). The correlation for post transition corrosion rate is:

Equation 7-1:
$$ds/dt = F \cdot C \cdot exp(-Q/RT)$$
,

with T temperature in [K], and C the rate constant. This temperature dependency is quite large (Q/R=14.200 K), as will be shown later. Thus, a significant corrosion rate increase will occur when the temperature further increases. The temperature that governs corrosion of Zr-FR-cladding is the one at the metal-oxide interface (Figure 7-22a) and increases with increasing oxide thickness. Thus, the heat flux (q"), the thermal conductivity of the oxide (λ) and its thickness (Sox) governs the temperature increase (Δ T) over the oxide.

Equation 7-2:
$$\Delta T = S_{ar} \cdot q'' / \lambda$$

Furthermore, any dense CRUD may have an additional effect on the corrosion temperature. The thermal conductivity value of the Zr-oxide layer, is most likely about 1.5 W/(m·K), as a comparison of the corrosion behaviour of FRs and isothermal coupons indicated. The expected significant temperature increase, with increasing oxide thickness at the very high LHGR existing in case of the highly enriched test FRs in KWO is consequently the reason for the large oxide thickness increase with increasing LHGR observed in Figure 7-21.

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Figure 7-22: Mechanistic aspects of Zr alloy corrosion under heat flux (a) and effect of irradiation and heat flux on corrosion of Zry-4 in PWR.

In 1985, the peak oxide values on Zry-4 FR cladding from several Siemens PWRs, operating under different thermal conditions exposed to increased burnups of 40-50 MWd/kgU were reported [Garzarolli et al., 1985b] in comparison with predictions obtained applying an out-of-reactor corrosion model (Figure 7-23). The maximum oxide thickness in this figure (>100 μ m) resulted from peak burnup FRs in Gösgen NPP, which have been reinserted for a fourth cycle. The figure indicates, that corrosion is initially similar as in out-of-reactor tests, but increases after some exposure time and that the critical burnup, where the corrosion rate increases, varies from PWR to PWR depending on the thermal conditions (coolant flow, LHGR, FR length, etc.) of the reactors. To confirm this, isothermal corrosion samples were exposed in the PWR KWO at 310 °C up to 1500 d. These tests (Figure 7-24) confirmed the irradiation induced corrosion increase at ~5 μ m, as indicated by Figure 7-22b and Figure 7-23.



Figure 7-23: Oxide layer thickness vs. burnup of PWR fuel rods from different Siemens reactors, with different coolant flow and LHGR [Garzarolli et al.,1985b].

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Corrosion in pressurized heavy water reactors

Corrosion of the Zr alloy pressure tubes (PTs), operating at high temperatures (t=250 °C-300 °C) with heavy water coolant (hydrogenated with LiOH addition) flowing through it, results in formation of an oxide layer on inside surface and uptake of deuterium. The early generation of the CANDU PHWRs had used Zrv-2 PTs, and the later Zr2.5Nb PTs, manufactured by either cold pilgering or cold drawing of hot extruded hollow bars. The oxide thickness and hydrogen/deuterium pickup of the PTs was estimated by PIE after the removal from different units after operating for a varying time. The CANDU PT data after 11 EFPY were reported by [Urbanic et al., 1987]. The corrosion behaviour of CANDU PTs is shown in Figure 8-1a versus distance from coolant inlet for PT removed from high flux regions of Pickering reactors. For both materials (Zry-2 and Zr2.5Nb), the measured oxide layers are higher at the outlet region than at the inlet region. The peak oxide thickness is significantly higher on Zry-2 PTs than on Zr2.5Nb PTs. Furthermore, for Zrv-2 PTs a clear temperature dependency ($O/R \approx 7000$ K) is observed. However, the deduced O/R value is lower than that of out-of-reactor or normal in-PWR corrosion (Q/R=12000-14200 K). The theoretical D pickup is shown in Figure 8-1b for the examined PTs, whose oxide thickness was shown in Figure 8-1a. Generally, deuterium uptake has been much less than 20% of theoretical for Zr-2.5Nb pressure tubes. For Zircaloy-2, the deuterium percent uptake remains between approximately 20 to 50% in the hotter part of the tubes (400-600 cm). Near the inlet, the high percentage of uptake in some tubes were attributed to additional deuterium ingress from outside the tube.



a) Oxide thickness vs PT height

b) Percent theoretical deuterium uptake



In case of the Zry-2 CANDU pressure tubes (PT) the axial oxide and HPUF profile indicate an acceleration of corrosion and HPUF at >5-10 μ m after an exposure of 3620 days (Figure 5-67 in Section 5.2).

