Multilayer interface tracking model of zirconium clad oxidation

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We present a numerical model to predict oxide scale growth and failure in zirconium clad exposed to water in out-of-pile conditions. The model includes the formation of two oxide sublayers on top of the metal clad, whose interfaces are tracked using a Stefan model coupled to diffusion kinetics. The kinetics is coupled to a thermal model that accounts for temperature gradient effects via thermo-migration inside the clad. The model also includes a mechanical failure criterion based on the accumulation of compressive stresses in the oxide near the interface with the metal. We present results of oxygen diffusion into the clad, oxide formation as a function of time, and oxide fragmentation by mechanical failure. We find that the growth of the oxide scale as the cubic root of time is recovered for a special charge distribution near the oxide interface. This charge distribution can be suppressed via alloying, which explains the square root scaling for certain Zr alloys. A sensitivity study has been conducted, showing that variations of $\pm \ 15\%$ in selected model parameters result in approximately $\pm \ 5\%$ changes in model predictions.

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1. Introduction

Corrosion of metallic structural materials is an extraordinarily broad phenomenon with implications in many areas of engineering [1–3]. In nuclear reactors cores, understanding the kinetics of corrosion of metallic components is particularly challenging, due to the compounded effects of high temperature, mechanical stresses, complex coolant and fuel chemistry, and irradiation [4,5]. In light-water nuclear reactors (LWR) zirconium alloys are used as cladding materials in fuel elements to provide a mechanical barrier with a low impact on neutron economy between the coolant (water) and the fuel [6–8]. In principle, Zr clad is subjected to corrosion from the coolant (water) and fuel sides, both by way of oxygen and hydrogen penetration. The oxidation and hydriding performance of zirconium fuel components in LWRs may limit the maximum fuel penetration. The oxidation and hydriding performance of zirconium fuel components in LWRs may limit the maximum fuel penetration.
corrosion of Zr [28–30]. This is partially due to the formation of a clearly distinguishable outer oxide scale and inner region where hydride platelets accumulate. In keeping with this distinction, in this paper we focus on the oxidation kinetics of Zr clad, assuming no cooperative effects from hydrogen on oxygen transport and reaction. An added challenge of considering Zr oxidation is the observation of an anomalous oxide layer thickness growth law that scales as $t^{1/3}$, in contrast to the classical $t^{1/2}$ scaling observed under the assumption of diffusion-limited kinetics [31–35]. There are several explanations that have been put forward to explain this anomaly, including charge imbalance [32], and hydrogen/oxygen coupling [30]. However, detailed experiments of zircaloy exposure to oxygen-only conditions have clearly revealed this cubic growth law, casting doubt on the role of hydrogen in facilitating a deviation from an ideally diffusive behavior [36–38]. Gondi and Missigoli [39] have put forward an explanation that rationalizes the cubic growth dependence based on the existence of a concentration gradient of anionic vacancies, which are generated at the oxide-metal interface and assumed to decay exponentially in space. Likhanskii and Evdokimov [28] take this line of thought further by relating the vacancy concentration gradient to differences in the Fermi level across the oxide/metal interface, which creates an electric field that is compensated by a differential vacancy concentration. Under such conditions—and when the Fermi level of metal is below that of the oxide—cubic growth develops.

As well, the zirconium oxide layer is known to lose its protective properties when it cracks catastrophically from the accumulation of compressive stresses at the oxide/metal interface. Cracking under compression can conceivably occur by either de-lamination and buckling or by shear cracking, both eventually leading to spall (fragmentation) [34]. This can also be aided by microstructural features such as grain boundaries and second-phase particles. Advanced alloys such as Zircaloy-2 and 4 and/or ZIRLO, however, are seen to reconstitute after the breakdown of the oxide layer, undergoing a renewed growth stage [13]. High temperature is also known to mitigate the breakdown of the oxide scale and above 300°C the oxide scale is expected to recover entirely. Nonetheless, the failure mechanisms of the Zr oxide layer are not yet fully understood, and a full thermo-mechanical model linking growth and failure is still lacking in the literature [8,29,40].

