

Review of Zircaloy Oxidation

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Abstract

This paper provides an overview of the kinetics for Zircaloy clad oxidation behaviour in steam and air during reactor accident conditions. The generation of chemical heat from metal/water reaction is considered. The effect of internal clad oxidation due to Zircaloy/VO₂ interaction is also discussed. Low-temperature oxidation of Zircaloy due to water-side corrosion is further described.

Introduction

The prediction of high temperature fuel rod behaviour is of particular importance for nuclear safety analysis. An understanding of fuel rod behavior has been well advanced through many decades of experimental research and efforts in modeling and code development (Van Uffelen, 2006). Various types of component and system computer codes have been developed by the international fuel community to describe nuclear fuel rod behaviour and performance during normal, upset and severe accident conditions (Cunningham, 2001; Lassmann, 1992; Gauntt, 2000; Dosanjh, 1989; Berna, 1985; Sills, 1979; Williams, 2005). These various codes describe the complex and linked phenomena associated with the thermo-mechanical and chemical behaviour of the fuel rod/bundle.

Zircaloy oxidation will affect the behaviour of fuel cladding during normal reactor operation. More importantly, it is also a key source of chemical heat due to metal-water reaction at high temperature during reactor accident situations. The uptake of oxygen can also embrittle the Zircaloy sheath. For instance, if the oxygen concentration over half of the clad wall thickness exceeds ~0.7 wt%, it can fail upon rewet during the introduction of emergency core cooling in a reactor accident (Sawatzky, 1978, Grandjean, 2008), or fail by overstrain under oxide cracks at strains as low as ~2% (Sagat, 1982).

Zircaloy Clad Oxidation

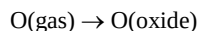
The oxidation of the Zircaloy cladding is an important consideration in light water/heavy water reactor accidents because this reaction will release heat and produce hydrogen/deuterium gas:



With a sufficient amount of water vapour, the cladding can be fully oxidized to ZrO₂ before the melting point of the metal is reached. On the other hand, as a significant amount of hydrogen gas can be produced in Eq. (1) with a large mass of Zirconium in the reactor core, the gas phase can become depleted in water vapour in the downstream locations of the fuel rods/bundle. In this case, the cladding does not completely oxidize and the ZrO₂ scale can dissolve into the remaining metal.

In the physical process of sheath oxidation (Olander, 1994(a)), with the absorption of oxygen by the sheathing, the steam mole fraction in the gas at the surface of the clad is smaller than that in the bulk gas, and the oxygen uptake rate by the solid depends on the water flux through the external gas phase boundary layer on the cladding surface where it decomposes. The O/Zr ratio in the solid at the surface is related to the water vapour-H₂ ratio in the adjacent gas by the thermochemistry of the O-Zr system. Oxygen in the solid at the surface moves through the oxide scale:

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The oxygen that arrives reacts with the substrate metal at the oxide/metal interface to produce the substoichiometric oxide ZrO_{2-x} which equilibrates with the substrate $\alpha\text{-Zr}$. The O/Zr ratio in the metal at the interface is the terminal solubility of oxygen in $\alpha\text{-Zr}$. Oxygen diffuses into the substrate metal from the oxide-metal interface



at a rate determined by the Fick's second law of diffusion.

Large accident modelling codes (Gauntt, 2000; Dosanjh, 1989; Berna, 1985; Fauske, 1990) generally describe the Zircaloy oxidation process using parabolic corrosion rate theory developed from laboratory experiments (Baker, 1962; Urbanic, 1978; Prater(a), 1987; Pawel, 1979(b); Schanz, 2004; Causey, 2005; Erbacher, 1987; Volchek, 2004; Fichot, 2004; OECD-NEA, 2010). For the parabolic rate law

$$w^2 = k_w t \quad (2)$$

where w is the mass of Zircaloy reacting per unit area with steam (kg m^{-2}), k_w is the reaction rate constant ($\text{kg m}^{-4} \text{s}^{-1}$), and t is time (s). The parabolic rate constant k_w , has the form

$$k_w = k_{w0} \exp\left(-\frac{Q}{RT}\right) \quad (3)$$

where k_{w0} , and Q are constants (see Table 1), R is the ideal gas constant ($= 8.31 \text{ J mol}^{-1} \text{ K}^{-1}$), and T is the temperature (in K) (Lewis, 1993(a)).

Table 1. Parametric values for parabolic rate constant for Zircaloy oxidation in steam

Investigators	Temperature range (K)	$k_{w0} (\text{kg}^2 \text{m}^{-4} \text{s}^{-1})$	$Q (\times 10^3 \text{ J/mol})$
Baker and Just	1273 to melting point	3.33×10^3	190
Urbanic and Heidrick	1323 to 1853	2.96×10^1	140
	1853 to melting point	8.79×10^1	138
Pawel et al.	1273 to 1773	2.94×10^2	167
Prater and Courtright	1783 to 2773	2.68×10^4	220

Recent experiments at 700 to 900°C with steam pressures from 0.1 MPa to 15 MPa suggests that the oxidation rate of Zircaloy-4 increases with the steam pressure; however, this pressure dependence does not appear at 1100°C (Pawel, 1979(a); Park, 2001). Zircaloy oxidation tests have also been conducted in various steam-hydrogen mixtures at temperatures between 1223 K and 1373 K (Furuta, 1978; Furuta, 1982). In these latter tests, the total weight gain varied with the hydrogen volume fraction and significantly decreased at a critical level of the hydrogen fraction. Hydrogen absorption occurred above a critical hydrogen fraction with the presence of a porous oxide. The hydriding resulted in a reduction of the Zircaloy-4 ductility. In addition, the oxidation kinetics of low-Sn Zircaloy-4 cladding has been investigated in the lower temperature range of 773 to 1253 K, where a cubic oxidation rate law is suggested (Nagase, 2003):

$$w^3 = k_w t \quad (4)$$

The rate constant obtained in these experiments in steam is shown in Figure 1.