The corrosion rate of Zry-4, irradiated in hydrogenated water under isothermal conditions, is initially similar as out-of-reactor, and increases after an oxide thickness of >2 to 7 μ m by a factor of 4-6, and accelerates at low temperatures and at high fluences, due to SPP dissolution, providing a corrosion enhancement of the factor of 7-40, depending on the temperature and the fast flux. Studies on the corrosion rate accelerated corrosion depends on the fast neutron flux (Figure 8-2). A pre-oxidation at higher temperatures (e.g. 350 °C) in the ATR decrease somewhat the critical fluence for the onset of the accelerated corrosion.

At a high flux (e.g. at $\sim 1.10^{14}$ n/cm²-s, >1MeV) as in the core of a PWR the normal increased corrosion would start at 290 °C after a time of about 1500 days (4 years). Afterwards the corrosion should be

increased by a factor of about 5. After a fluence of $1 \cdot 10^{22} \text{ n/cm}^2$, what in the case of a typical PWR flux would be reached after about 5 years, the irradiation induced SPP dissolution would lead to a heavily accelerated corrosion. At the low flux of $2.5 \cdot 10^{13} \text{ n/cm}^2$ -s (>1MeV) the accelerated corrosion will start at a lower fast fluence (according Figure 8-2 at about $6.1 \cdot 10^{21} \text{ n/cm}^2$), corresponding to an exposure time of about 8 years. From this moment the corrosion rate will increase, according Figure 7-44 in Section 7.1.2, to a rate of about 0.025 µm/d. In Figure 8-3 the reported measured maximum PT oxide data from PHWRs and N-Reactor are shown in comparison with the prediction for SPP dissolution induced corrosion, indicating that the measured and predicted data fit well. It must be pointed out that at high exposure times the fast fluence is rather high (> $5 \cdot 10^{21} \text{ n/cm}^2$), and consequently other aspects, such as the irradiation induced SPP dissolution, may contribute to the observed corrosion acceleration.



Figure 8-2: Correlation between fast neutron flux and the onset fluence of accelerated corrosion. Data from [Kammenzind et al., 1996; Hillner et al., 2000; Bajej et al., 2016; and Garzarolli et al., 2002a].



Figure 8-3: Comparison of Zircaloy corrosion data with predictions from low flux PWR test results.

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9 Sensitivity against alloying impurities

An important aspect for the development of the Zr-alloys was the improvement of the sensitivity of corrosion against material impurities.

Nitrogen has a significant effect on corrosion. At >30 ppm N, Zr exhibits an accelerated corrosion within short times even in 315 °C water (Figure 3-4), Zircaloy-2/4 and E110 show increased corrosion at >130 ppm N (Figure 9-1). E110 is more sensitive to N than Zircaloy-2/4. Whereas Zr exhibits accelerated corrosion within short times even in 315 °C water at >30 ppm N, Zry-2/4 and E110 show increased corrosion only at >130 ppm N.



Figure 9-1: Effect of N on the corrosion behaviour of Zr, Zircaloy-2/4 and Zr1Nb.

Corrosion of Zr is very much increased at high **carbon** contents. In case of M5 alloy, increase of corrosion with increasing C content starts at a rather low C content (30 ppm) as can be seen from Figure 9-2. According ASTM, C is limited to $\leq 120/270$ ppm for Zircaloy-2/4. In case of E110 alloy, C is limited to ≤ 70 pm. In PWR corrosion of Zry-4 increases with increasing carbon content (Figure 9-3). For a corrosion-optimized PCA alloy, the max C content was limited to 120 ppm [Garzarolli et al., 1990]. The in BWR corrosion of Zr alloy-cladding increases with increasing C content, and the increase is even higher than in the case of the uniform in-PWR corrosion (Figure 9-4). The corrosion rate increases heavily in case of Zry-2/4 in-BWR at >40 ppm (nodular corrosion), especially, if fabricated at higher temperatures, at A=5E-18h, than the LTP condition (A~5E-19h). The corrosion of M5 increases moderately at >40 ppm C in out-of-reactor tests in 400 °C steam, and in PWR in case of Zry-4 at about >70 ppm C (Figure 9-5). In out-of-reactor tests at 500 °C the effect of C on nodular corrosion is much lower [Weidinger et al., 1987].



a) Corrosion of Zr

b) Corrosion of M5

Figure 9-2: Effect of carbon on the corrosion behaviour of Zr and M5.