With the objective of shedding new light on these and other issues by using new computational and experimental understanding, in this paper, we present an comprehensive oxidation model of Zr formulated from first principles reaction kinetics and fundamental thermodynamics and mechanics. The model is parameterized using electronic structure calculations and experiments and captures both the protective oxide layer growth and runaway growth after oxide scale fragmentation. First, we describe the fundamental chemistry and phenomenology of the oxidation process followed by a mathematical formulation of the model. We then provide numerical results under a number of conditions relevant to LWR operation. We finalize with a discussion of the results and the implications of our modeling approach for zircalloy corrosion.

2. Chemical reaction kinetics model

2.1. Low-temperature Zr oxide reaction chemistry

Uniform corrosion of Zr can be considered an electrochemical process defined by the cathodic reduction of water:

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

(1)

and an anodic oxidation step:

$$\text{Zr} + 2\text{O}^{2-} + 2\text{V}_{\text{ZrO}_2}^0 \rightarrow \text{ZrO}_2 + 4\text{e}^-$$

(2)

which, when combined, leads to the standard stoichiometric reaction:

$$\text{Zr} + 2\text{H}_2\text{O} \rightarrow \text{ZrO}_2 + 2\text{H}_2$$

(3)

with $\text{V}_{\text{ZrO}_2}^0$ denoting a structural oxygen vacancy in $\text{ZrO}_2$. In the above reaction, we have chosen to write the hydrogen term in terms of molecular hydrogen $\text{H}_2$. However, we note that a portion of that hydrogen can remain as atomic hydrogen and either stay dissolved in water or penetrate the solid clad and contribute to internal hydride formation. We will get back to this issue in Section 4. Reaction (3) represents an ideal stoichiometric reaction of stable chemical species. However, in conditions of impoverished oxygen concentration such as near the oxide/metal interface, an incomplete reaction (3) may occur, leading to the formation of non-stoichiometric $\text{ZrO}_x$. It is generally thought that the monoclinic $\alpha$-$\text{ZrO}_2$ phase admits a negligible range of non-stoichiometry, undetectable by conventional techniques [41]. Conversely, metallography [42] and mass spectroscopy [43] measurements have established the concentration limit of the sub-stoichiometric tetragonal $\beta$-$\text{ZrO}_2$ phase at $x < 0.02$. This is not a minor detail, as such small deviations, among other factors, may be behind the stabilization of tetragonal zirconia (which at ambient pressure occurs only above 1200°C, cf. refs. [41,44]) near the interface, in coexistence with the monoclinic phase. As well, nonstoichiometry may play a role in the emergence of a local charge imbalance at the oxide/metal interface, as will be discussed below.

Experimental [41] and computational [44] descriptions of the phase diagram below 1200 K agree that the first compounds that appear after the metal-solid solution phase ($\alpha$-$\text{Zr}$) are ordered $\text{ZrO}_2$ hexagonal metallic compounds—sometimes termed ‘suboxides’—with stoichiometries ranging from $z = 1/6$ to $z = 1/2$ (which are often designated by descriptors such as $\alpha_{2/3}, \alpha_{2/3}$, or $\alpha_{1/2}$) [41]. After that, the experimental data are inconclusive as to the phases to be expected. However, recent density functional theory (DFT) calculations suggest that a line compound with perfect stoichiometry $\text{ZrO}$ ($z = 1$) emerges in coexistence with the metallic $\alpha'$ phase ($\text{ZrO}_{1.2}$) all the way to the monoclinic zirconia phase boundary ($\alpha$-$\text{ZrO}_2$), which starts to nucleate at 1/2 oxygen atomic fraction [44]. This phase, known as $\delta'$, forms in a distorted simple hexagonal crystal lattice akin to that of $\text{a}$-$\text{TiO}$. Recent experimental measurements in several $\text{Zr}$-based systems show clear evidence of the formation of this phase (as well as $\text{ZrO}_{1.2}$) behind the zirconia layer in specimens exposed to 360°C water [45–47].