In parabolic corrosion rate theory, the increment in the oxygen absorbed in a time step Δt is taken to be the minimum of $\dot{w}\Delta t$, n_{Zr} or $n_w/2$, where $\dot{w}$ is the molar rate of oxygen absorption per square centimeter of cladding, given by parabolic rate theory, and n_{Zr} and n_w are the moles of zirconium and H_2O (or D_2O) per unit cladding surface area in the node at the start of the time step. These three conditions represent parabolic corrosion in unlimited steam, zirconium availability, and steam availability, respectively. The laboratory corrosion experiments that underlie the above method are isothermal, usually conducted in unlimited

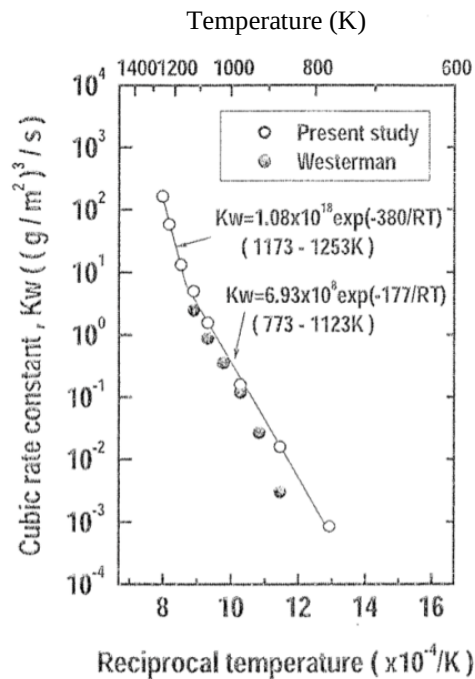


Figure 1. Rate constant for cubic oxidation kinetics in steam from 773 to 1253 K (taken from Ref. (Nagase, 2003)).

steam environments, and are restricted to metal specimens whose thickness is large compared with the scale thickness. Under these conditions, the rates of oxygen uptake and of growth of the oxide scale are theoretically proportional to the square root of time as shown in Eq. (2) at high temperature (Pawel, 1979(b)). However, with steam-H₂ gas present in a degraded reactor accident and finite sheath thickness, the conditions required for a parabolic behavior may not be fulfilled. The effect of scale dissolution in the substrate metal, which occurs in steam-starved gases as well as the effect of oxygen concentration reaching the solubility limit across the sheath volume, cannot be modelled by parabolic kinetics. The presence or absence of a ZrO₂ scale on the cladding has an important effect on the uptake of hydrogen by the metal, which can affect the course of the fuel dissolution process when the metal melts in higher temperature accident scenarios.

The oxidized cladding has a complex morphology. For instance, two other contiguous metallic phases of zirconium can exist for the partially-oxidized Zircaloy cladding in addition to the zirconia layer. Since the mechanical properties of these layers are strongly influenced by oxygen distribution, an accurate prediction of the layer thicknesses, oxygen profile and reaction rates are needed. In summary, a more complicated model is needed to predict the Zircaloy oxidation behaviour to more accurately predict the oxidation kinetics, as well as the sheath deformation behaviour and time of failure. In addition, as mentioned, parabolic kinetics cannot handle the scale dissolution behaviour in reducing environments.

A variety of structures result in oxidized Zircaloy that depends on the temperature and oxygen concentration (Iglesias, 1985). At temperatures below 1144 K, an outer layer of zirconia results adjacent to a layer of alpha Zr (α) that contains oxygen in solid solution. On the other hand, at temperatures above 1255 K, at least three layers are observed: (i) an external zirconia layer, (ii) an intermediate "oxygen-stabilized" α layer and (iii) an inner layer of base metal comprised of transformed beta Zr (β). Between this temperature range, the transformed β forms at the triple point of the α grains, where three structures form: (i) an outside layer of zirconia, (ii) an α layer adjacent to the zirconia layer and (iii) an internal layer of transformed β combined with undissolved α . With cooling, the β phase will transform back to the α phase in which the oxygen concentration is significantly different from that of the oxygen-stabilized α and "prior β ". Moreover, under certain conditions, the α layer can also consist of two sublayers (α_1 and α_2) (Iglesias, 1985). The prior β material can also reveal structural changes where, if enough oxygen is absorbed, " α incursions" may form with a growth of oxygen-enriched α into β . Although the boundaries between the different phases are generally planar, irregular boundary surfaces can be formed at low temperatures or by the appearance of the secondary phenomenon previously mentioned. Figure 2 shows the boundaries for the exiting phases (Prater, 1987(b)).

As mentioned, diffusion theory has been applied to describe the corrosion of cladding for general transient conditions for finite specimens (Iglesias, 1985; Malang, 1975; Hofmann, 1987). These accurate models require the numerical solution of partial differential equations representing Fickian diffusion in each layer:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \quad (5)$$

Here D is the diffusion coefficient, C is the oxygen concentration and x is the spatial coordinate. These partial differential equations are also subject to specified oxygen concentration values at each of the layer boundaries and oxygen conservation relationships as the boundaries move. This moving boundary problem has been solved as the FROM (Full Range Oxidation Model) computer code, which predicts the various corrosion layer thicknesses, transition from two phase to three phase oxidation, and oxygen concentration profiles in the Zircaloy sheath (Iglesias, 1985). This latter treatment also incorporates non-equilibrium boundary concentrations that improve the prediction of the oxide layer thickness during fast temperature transients.

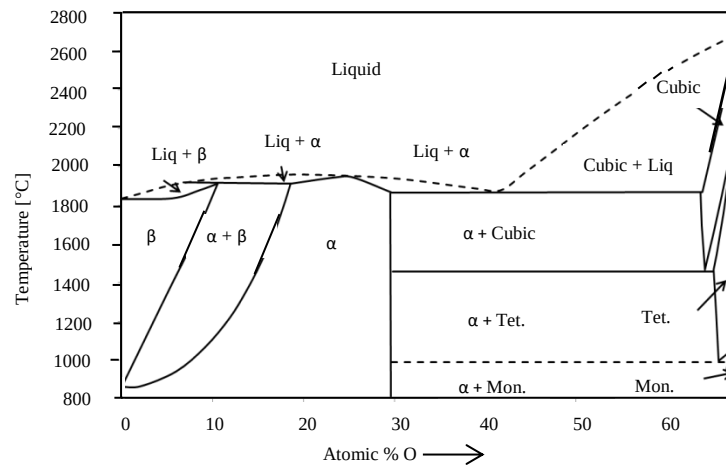


Figure 2. Zirconium-Oxide phase diagram.