Figure 9-3: Influence of the carbon content on the in PWR corrosion [Garzarolli et al., 1990].

10 Allowable extend of corrosion

An important aspect is to avoid (1st) any corrosion-driven FR defect and (2nd) a cladding corrosion induced modification of the cladding that affects the FR behaviour under accident condition (e.g. RIA and LOCA) and under dry storage conditions.

Corrosion driven PWR FR cladding, operating at 300-350 °C, and FA component defect can be induced by the following processes:

- a) Local CRUD induced significantly increased corrosion,
- b) Heat flux induced local corrosion acceleration,
- c) Hydride blister formation at local oxide spalling position,
- d) Li induced increased corrosion,
- e) Impurity induced increased local corrosion or HPU.

In BWRs, where the temperature is much lower (<300 °C), FR and FA components defects can be induced by:

- a) Local CRUD induced significantly increased corrosion,
- b) Massive enhanced corrosion (e.g. nodular corrosion),
- c) Extremely accelerated HPUF, especially with Zry-2 FA components,
- d) Impurity induced increased local corrosion or HPU.

The state of knowledge on CRUD induced corrosion acceleration is detailed described in the Volume I.

The **heat flux induced local corrosion acceleration** was studied especially in early days with experimental Zry-4 FRs and FAs with increased enrichment exposed under the most limiting power history. Three different processes were observed, that can lead to significant FR cladding damage.

- **1)** At a very high heat flux an excessive corrosion may occur at above a certain oxide thickness, as was observed on experimental high enriched (>5%) FRs, exposed in the PWR KWO for 2 yearly cycles for 625 EFPD (Figure 10-1). These high-power experiments (at a surface heat flux of up to 140 W/cm) performed in the early 1970ies showed a peak oxide that increased heavily with increasing linear heat generation rate (LHGR) prevailing during the last cycle (Figure 10-1). At the peak LHGR value (470 W/cm, and a heat flux of 140 W/cm²), a corrosion related failure was observed due to the formation of tangential cracks in the oxide layer with thickness of >50 μm, resulting in a very high local high temperature increase (creating even local cladding recrystallization as PIE showed) and a dramatic acceleration of the local corrosion rate. The formed thick oxide was spalled off, but the local thinning of the wall became obvious.
- 2) Other potential reason of corrosion induced failures were observed from the experimental irradiation of 4 FAs with an increased enrichment during the 3rd irradiation cycle, where the FAs were exposed at a high LHGR (235 W/cm). At the end of the third exposure cycle >10% of the FRs (87) of these 4 FAs failed, at a peak oxide thickness of 140-190 μm (Figure 10-2). The failures occurred at local positions with a peak oxide thickness of ≥140 mm exposed at the local heat flux values of 70 W/cm² during the last cycle, mainly due to very large hydride blisters (up to 90% of the wall thickness) at oxide spallation locations. The experience with thick oxide layers gained by Siemens up to 1985 is summarized in the Figure 10-2.
- **3)** The 3rd potential reason for PWR corrosion failures is the LiOH induced accelerated corrosion. During the experimental irradiation of 4 FAs with an increased enrichment during the 3rd cycle also Li induced failures were observed, which were described in Section 4.7.4. LiOH induced defects occurred, when the average Li content in the oxide layer became >200 ppm, as Figure 4-98 in Section 4.7.4 shows. The average Li content in the oxide layer depends on (1st) the Li content in the coolant, (2nd) the oxide layer thickness, and (3rd) on the heat flux, as

11 Corrosion modelling and predictions

Corrosion of the Zr-alloy cladding and structural components proceeds quite different in different reactor systems, such as PWR, VVER, BWR, RBMK, and CANDU reactors, due to the different FR surface temperatures and water chemistry in the different types of power reactors. FR corrosion in PWRs is particularly affected by the thermohydraulic characteristics of the PWR and the fuel duty. Therefore, it is necessary to deduce corrosion constants from the measured oxide data that can be applied for predictions of the corrosion behaviour in any PWR. The deduced corrosion constants can also allow a comparison of different material compositions and conditions for a future optimization of the Zr-alloys used for PWR fuel. The ANT International Report "PWR Zr Alloy Cladding Water Side corrosion analysis methods of measured oxide data and oxide thickness prediction. In the following only a summary of this report is given.