In view of this picture, and to be consistent with the most recent experimental evidence, we design our model to consist of three consecutive layers ($\alpha$-$\text{ZrO}_2$)$(\delta' - \text{ZrO})$($\alpha$-$\text{Zr}$) separated by two distinct interfaces evolving in time according to chemical, thermal, and mechanical constraints. In the following, the use of the word ‘oxide’ is applied only to the $\alpha$-$\text{ZrO}_2$ layer.

2.2. Qualitative picture of the structural growth of zirconia films

The oxygen ions available from the reduction of water at the clad outer surface penetrate in the Zr matrix via diffusion. Under in-pile conditions, diffusion occurs against a temperature gradient of approximately 60 K over 600 μm [48], which accelerates oxygen transport as it penetrates the clad. As the oxygen concentration builds up, the resulting Zr-O mixtures evolve through the different phases discussed above. When the ratio of O and Zr atoms reaches a value of 1:1 corresponding to the $\delta'$-$\text{ZrO}_2$ phase, a well-defined interface appears, separating the ZrO from the region containing
the metal and other suboxides. As the atomic fraction of oxygen approaches 2/3, the oxide forms, resulting in a second interface separating it from the δ’ phase. However, because the monoclinic ZrO2 phase that corresponds to low temperature Zr oxide does not form under sub-stoichiometric conditions, the first oxide phase to emerge is a tetragonal β-ZrO2-x phase. The tetragonal phase is believed to be stabilized at low temperatures by the compressive stresses that develop between the α-Zr matrix which opposes the transformation to the less dense monoclinic form. In addition, the stability of the tetragonal phase can be aided by keeping the oxide particle size at less than approximately 30 nm, due to lower surface energies compared with monoclinic.

The oxide that starts to form consists of arrays of nano-crystals of ZrO2-x (roughly equiaxed for in-pile conditions), with columnar out-of-pile [48], with many different orientations relative to the orientation of the Zr grain on which they form. As just discussed, the internal structure of these crystallites is tetragonal zirconia, and although their crystallographic orientation is typically very difficult to establish, one should expect these crystallites to grow with orientations that minimize the stress due to the volume change on going from Zr to zirconia (the Pilling-Bedworth ratio of 1.56). Recent work has indeed established that the oxide consists mainly of well-oriented columnar monoclinic grains aligned with (001) directions parallel to the metal/oxide interface, with sporadic tetragonal grains interspersed throughout the oxide with orientations significantly deviated from the expected [54]. At this stage, free oxygen diffusion is thought to occur preferentially along the grain boundaries of these oxide crystals within the ZrO2-x layer, which accelerates oxygen transport with respect to bulk diffusion. Weight loss experiments show that the oxide scale thickness under these conditions grows as t^{1/2} [34,48,55,56].

As the oxygen continues to penetrate the clad, the stoichiometric oxide concentration is first reached near the environment side. This prompts the oxide crystals to begin transforming into a more stable monoclinic phase. This tetragonal → monoclinic transformation is martensitic and results in the generation of microcracks—possibly compounded by residual stresses developed during the metal-to-oxide transformation—in the oxide due to the volume change associated with the phase change [54,57,58]. As the oxide thickens, it transitions to a t^{1/3} growth dependence (at least under PWR operating temperatures [8,13,48,53,55,59]), the mechanisms of which are not fully understood. Further oxide thickness results in the eventual activation of cracks, leading to Stage 2 kinetics. Thus, at any given point, one expects a layer of tetragonal zirconia oxide to exist adjacent to the oxide/ZrO2 (or metal) interface where the free oxygen concentration is less than stoichiometric, whereas at the oxide/water interface these crystallites transform to monoclinic zirconia with an intrinsic distribution of cracks. We have modeled the coexistence of the two allotropes of ZrO2 in a previous study [60]. In this work, however, we make no distinction between sub-stoichiometric tetragonal zirconia and monoclinic zirconia, which are both bundled into a single ‘oxide’ layer.