An “integral diffusion technique” has been further developed as a compromise between the computationally simple yet physically oversimplified parabolic kinetic technique and the highly descriptive but analytically complex full diffusion theory treatment (Olander, 1994(a)). In this method, the exact concentration distribution of oxygen in the metal phase is replaced by an approximate distribution that fits the boundary and initial conditions. This distribution is coupled to the linear oxygen concentration profile in the oxide layer (and ultimately to the steam mole fraction in the bulk gas). However, this treatment oversimplifies the duplex α -Zr and β -Zr metal phase as a single metal layer (with the diffusion properties of α -Zr). Thus, this technique fails to accurately model the structural properties of the sheath, which is particularly important in order to determine the timing of sheath failure. The detailed morphological state of the sheathing is important because it determines: (i) the mechanical properties of the clad and thus the timing of clad failure; (ii) the heat released by the oxidation process and hydrogen dissolution in the cladding; and (iii) the capacity of the metal to dissolve fuel when the cladding melts at $\sim 2000^\circ\text{C}$.

Oxidation of the Zircaloy sheath in air is also an important phenomenon because of the possibility of fuel handling accidents. Single-effects experiments with air oxidation from ~ 500 to 1000°C , as well as multi-element testing in the CODEX facility simulating air ingress for Pressurized Water Reactor (PWR)-type fuel, have been performed (Vermoyal, 2001; Natesan, 2004; Duriez, 2005; Suzuki, 1986; Hozer, 2006). In the reaction between Zircaloy-4 and air and in steam and nitrogen-containing atmospheres at temperatures above 800°C , there is a degradation of the cladding material with formation of zirconium nitride and its re-oxidation (Steinbrück, 2009). Breakaway oxidation in air shows similar characteristics to that of steam, where the only difference is due to the formation of zirconium nitrides that affect the characteristics of the zirconia phase. This is supported by the experimental evidence that the oxide thickness at transition is similar for oxidation in steam or air (Leistikov, 1978; Duriez, 2005). Although parabolic correlations may be applied for oxidation in air, this is only appropriate for high temperatures ($>1400^\circ\text{C}$) and for pre-oxidized cladding ($\geq 1100^\circ\text{C}$), i.e., under all other conditions, faster kinetics are observed to occur (Steinbrück, 2009) probably due to a less protective oxide layer by the crystallographic mismatch between zirconia and zirconium nitrides. This is consistent with similar behaviour reported for Zircaloy oxidation in environmental mixtures of steam and nitrogen (Steinbrück, 2009).

Measurements have also been made on the loss of ductility and embrittlement of Zircaloy-4 cladding by oxidation and hydriding under LOCA conditions and with a water quench (Furuta, 1981; Furuta, 1984; Uetsuka, 1981; Uetsuka, 1983; Nagase, 2004; Nagase, 2005; Kim, 2005; Kim, 2006). In particular, the LOFT FP-2 test was a relatively large in-reactor experiment to determine the effect of reflood for a severely damaged core assembly (Jensen, 1989; Hobbins, 1990). A large fraction of the bundle inventory of the LOFT FP-2 bundle was available for subsequent oxidation during reflooding. This experiment showed that significant H_2 generation can be expected during reflooding, which is largely dependent on the degree of prior oxidation and reflood thermalhydraulic conditions. An upper debris bed was also observed in the LOFT FP-2 test when coolant was introduced into the hot bundle, resulting in a thermal shock and fragmentation of the oxidized fuel rods.

Acceptance criteria for preventing fuel failure due to oxygen and hydrogen embrittlement with water quench by the emergency core coolant system has been proposed by a number of investigators (Sawatzky, 1978; Furuta, 1984; Erbacher, 1987; Chung, 2005; Nagase, 2009).

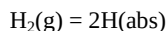
Chemical Heat Generation by Clad Oxidation/Hydriding

All transient reactor analysis codes compute the oxidative heat release from the standard enthalpy change for the reaction in Eq. (1) (Gauntt, 2000; Dosanjh, 1989; Berna, 1985; Sills, 1979). However, during a substantial portion of the accident, the corrosion product is not the stoichiometric oxide (Olander, 1994(b)). In the steam-starved regions, the principal final state is oxygen dissolved in the metal so that the heat release is in accordance with the reaction:



The partial molar enthalpy of solution of oxygen in Zr depends on the O/Zr ratio of the metal, where calorimetric data permit estimation of this quantity (Boureau, 1984). For typical oxygen contents in the metal, the heat of solution of oxygen is 3-5% more negative than the heat of formation of stoichiometric ZrO_2 . Hence, after subtracting the heat of formation of $H_2O(g)$, the heat release for the reaction in Eq. (6) is 6-10% larger than that for Eq. (1) (Olander, 1994(b); Olander, 1995(b)).

It is generally assumed that the hydrogen solubility in Zircaloy is negligible at high temperatures. Although the phase diagram of the H-Zr system shows that zirconium hydrides do not form at temperatures above about 1200 K (Kubaschewski, 1976), measurements of the high-temperature solubility of hydrogen in Zircaloy, however, show that dissolution as interstitial atoms is significant particularly at a higher system pressure (Moalem, 1991; Yamanka, 1995; Yamanka, 1997). For high steam flow rates, the outer sheath surface is covered with a protective ZrO_2 scale. Hence, because of the low solubility of hydrogen in ZrO_2 (Park, 1991), H absorption is restricted to just the pick-up fraction that results during Zircaloy oxidation. This amount is quite small because of the low hydrogen permeability of the coherent oxide scale produced by oxidation above ~1300 K. When a ZrO_2 scale separates the external gas from the metal, the gas in the gap consists of only He and Xe, except for short distances from a rupture site with rod failure, where some hydrogen and, to a lesser extent, steam are present. On the other hand, with a low steam flow rate, the external gas quickly becomes steam-starved and, shortly thereafter, the oxide scale dissolves into the metal. Downstream regions of the reactor core that contain Zircaloy without an oxide scale are inevitably in contact with a gas that is nearly pure H_2 , which dissolves in the metal according to the reaction:



The equilibrium of this reaction is given by Sievert's law:

$$\frac{C_H}{\sqrt{p_{H_2}}} = \exp\left(\frac{\Delta S_H}{R}\right) \exp\left(-\frac{\Delta H_H}{RT}\right) \quad (7)$$

where C_H is the H/Zr ratio of the metal in equilibrium with the gas containing H_2 at a hydrogen gas partial pressure p_{H_2} (atm). The thermochemical properties of hydrogen dissolution in Zircaloy are given in Table 2 (Moalem, 1991; Yamanka, 1995; Steinbrück, 2004). However, some discrepancy is seen in the measured values shown in Table 2. Hydrogen dissolution is typically neglected in accident analysis even though the above data suggest that the solubility is significant at temperatures as high as 2000°C. The principal consequences of hydrogen retention by the metal are twofold (Olander, 1994(b); Olander, 1995(b)): (i) The unoxidized metal acts as a sink of hydrogen, which can alter the timing of hydrogen release; hydrogen absorbed in the metal

in the steam-starved regions of the core is released on subsequent oxidation, because of the low solubility of hydrogen in zirconia.
 (ii) Hydrogen absorption by zirconium releases heat.

Table 2. Thermophysical Properties for Hydrogen Dissolution in Zircaloy

Investigator	ΔH_H (kJ/mol)	ΔS_H (J/mol-K)
(Moalem, 1991)	-63	-54
(Yamanaka, 1995)	- 246 (alpha), -252 (beta)	- 38 (alpha), -25 (beta)
(Steinbrück, 2004)	-65	-101

The normal approach for estimating heat release in accident codes is by oxidative heating, which is valid during the early stages of a transient because the principal oxidation product is ZrO_2 , where the oxide scale has not appreciably dissolved in the metal so that no hydrogen is absorbed in this time period. This oxidative heating is based on the total amount of oxygen absorbed, assuming that the heat released per gram atom of oxygen absorbed by the metal is one-half of the standard enthalpy of the reaction in Eq. (1). As previously discussed, in steam-starved regions, one must further consider the effect of hydrogen absorption in metallic Zr. Moreover, hydrogen absorption can result in a sharp increase in the heat release with dissolution of only 10% of the corrosion-product hydrogen in cladding without an oxide scale, i.e., while not as exothermic as oxidative heating, hydrogen uptake can nearly double the contribution from oxidation alone (Olander, 1994(b)). This additional heating effect is the sum of the product of the hydrogen content of the metal and the enthalpy of solution of hydrogen. The cumulative heat release will decrease with a reduction in the solubility of hydrogen in Zr as the temperature increases (Olander, 1994(b)). Desorption of hydrogen from the cladding is endothermic, which consumes more heat than is typically provided by the continuing oxidation process.

Internal Zircaloy Oxidation due to Zircaloy/Uranium Dioxide Interaction

Under high-temperature conditions, a combined external and internal oxidation of the fuel sheathing can occur due to a reaction of steam on the outside surface of the sheath and from the UO_2 on the inside surface. The UO_2 and Zr can interact chemically at temperatures as low as 1273 K, leading to a complex series of reaction layers (Dienst, 1984) where, from both internal and external oxidation, the following reaction layers can be formed: $[UO_2 + U] \rightarrow [\alpha-Zr(O)_a + (U,Zr)] \rightarrow (U,Zr)_{alloy} \rightarrow \alpha-Zr(O)_b \rightarrow \beta-Zr \rightarrow \alpha-Zr(O)_c \rightarrow ZrO_2$. This internal interaction requires a substantial external overpressure to promote good solid-solid contact between the fuel and cladding. For instance, experiments have been conducted at overpressures of 4 MPa (Dienst, 1984) and 1 MPa (Hutchings, 1984). In the CANDU fuel design, the thin sheath will creep down onto the fuel under the conditions of the high pressure coolant. However, contact between the sheath and fuel can be lost during the transient with sheath lift off due to fission gas release into the (small) free void space of the fuel element and depressurization with coolant blowdown, as well as with the eventual bursting of the sheath. Thus, with an open gap during an accident, any direct fuel/sheath interaction is suppressed and no uranium is transferred from the fuel to the sheathing as long as the sheath is solid. If the gap contains hydrogen, fuel reduction can occur as oxygen moves from the fuel to the sheathing by the H_2O-H_2 transport mechanism, driven by the difference in the oxygen potential between the fuel surface and the sheathing inner wall. However, the extent of fuel reduction and cladding oxidation by this mechanism is minor (Olander, 1994(b)).

At temperatures above ~1470 K, steam oxidation of Zircaloy and stainless steel produces a significant temperature escalation. With the melting of the as received metallic Zircaloy-4 cladding (2030 K) or metallic oxygen-stabilized $\alpha-Zr(O)$ phase (2245 K), the solid UO_2 may be partially dissolved and liquefied ~1000 K below its melting temperature. The driving force for the reaction is diffusion of oxygen from the UO_2 into the sheathing. This process has been extensively studied in single-effect laboratory crucible experiments (Dienst, 1984; Rosinger, 1985; Hofmann, 1988; Nikolopoulos, 1984; Kim, 1988; Hayward, 1994(a); Hayward, 1994(b); Olander, 1995(a); Hayward, 1996(a); Hayward, 1996(b); Veshchunov, 1996; Olander, 1996; Hayward, 1999(a); Hayward, 1999(b); Hofmann, 1999; Mueller, 2004; Stuckert, 2002; Adroguer, 2005).

In hydrogen-rich regions of the core, the outer oxide scale is not present on the cladding, which is all-metal with oxygen in solid solution. On melting of the cladding, the liquid metal contacts the solid fuel and dissolution of the fuel begins. The endothermic reaction of UO_2 dissolution in U-Zr-O melts and the melting of $\alpha Zr(O)$ sheathing is affected by the supply of heat. In addition to receiving additional oxygen, uranium from the fuel dissolves in the liquid metal forming a U-Zr-O melt. Dissolution continues until the melt is saturated in both oxygen and uranium (Olander, 1995(b)). The fuel dissolution process has been detailed, for example, in (Olander, 1996), where it is shown that diffusion in the growing U-Zr-O melt is rapid and the liquid phase concentration remains at saturation. Reduction of the fuel by oxygen diffusion affects the amount of oxygen in the melt.