In most models the evaluation of the in-PWR corrosion is based on the out-of-reactor corrosion behaviour of Zr-alloys in oxygen free water, assuming at first the formation of a dense protective oxide film. Initially, the corrosion follows an approximate cubic law, where the corrosion rate decreases with increasing oxide layer thickness (S) and time (t):

Equation 11-1:

 $S^3 = k \cdot t$

At a certain oxide thickness, the so-called transition thickness ($S_{Trans} = 1.5-3 \mu m$), the oxide layer becomes porous causing a rate transition. After this transition, the corrosion rate is constant and is governed by the thickness and quality of the innermost part of the oxide layer (the barrier layer), that controls the corrosion rate. The thickness of the barrier layer is always less than the total oxide thickness, even in the pre-transition range. The corrosion rate (ds/dt) before and after the rate transition shows an exponential temperature dependence. For the post transition corrosion rate, which is most important for in-PWR corrosion modelling, the following equation is used:

Equation 11-2: $ds/dt = C \cdot exp(-Q/RT)$,

where C is the corrosion constant, that depends on Zr-alloy composition and final heat treatment condition, Q is the activation energy, R the gas constant, and T the absolute temperature. The temperature effect on corrosion rate is related to the increased transport rate of the corrosion species responsible for the oxide growth (electrons and/or oxygen ions) with increased temperature. The activation temperature, Q/R, is reported to be between 11000 and 16000 K and appears to be quite independent of the Zr-alloy composition and final heat treatment condition.

Several models to predict the PWR fuel cladding corrosion behaviour have been proposed over the years. Some of them are listed in the Table 11-1 together with the information on the basic concept and the most important parameters, such as the used corrosion rate constants and activation temperatures for the pre- and post-transition range, the transition thickness, as well as the applied thermal conductivity of the oxide layer. Most models assume that there is an initial period where corrosion is similar as that of out-of-reactor and that corrosion rate is only increased above a certain in-PWR transition oxide thickness, which varies between 2 and 6 μ m.

 Table 11-1:
 Basic concept used corrosion rate constants, activation temperatures, transition thickness, and applied thermal conductivity of the oxide layer for different models to predict PWR Zry-4 cladding corrosion [Garzarolli & Garzarolli, 2012].

Model	Basic assumption on corrosion rate	Pre Q/R K	etransition Rate const (μm/d)	n	Transition at (µm)	Post Q/R K	transition Rate const (μm/d)	Thermal cond. of oxide layer W/(cm⋅K)	References
EPRI/KWU4/CE5	increases after transition depending on fast flux (for Zry-4)	16266	6.30E+09	3	2.2-2.4	13775	8.04E7+2.59E8 * (7.46E-15 * φ) ^{0.26}	0.015	[Garzarolli et al, 1982a]
Siemens	is as out reactor up to transition and increases then by FF (~4 for Zry-4)	14200	1.50E+08	1	~5	14200	1.5E8*FF	0.015	[Garzarolli et al, 1985a,1993,1996a]
Advanced Nuclear Fuel (ANF)	1978 MATPRO model, increases by temperature dependent A and independent E	15660	4.97E+9*A	3	1.3–1.9	14080	8.288E+7*A*E	0.0173	[Van Swam & Shann, 1991]
British Nuclear Fuels Limited (BNFL)	increases after transition by FF, depending on fast flux and material, Recrystallized (RX)-degree, H-content, Li-content	16250	5.07E+13	3	2.2	14172	1.5E8*FF	0.015 at <48 µm 0.008 at >65 µm	[Polley et al, 1992]
ABB	increases linearly with fast flux and the oxide thickness >6 μm	16260	1.34E+10	3	2.3-2.6	13775	1.04E8* (1+F · φ · (Sox-6)	0.022	[Forsberg et al, 1995]
EPRI-PFCC	increases after transition depending on fast flux, Fe-cont., Sn-cont., SPP-size, H-cont., Li-cont	16952	5.88E+10	3	2	12500 at <400 ppmH 4600 at 18800 ppmH	C - $\phi^{0.25}$	0.015	[Levy et al, 1995] [Cheng et al, 1996]
CEA®/EDF7/ FRAMATOME	follows repeated transition and increases in PWR after transition to ≈2 and >18 μm to≈5 (for Zry-4)	16000	6.92E+09	3	1.75 for Zry-4 2.08, M2	16000		0.022 (>18 µm 0.008)	[Pêcheur et al, 2004]
φ = fast neutron flux in n/cm ⁵ s, F or FF = fitting factor, Sox = oxide thickness, A=120°exp(-0.0071°T), E = temperature independent multiplication factor									
									ANT International, 2012