2.3. Kinetic model

To predict the evolution of the interfaces that define the limits of the different layers, we resort to a Stefan model [61]. The Stefan formulation has been widely used to solve moving boundary problems involving mass and heat transport [61–63]. In the present study, interfaces move as a consequence of oxygen flux discontinuities resulting from diffusion in different media. The geometry considered for the model is shown in Fig. 1. As the figure shows, with three distinct layers of different composition—representing, respectively, ZrO2, ZrO, and α-Zr (and its suboxides)—, two evolution equations must be defined for the two interfaces separating each layer. The first for s1, the ZrO2/ZrO interface, and the second, s2, for the ZrO/metal interface:

\[ \frac{d s_1}{d t} = \frac{J_{II}}{Z_{PZr}} - \frac{D_{II}}{Z_{PZr}} \frac{\partial C_{II}}{\partial y} \]  
\[ \frac{d s_2}{d t} = \frac{J_{II}}{Z_{PZr}} - \frac{D_{II}}{Z_{PZr}} \frac{\partial C_{II}}{\partial y} \]  

where the roman numeral I refers to the ZrO2 layer and II to ZrO (cf. Fig. 1). J1 and JII are the mass fluxes, D1 and DII the oxygen diffusivities, and \( Z_{PZr} \) is the atomic density of the metal. Determination of the fluxes requires solving a general mass balance equation of the type:

\[ \frac{\partial C_i}{\partial t} = \nabla (D_i \nabla C_i) + \frac{J_{II}}{Z_{PZr}} \nabla C_i + \frac{q_{II}}{K_T} \nabla (C_i \Phi) \]  

also known as the drift-diffusion equation [64]. The i subindex refers to zones I, II, and III. The terms on the r.h.s. of eq. (6) are:

- The first term is standard Fickian diffusion in the presence of a concentration gradient.
- The second term is the so-called thermo-migration contribution, which depends on the temperature gradient and where U is the activation energy for diffusion. According to the classical theory of thermomigration (also known as Soret-Ludwig effect), vacancy mediated motion of substitutional atoms is expected to occur down the temperature gradient, while interstitial solutes move in the opposite direction. Experiments and calculations [65,66] have provided evidence of oxygen diffusion in α-Zr down the temperature gradient, suggesting an interstitial diffusion mechanism. According to convention, such thermomigration is labeled ‘positive’, and thus we show it as additive in the equation.

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1 Although it is not clear that this ZrO layer can be considered a barrier layer.
2 Defined as PBR = \( \frac{V}{Z_{PZr}} \) = \( \frac{\partial C_{II}}{\partial y} \) = 1.56, where V is the molar volume and \( \rho \) the atomic density.
3 Not eliminated completely despite the orientation relations among zirconia crystallites alluded to above.
The third term represents electro-migration, where $q$ is the charge of the diffusing species (e.g. $-1$ for electrons), and $\phi$ is the electrical potential, which can be determined by solving Poisson’s equation:

$$\nabla^2 \phi = -\frac{\rho}{\varepsilon}$$

(7)

where $\rho$ is the charge density and $\varepsilon$ is the dielectric permittivity.

As discussed in Section 2.1, with the buildup of O in the metal, a series of configurations ranging from a solid solution to various subsaturated intermetallic phases begin to form. These phases effectively immobilize oxygen by dissolving it internally and removing it from the free oxygen concentration. The relevance of each of the terms in eq. (6) depends on the chemistry and kinetics in each layer, which we discuss next.

2.3.1. Zone I: formation of the Zr-O solid solution

As free oxygen penetrates into the clad, a Zr-O solid solution is formed. In accordance with the zirconium-oxygen phase diagram [44], at the temperatures of interest here of 600 ~ 660 K oxygen is soluble up to around 20 at%. In the metallic layer, local charge equilibrium is assumed so that drift due to electro-migration can be neglected. However, the existing temperature gradient activates thermo-migration. The resulting equation is:

$$\frac{\partial c_i}{\partial t} = D_i \left( \frac{\partial^2 c_i}{\partial y^2} + \frac{U_i}{kT^2} \frac{\partial c_i}{\partial y} \frac{\partial \phi}{\partial y} \right)$$

(8)

where $D_i = D_i^T \exp \left( -\frac{\lambda y}{kT} \right)$ is the diffusivity of oxygen in a-Zr, assumed to be independent of the oxygen content.