The effect of an oxide scale will also reduce the extent of fuel liquefaction because less metal is available to dissolve uranium when a melt forms. In addition, the high concentration of oxygen in the oxide layer will increase the oxygen content of the melt, thus depressing the uranium solubility. It is suggested that the fraction of the fuel pellet that is dissolved by the initial liquefaction is small (Olander, 1996).

Zircaloy Corrosion at Low Temperature

During normal reactor operation, the outer cladding surface of the fuel rods will corrode very slowly on the waterside of the cladding. This reaction at low temperature proceeds through the reaction in Eq. (1). Part of the hydrogen generated in this reaction diffuses into the metal. At the start of the oxidation process, all of the hydrogen may be absorbed. However, the rate of absorption readily decreases from a maximum during the first 10 mg dm^{-2} oxidation to a typical plateau (Clayton, 1989; Cox, 1963; Cox, 2005). The pickup fraction (defined as the amount of hydrogen in the metal to the total amount produced during the corrosion reaction) for Zircaloy-4 is usually between 5 and 25%. In the case of defective fuel, with the addition of internal clad corrosion, the hydrogen that is not absorbed by the cladding is released into the fuel-to-clad gap of the defected rod, thereby enriching the steam atmosphere in hydrogen, which will affect the oxygen potential in the fuel-to-clad gap thereby inhibiting the fuel oxidation reaction (Higgs, 2007).

The kinetics for the waterside corrosion have been extensively studied (Parry, 1980; Stehle, 1984; Peters, 1984; Almarshad, 1991). In the 523 to 673 K temperature range, the corrosion process of Zircaloy starts with the formation of a thin protective oxide that grows with an approximate cubic rate law. After a certain thickness is reached, a transition occurs where cracks develop in the oxide film structure. These cracks provide easier access of the oxygen to the oxide-metal interface, resulting in a breakaway regime that is characterized by linear kinetics. An enhancement factor for water-side corrosion is seen for in-reactor conditions, with a factor ranging from 1 to 3 in pressurized water reactors, and 10 for boiling water reactors (Pickman, 1994). For a defected fuel element operating at $\sim 50 \text{ kW m}^{-1}$, an enhancement of ~ 50 has been suggested for enhanced corrosion on the inside cladding surface due to bombardment by energetic fission fragments (Lewis, 1993(b)).

References

- Adroguer, B., Bertrand, F., Chatelard, P., Cocuau, N., Van Dorsselaere, J.P., Bellenfant, L., Knocke, D., Bottomley, D., Vrtlikova, V., Belovsky, L., Mueller, K., Hering, W., Homann, C., Krauss, W., Miasoedov, A., Schanz, G., Steinbrueck, M., Stuckert, J., Hozer, Z., Bandini, G., Birchley, J., von Berlepsch, T., Kleinhietpass, I., Buck, M., Benitez, J.A.F., Virtanen, E., Marguet, S., Azarian, G., Caillaux, A., Plank, H., Boldyrev, A., Veshchunov, M., Kobzar, V., Zvonarev, Y., and Goryachev, A., "Core Loss During a Severe Accident (COLOSS)," Nuclear Engineering and Design 235(2-4) (2005) 173-198.
- Almarshad, A.I.A., and Klein, A.C., "A Model for Waterside Oxidation of Zircaloy Fuel Cladding in Pressurized Water Reactors," J. Nucl. Mater. 183 (1991) 186.
- Baker, L., and Just, L.C., "Studies of metal-water reactions at high temperatures," Rep. ANL-6548, Argonne National Laboratory, Argonne, IL, 1962.
- Berna, G. A., et al., "RELAP5/SCDAP/MOD0 Code Manual," EGG-RTH-7051, EG&G, September 1985.
- Boureau, G., Gerdanian, P.; J. Phys. Chem. Solids, 4, 141 (1984).
- Causey, R.A., Cowhill, D.F., Nilson, R.H., "Review of Oxidation Rate of Zirconium Alloys," SAND2005-6006, Sandia Repot, November 2005.
- Chung, H. M., "Fuel Behavior under Loss-of-Coolant Accident Situations," Nuclear Engineering and Technology, Vol. 37, No.4, August 2005.
- Clayton, J.C., "Internal Hydriding in Irradiated Defected Zircaloy Fuel Rods," Proc. 8th Int. Sym. Zirconium in the Nuclear Industry, STP 1023, p. 266, American Society for Testing and Materials (1989).
- Cox, B., "Some Factors Which Affect the Rate of oxidation and Hydrogen Absorption of Zircaloy-2 in Steam," AERE-R4348, Atomic Energy Research Establishment (Nov. 1963).
- Cox, B., "Some thoughts on the mechanisms of in-reactor corrosion of zirconium alloys," Journal of Nuclear Materials 336 (2005) 331-368.
- Cunningham, M.E., Beyer, C.E., Medvedev, P.G., Berna, G.A., "FRAPTRAN: A Computer Code for the Transient Analysis of Oxide Fuel Rods," NUREG/CR-6739, Vol. 1, PNNL-13576, 2001.
- Dienst, W., Hofmann, P. and Kerwin-Peck, D., "Chemical Interactions Between UO_2 and Zircaloy from 1000 to 2000°C," Nucl. Technol. 65 (1984) 109.