There are different models for analysis and prediction of in-PWR corrosion behaviour of Zr alloys. The models apply different (a) transition thickness (1,75-5 μ m), (b) temperature dependency (Q/R=12500-18800 K), and (c) thermal conductivity of the oxide layer (0.008-0.022 W/cm·K). It must be pointed out that conclusion from analysis with a particular model cannot be compared with conclusions derived with another model. For this report it was decided to apply the Siemens model with its corrosion constants (as default constants), because it allows comparison with the corrosion constants (enhancement factors) of the largest published data base for very different material composition and final heat treatment conditions.

[Garzarolli & Goll, 1993] reported that the **post irradiation measurements of 30-150 μm oxide layer thickness on Zry-4 PWR cladding tubes in boiling water showed rather high thermal conductivities** (0.03-0.06 W/(cm·K)) much higher than diffusivity measurements in vacuum of cladding samples with 15-50 μm thick oxide layers (0.015-0.018 W/(cm·K)), as can be seen from Figure 11-1. They pointed out that the lower values may be a result of cracks formed in the oxide layer either due to the differential expansion of Zr metal and oxide during operation or during handling.

At larger oxide thicknesses, the oxide growth rate will accelerate due to the **low thermal conductivity of the oxide** resulting in a significant increase of the oxide/metal interface temperature. which in turn will cause an increase of the corrosion rate thermal feedback. Thermal conductivity values ranging from 0.008 to 0.022 W/(cm·K) have been used in different codes.

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Nomenclature

AREVA	French Equipment Manufacturer, today Framatome
ASTM	American Society for Testing and Materials
ATR	Advanced Test Reactor
BF	Browns Ferry
BU	Burnup
BWR	Boiling Water Reactor
CANDU	CANada Deuterium Uranium type of Reactor
CE	Combustion Engineering
CGR	Crack Growth Rate
СНС	Critical Hydrogen Concentration
CILC	CRUD Induced Localized Corrosion
CPNPP	Comanche Peak Nuclear Power Plant
CR	Control Rod
CRUD	Chalk River Unidentified Deposits
CVCS	Chemical and Volume Control System
CW	Cold Work
CWSR	Cold Work Stress Relieved
DNB	Departure from Nuclear Boiling
DNBS	Dresden Nuclear Power Station
DR-3	DIDO class experimental reactor
DZO	Depleted Zinc Oxide
DX	Duplex
EC	Eddy Current
EdF	Electricite de France
EFID	Effective Full insertion days
EFPD	Effective Full Power Day
EFPY	Effective Full Power Years
ЕНС	Electro-Hydraulic Control
EPRI	Electric Power Research Institute, USA
ETR	Experimental Test Reactor
et al	et alia