- Dosanji, S. S., (Ed.), "MELPROG-PWR/MOD1: A Two-Dimensional, Mechanistic Code for Analysis of Reactor Core Melt Progression and Vessel Attack Under Severe Accident Conditions," Sandia National Laboratories, NUREG/CR-5193, SAND88-1824, May 1989.
- Duriez, C., Drouan, D., and Dupont, T., "The MOZART Program on Air Cladding Oxidation: Results on Bare Zircaloy-4 in the Range 600-1000°C," Proceedings of the 25th Meeting of the Phebus FP Bundle Interpretation Circle, Aix-en-Provence, 2005 October 19.
- Erbacher, F. J., and Leistikow, S., "Zircaloy Fuel Cladding Behavior in a Loss-of-Coolant Accident: A Review," ASTM-STP 939, American Society for Testing and Materials, 1987, p. 451-488.
- Fauske and Associates, "MAAP3.0B Computer Code Manual," EPRI Rep. NE-7071-CCML, November 1990.
- Fichot, F., Adroguer, B., Volchek, A., and Zvonarev, Yu., "Advanced Treatment of Zircaloy Cladding High-Temperature Oxidation in Severe Accident Code Calculations. Part III. Verification Against Representative Transient Tests," Nuclear Engineering and Design 232(1) (2004) p. 97-109.
- Furuta, T., and Kawasaki, S., "Reaction Behavior of Zircaloy-4 in Steam-Hydrogen Mixtures at High Temperature," J. Nucl. Mater. 105(2/3) (1982) 119-131.
- Furuta, T., Kawasaki, S., and Hashimoto, M., Zircaloy-Clad Fuel Rod Burst Behavior under Simulated Loss-of-Coolant Condition in Pressurized Water Reactors, Journal of Nuclear Science and Technology, 15[10], p. 736-744 (October 1978).
- Furuta, T., Uetsuka, H., and Kawasaki, S., "Ductility Loss of Zircaloy Cladding by Inner-Surface Oxidation During High Temperature Transient," J. Nucl. Sci. Technol. 18(10) (1981) 802-810.
- Furuta, T., Uetsuka, H., and Kawasaki, S., "Estimation of Conservatism of Present Embrittlement Criteria for Zircaloy Fuel Cladding Under LOCA," ASTM-STP 824, American Society for Testing and Materials, 1984, p. 734-746.
- Gauntt, R. O., Cole, R. K., Erickson, C. M., Gido, R. G., Gasser, R. D., Rodriguez, S. B., and Young, M. F., "MELCOR Computer Code Manuals, Version 1.8.5," May 2000, NUREG/CR-6119, SAND-2417/2, May 2000.
- Grandjean, C., Hache, G., "A state-of-Art Review of Past Programmes Devoted to Fuel Behaviour Under Loss-of-Coolant Conditions, Part 3: Cladding Oxidation Resistance to Quench and Post-Quench Loads," IRSN Technical Report, DPAM/SEMCA 2008-093, 2008.
- Hayward, P.J. and George, I.M., "Dissolution of UO₂ Fuel by Molten Zircaloy-4, Part 1: Solubility from 2000 to 2200°C," J. Nucl. Mater. 208 (1994) 35 (a).
- Hayward, P.J. and George, I.M., "Dissolution of UO₂ Fuel by Molten Zircaloy-4, Part 2: Phase Evolution During Dissolution and Cooling," J. Nucl. Mater. 208 (1994) 43 (b).
- Hayward, P.J. and George, I.M., "Dissolution of UO₂ Fuel by Molten Zircaloy-4, Part 3: Solubility from 2000 to 2500°C," J. Nucl. Mater. 232 (1996) 1 (a).
- Hayward, P.J. and George, I.M., "Dissolution of UO₂ Fuel by Molten Zircaloy-4, Part 4: Phase Evolution During Dissolution and Cooling of 2000 to 2500°C Specimens," J. Nucl. Mater. 232 (1996) 13 (b).
- Hayward, P.J. and George, I.M., "Dissolution of ZrO₂ in Molten Zircaloy-4," J. Nucl. Mater. 265 (1999) 69-77 (a).
- Hayward, P.J., Hofmann, P., Stuckert, J., Veshchunov, M.S. and Berdyshev, A.V., "UO₂ Dissolution by Molten Zircaloy. New Experimental Results and Modelling," FzK Report FZKA-6379 / INV-CIT-99-P029, 1999 Dec. (b)
- Higgs, J.D., Lewis, B.J., Thompson, W.T. and He, Z., "A conceptual model for the fuel oxidation of defective fuel," J. Nucl. Mater. 366 (2007) 99-128
- Hobbins, R.R., McPherson, G.D., in: Proceedings of the Open Forum on the OECD/LOFT Project, Achievements and Significant Results, Madrid, Spain, 9-11 May 1990, Organization of Economic Cooperation and Development, 1991.
- Hofmann, P., and Neitzel, H.J., "Experimental and theoretical results of cladding oxidation under severe fuel-damage conditions," 7th symposium, ASTM STP 939, 1987, pp.504-538.
- Hofmann, P., Stuckert, J., Miasoedov, A., Veshchunov, M.S., Berdyshev, A.V. and Boldyrev, A.V., "ZrO₂ Dissolution by Molten Zircaloy and Cladding Oxide Shell Failure. New Experimental Results and Modelling," FzK Report FZKA-6383 / INV-CIT-98-P026, Dec 1999 (in English).
- Hofmann, P., Uetsuka, H., A.N. Wilhelm and E.A. Garcia, "Dissolution of Solid UO₂ by Molten Zircaloy and Its Modelling," in: IAEA/OECD International Symposium on Severe Accidents in Nuclear Power Plants, Sorrento, Italy, 21-25 March 1988 (IAEA-SM-296/99), p. 3.
- Hozier, Z., Maroti, L., Windberg, P., Matus, L., Nagy, I., Gyenes, G., Horvath, M., Pinter, A., Balasko, M., Czitrovszky, A., Jani, P., Nagy, A., Prokopiev, O., and Toth, B., "Behavior of VVER Fuel Rods Tested Under Severe Accident Conditions in the CODEX Facility," Nucl. Technol. 154 (2006) 302-317.
- Hutchings, W.G., and Rosinger, H.E., "The UO₂/Zircaloy interaction: a metallographic examination," Proc. ASM Metals Congress, Detroit, IL, 1984.
- Iglesias, F.C., Duncan, D.B., Sagat S., and Sills, H.E., "Verification of the FROM Model For Zircaloy Oxidation During High Temperature Transients," J. Nucl. Mater. 130 (1985) 3644

- Jensen, S.M., Akers, D.W., Pregger, B.A., "Postirradiation Examination Data and Analysis for OECD LOFT Fission Product Experiment LP-FP-2," OECD LOFT-T-3810, vol. 1, Organization of Economic Cooperation and Development, December 1989.
- Kim, J. H., Choi, B. K., Baek, J. H., and Jeong, Y. H., "Effects of Oxide and Hydrogen on the Behavior of Zircaloy-4 Cladding During the Loss of Coolant Accident (LOCA)," Nuclear Engineering and Design, 236 (2006), 2386-2393.
- Kim, J.H., Lee, M.H., Choi, B.K., and Jeong, Y.H., "Embrittlement Behavior of Zircaloy-4 Cladding During Oxidation and Water Quench," Nucl. Engin. Design 235(1) (2005) 67-75.
- Kim, K.Y., and Olander, D.R., "Dissolution of UO_2 by Molten Zircaloy," J. Nucl. Mater. 154 (1988) 85.
- Kubaschewski, O., "Zirconium: physico-chemical properties of its compounds and alloys," IAEA Special Issue 6 (1976).
- Lassmann, K., "TRANURANUS: A Fuel Rod Analysis Code Ready for Use", J. Nucl. Mater. 188 (1992) 295-302.
- Leistikov, S., Schanz, G., Berg, H., "Kinetics and Morphology of Isothermal Steam Oxidation of Zircaloy at 700-1300°C," KfK-2587, March 1978.
- Lewis, B.J., Cox, D.S., and Iglesias, F.C., "A kinetic model for fission-product release and fuel oxidation behaviour for Zircaloy-clad fuel elements under reactor accident conditions," J. Nucl. Mat. 207 (1993) 228-241 (a)
- Lewis, B.J., MacDonald, R.D., Ivanoff, N.V., and Iglesias, F.C., "Fuel Performance and Fission Product Release Studies for Defected Fuel Elements", Nucl. Technol. 103 (1993), 220-245 (b).
- Malang, S., "SIMTRAN I-A computer code for the simultaneous calculation of oxygen distributions and temperature profiles in Zircaloy during exposure to high-temperature oxidizing environments," Rep. ORNL-5083, Oak Ridge National Laboratory, Oak Ridge, TN, 1975.
- Moalem, M., and Olander, D.R., "The high-temperature solubility of hydrogen in pure and oxygen-containing zircaloy," J. Nucl. Mater. 178 (1991) 61.
- Mueller, K., Goryachev, A.V., Smirnov, V.P., Svyatkin, A.M., Stuckert, J., Veshchunov, M.S. and Berdyshev, A.V., "Simultaneous Dissolution of UO_2 and ZrO_2 by Molten Zircaloy. New Experiments and Modelling," FzK / EU Report FZKA-6947 / SAM-COLOSS-P-074, Jan 2004.
- Nagase, F., Chuto, T., and Fuketa, T., "Behavior of High Burn-up Fuel Cladding Under LOCA Conditions," Journal of Nuclear Science and Technology, Vol. 46, No. 7, PP. 763-769 (2009).
- Nagase, F. and Fuketa, T., "Behavior of Pre-Hydrated Zircaloy-4 Cladding Under Simulated LOCA Conditions," J. Nucl. Sci. Technol. 42(2) (2005) 209-218.
- Nagase, F. and Fuketa, T., "Effect of Pre-Hydrating on Thermal Shock Resistance of Zircaloy-4 Cladding Under Simulated Loss-Of-Coolant Accident Conditions," J. Nucl. Sci. Technol. 41(7) (2004) 723-730.
- Nagase, F., Otomo, T. and Uetsuka, H., "Oxidation Kinetics of Low-Sn Zircaloy-4 at the Temperature range 773 to 1,573 K," J. Nucl. Sci. Technol. 40(4) (2003) 213-219.
- Natesan, K., Soppet, W.K., "Air Oxidation Kinetics for Zr-Based Alloys," NUREG/CR-6846, March 2004.
- Nikolopoulos, P., Hofmann, P., and Kerwin-Peck, D.K., "Determination of the Interfacial Energy and Work of Adhesion in the UO_2 /Zircaloy-4 Diffusion Couple," J. Nucl. Mater. 124 (1984) 106.
- OECD-NEA Report, "Nuclear Fuel Behaviour under Loss-of-Coolant Accident (LOCA) Conditions," Organization for Economic Cooperation and Development (OECD), Nuclear Energy Agency (NEA), NEA No. 6846 (2010).
- Olander, D.R., "Interpretation of laboratory crucible experiments on UO_2 dissolution by liquid uranium," J. Nucl. Mater., 224 (1995) 254 (a).
- Olander, D.R., "Materials chemistry and transport modeling for severe accident analyses in light-water reactors, I: External cladding oxidation," Nucl. Eng. Des. 148 (1994) 253-271 (a).
- Olander, D.R., "Materials chemistry and transport modeling for severe accident analysis in light-water reactors, II: Gap processes and heat release" Nucl. Eng. Des. 148 (1994) 273-292 (b).
- Olander, D.R., "Materials chemistry and transport modeling for severe accident analyses in light-water reactors III. Fuel dissolution by molten cladding," Nuclear Engineering and Design 162 (1996) 257-270.
- Olander, D.R., "Thermodynamics and transport processes in reactor fuel," Pure & Appl. Chem., Vol. 67, No. 6, pp. 1003-1010, 1995(b).
- Park, K., Taegeun, Y., Sungkwon, K., Kim, H.G., Jeong, Y., and Kim, K., "High Temperature Oxidation of Zirconium Base Alloy in Steam," 7th International CANDU Fuel Conference, Kingston, Ontario (Canada) 23-27 Sep 2001, ISBN 0-919784-71-2 (v.2) p. 3B.1-3B.10.
- Park, K.H., and Olander, D.R., "Hydrogen dissolution in and release from nonmetals: III, tetragonal zirconia," J. Am. Ceram. Soc. 74 (1991) 72.
- Parry, G.W., and Smerd, P.G., "Review of PWR Fuel Rod Waterside Corrosion Behavior," NP-1472, Electric Power Research Institute (Aug. 1980).
- Pawel, R.E., Cathcart, J.V., and Campbell, J.J., "The Oxidation of Zircaloy-4 at 900 and 1100°C in High Pressure Steam," J. Nucl. Mater. 82(1) (1979) 129-139 (a).
- Pawel, R.E., J. Electrochem. Soc. 126 (1979) 1111 (b).