FA	Fuel Assembly
FF	Fitting Factor
FGR	Fission Gas Release
FR	Fuel Rod
FW	Feed Water
GB	Grain Boundary
GE	General Electric
GNF	Global Nuclear Fuel
GT	Guide Thimble
HBWR	Halden Boiling Water Reactor
НТ	High Temperature
НТР	High Thermal Performance
HPST	High Pressure Steam Test
HPU	Hydrogen Pick-Up
HPUF	Hydrogen Pick-Up Fraction
HWC	Hydrogen Water Chemistry
IAEA	International Atomic Energy Agency
IASCC	Irradiation Assisted Stress Corrosion Cracking
IPHT	In Process Heat Treated
KKB	KernKraftwerk Borsele
KKL	KernKraftwerk Leibstadt
KRB	KernReaktor Brunsbuttel
KWL	KernkraftWerk Lingen
KWO	Kraftwerk Obrigheim (Nuclear Power Plant Section of Siemens)
KWU	Kraftwerk Union (Nuclear Power Plant Section of Siemens)
LHGR	Linear Heat Generation Rate
LOCA	Loss of Coolant Accident
LTA	Lead Test Assembly
LTP	Low Temperature Processed
LWR	Light Water Reactor
MDA	Mitsubishi Developed Alloy
MW	Mega Watt

MZFR	Heavy Water Research Reactor in Germany now decommissioned
NDA	New Developed Alloy
NFI	Nuclear Fuel Industry
NMCA	Noble Metal Chemical Application
NNFD	Nippon Nuclear Fuel Development
NPP	Nuclear Power Plant
NRC	Nuclear Regulatory Commission
NRU	National Research Universal reactor
NWC	Normal Water Chemistry
OECD	Organisation of the cooperative performance of the Halden Reactor
OD	Outer Diameter
OLNC	On-Line Noble Metal Chemistry
0/W	Oxide/Water
PCI	Pellet cladding interaction
PIE	Post irradiation examination
ppb	part per billion = $\mu g/kg$
ppm	part per million = mg/kg
PR	Partially Recrystallized
РТ	Pressure Tubes
PWR	Pressurized Water Reactor
PHWR	Pressurized Heavy Water Reactor
RBMK reactor)	Reactor Bolshoi Mozhnosti Kanalov (in English Large Boiling Water Channel type
REDOX	REDuction-OXidation
RX	Recrystallised
RXA	Recrystallised Annealed
SCC	Stress Corrosion Cracking
SCW	super critical water
SEM	Scanning Electron Microscope
SG	Steam Generator
SGHWR	Steam Generating Heavy Water Reactor
SHE	Standard Hydrogen Electrode
SIMS	Secondary Ion Mass Spectrometry

SNB	Sub-cooled Nucleate Boiling
SPP	Second Phase Particle
SR	Stress Relieved
SS	Stainless Steels
STEM	Scanning Transmission Electron Microscopy
STR	Special Topic Report
ТМ	Transition Metals
TEM	Transmission Electron Microscope
TMI	Three Mile Island
UKAEA	UK Atomic Energy Authority
UV	Ultraviolet Light
VAK	Versuchs Atomkraftwerk Kahl
VVER	Voda Voda Energo Reactor (Russian Acronym for the Russian type of PWR)
ZIRAT	ZIRconium Alloy Technology
ZIRLO	ZIRconium Low Oxidation
Zr alloy	Zircaloy

Unit conversion

TEMPERATURE				
°C + 273.15	= K °C ×	1.8 + 32 = °F		
T(K)	T(°C)	T(°F)		
273	0	32		
289	16	61		
298	25	77		
373	100	212		
473	200	392		
573	300	572		
633	360	680		
673	400	752		
773	500	932		
783	510	950		
793	520	968		
823	550	1022		
833	560	1040		
873	600	1112		
878	605	1121		
893	620	1148		
923	650	1202		
973	700	1292		
1023	750	1382		
1053	780	1436		
1073	800	1472		
1136	863	1585		
1143	870	1598		
1173	900	1652		
1273	1000	1832		
1343	1070	1958		
1478	1204	2200		

	Radioactivity
1 Sv	= 100 Rem
1 Ci	= 3.7 × 10 ¹⁰ Bq = 37 GBq
1 Bq	= 1 s ⁻¹

N	IASS
kg	lbs
0.454	1
1	2.20

ANCE
x (mils)
0.02
0.04
0.20
0.39
0.79
0.98
1.00
3.94

PRESSURE				
bar	MPa	psi		
1	0.1	14		
10	1	142		
70	7	995		
70.4	7.04	1000		
100	10	1421		
130	13	1847		
155	15.5	2203		
704	70.4	10000		
1000	100	14211		

STRESS INTENSITY FACTOR		
MPa√m	ksi√inch	
0.91	1	
1	1.10	