- Peters, H.R., "Improved Characterization of Aqueous Corrosion Kinetics of Zircaloy-4, Proc. 6th Int. Sym. Zirconium in the Nuclear Industry, ASTM-STP 824, p. 507, American Society for Testing and Materials (1984).
- Pickman, D. O., "Zirconium Alloy Performance in Light Water Reactors: A Review of UK and Scandinavian Experience," ASTM-STP 1245, American Society for Testing and Materials, 1994, pp. 19-32.
- Prater, J.T., and Courtwright, E.L., "Oxidation of Zircaloy-4 in Steam at 1300°C to 2400°C," Proc. 7th Int. Symp. on Zirconium in the Nuclear Industry, ASTM Spec. Tech. Publ. 939 (1987) 489 (a).
- Prater, J.T., and Courtwright, E.L., "Properties of Reactor Fuel Rods Material at High Temperatures," NUREG/CR-4891 July 1987 (b).
- Rosinger, H.E., Rondeau, R.K., Demoline, K., and Ross, K.J., "The Interaction and Dissolution of Solid UO_2 by Molten Zircaloy-4 Cladding in an Inert Atmosphere or Steam," 6th Annual Conference of the Canadian Nuclear Society, Ottawa, Ontario, June 3-4, 1985, p. 16.33.
- Sagat, S., Sills, H.E., Walsworth, J.A., Foote, D.E., and Shields, D.F., "Deformation and Failure of Zircaloy Fuel Sheaths Under LOCA Conditions," 6th International Conference on Zirconium in the Nuclear Industry, Vancouver, Canada 1982 June 28 to July 01 (also AECL-7754, 1982).
- Sawatzky, A., "A Proposed Criterion for the Oxygen Embrittlement of Zircaloy-4 Fuel Cladding," 4th International Conference on Zirconium in the Nuclear Industry, Stratford-upon-Avon, 1978, p. 479-496.
- Schanz, G., Adroguer, B., and Volchek, A., "Advanced Treatment of Zircaloy Cladding High-Temperature Oxidation in Severe Accident Code Calculations Part I. Experimental Database and Basic Modelling," Nuclear Engineering and Design 232(1) (2004) p. 75-84.
- Sills, H.E., "ELOCA Fuel Element Behaviour during High-Temperature Transients", AECL Report AECL-6357, 1979.
- Stehle, H., Garzarolli, F., Garde, A.M., and Smerd, P., "Characterization of ZrO_2 Films Formed In-Reactor and Ex-Reactor to Study Factors Contributing to the In-Reactor Waterside Corrosion of Zircaloy," Proc. 6th Int. Sym. Zirconium in the Nuclear Industry, ASTM-STP 824, p. 483, American Society for Testing and Materials (1984).
- Steinbrück, M., "Hydrogen absorption by zirconium alloys at high temperatures," J. Nucl. Mater. 334 (2004) 58-64.
- Steinbrück, M., "Prototypical experiments relating to air oxidation of Zircaloy-4 at high temperatures," J. Nucl. Mater. 392 (2009) 531-544.
- Stuckert, J., Miassodov, A., Hayward, P.J., Hofmann, P. and Veshchunov, M., " ZrO_2 and UO_2 Dissolution by Molten Zircalloy," Proceedings of the International Conference Nuclear Energy in Central Europe 2002, Kranjska Gora, Slovenia, 9-12 Sep 2002, electronic, 8 p.
- Suzuki, M., and Kawasaki, S., "Oxidation of Zircaloy Cladding in Air," J. Nucl. Mater. 140(1) (1986) 32-43.
- Uetsuka, H., Furuta, T., and Kawasaki, S., "Failure-Bearing Capability of Oxidized Zircaloy-4 Cladding under Simulated Loss-Of-Coolant Condition," J. Nucl. Sci. Technol. 20(11) (1983) 941-950.
- Uetsuka, H., Furuta, T., and Kawasaki, S., "Zircaloy-4 Cladding Embrittlement due to Inner Surface Oxidation under Simulated Loss-of-Coolant Condition," J. Nucl. Sci. Technol. 18(9) (1981) 705-717.
- Urbanic, V.F., and Heidrick, T.R., "High-Temperature Oxidation of Zircaloy-2 and Zircaloy-4 In Steam," J. Nucl. Mater. 75 (1978), pp. 251-261 (also AECL Report AECL-6149).
- Van Uffelen, P. "Modelling of Nuclear Fuel Behaviour," European Commission Directorate-General Joint Research Centre Institute for Transuranium Elements, EUR 22321 EN ISSN 1018-5593 (2006).
- Vermoyal, J.J., Dessemond, L., Hammou, A., and Frichet, A., "In Situ Characterization of Zircaloy-4 Oxidation at 500 °C in Dry Air," J. Nucl. Mater. 298(3) (2001) 297-308.
- Veshchunov, M.S., Hofmann, P., and Berdyshev, A.V., "Critical Evaluation of Uranium Dioxide Dissolution by Molten Zircaloy in Different Crucible Tests," J. Nucl. Mater. 231 (1996) 1.
- Volchek, A., Zvonarev, Yu., and Schanz, G., "Advanced Treatment of Zircaloy Cladding High-Temperature Oxidation in Severe Accident Code Calculations Part II. Best-Fitted Parabolic Correlations," Nuclear Engineering and Design 232(1) (2004) p. 85-96.
- Williams, A.F., "The ELOCA Fuel Modelling Code: Past, Present And Future," 9th International CNS Conference on CANDU Fuel, Belleville, Ontario, Canada, September 18-21, 2005.
- Yamanaka, S., Higuchi, K., and Miyake, M., "Hydrogen Solubility in Zirconium Alloys," J. of Alloys and Compounds 231 (1995) 503-507.
- Yamanaka, S., Miyake, M., and Katsura, M., "Study on the Hydrogen Solubility in Zirconium Alloys," Journal of Nuclear Materials 247 (1997) 315-321.