2.3.2. Zone II: diffusional growth of the $\delta'$-ZrO layer

At an atomic fraction of 0.5, the first line compound appears with the formation of the $\delta'$ phase. Line compounds are no longer capable of immobilizing oxygen, as they correspond to saturated phases. This results in the formation of a distinct ZrO layer with a fixed composition, clearly seen in atom probe tomography experiments as a plateau in the measured oxygen concentration at 50% [45–47]. As above, charge equilibrium is assumed so that the mass balance equation reads:

$$\frac{\partial c_i}{\partial t} = D_B \left( \frac{\partial^2 c_i}{\partial y^2} + \frac{U_B}{kT^2} \frac{\partial c_i}{\partial y} \frac{\partial \phi}{\partial y} \right)$$

(9)

where $D_B$ is the diffusivity of oxygen in ZrO.

2.3.3. Zone III: growth of the oxide scale

As in zone II, the growth of zone III, referred to as oxide scale hereafter, is driven by an oxygen flux imbalance at the ZrO/ZrO2 interface. However, for completeness of the model, it is necessary to account for the electric field created by charged species gradients, including oxygen anions and electrons. Therefore, the complete equation is used for this layer:

$$\frac{\partial c_{\text{III}}}{\partial t} = D_{\text{III}} \left[ \frac{\partial^2 c_{\text{III}}}{\partial y^2} + \frac{U_{\text{III}}}{kT^2} \frac{\partial c_{\text{III}}}{\partial y} \frac{\partial \phi}{\partial y} \right] + q \left( \frac{\partial c_{\text{III}}}{\partial y} \frac{\partial \phi}{\partial y} + c_{\text{III}} \frac{\partial^2 \phi}{\partial y^2} \right)$$

(10)

where $D_{\text{III}}$ is the oxygen diffusivity in the oxide.

As Couet et al. [67] have discussed, the existence of an oxygen concentration gradient across the oxide layer has not been firmly established experimentally, although several studies make use of this concept to explain non-parabolic growth in corroded Zr [28,68]. Couet et al. have developed kinetic models that ensure charge balance between the anionic and cationic mass flows giving rise to zero charge current condition [67]. Here, in the spirit of the results by Beie et al. [69], who measured the voltage difference between the metal and the oxide surfaces in non-stoichiometric ZrO2-x, we adopt a simpler approach by using a fast-decaying charge density distribution concentrated near the interface with the ZrO layer:

$$\rho(y) = \rho_0 \exp \left( -\frac{s_1 - y}{\lambda} \right)$$

(11)

where $\rho_0$ is that charge density at the interface and $\lambda$ is a spatial constant. We reiterate that the justification for using this expression for the charge density lies in the existence of a thin layer of ZrO2-x, where non-stoichiometry and high compressive stresses can result in extra oxygen vacancies that can trap electrons and create a charge gradient, as has been discussed by Bell et al. [70,71]. From a numerical point of view, expression (11) is straightforward to integrate, which allows us to write the electrical potential and its first derivative as:

$$\phi(y) = -\frac{\lambda^2 \rho(y)}{\varepsilon}, \nabla \phi(y) = -\frac{\lambda \rho(y)}{\varepsilon}$$

During Stage 1 growth, equations (8)–(10) can be solved in one dimension ($y$) using the finite difference model subjected to the following dynamic boundary conditions:

$$c_i(y, 0) = 0, y > s_2$$

$$c_i(s_2, t) = c_{i1}(s_2, t) + \rho_{Zr}$$

$$c_{i1}(s_1, t) = c_{i2}(s_1, t) + 2\rho_{Zr}$$

$$c_{i2}(0, t) = C_0$$

$$\frac{\partial c_{\text{III}}(L, t)}{\partial y} = 0$$

where $C_0$ is the (constant) oxygen concentration available at the outer clad surface. The first condition trivially states that the oxygen content in the clad at the beginning of time is zero. The next two ensure the continuity of oxygen concentration at the interfaces while the third fixes the oxygen concentration in the environment to a value set by the water chemistry, temperature, pressure, etc. Finally, the last one simply reflects the fact that no free oxygen can escape the clad into the fuel side, i.e. $j_i(L, t) = 0$, where $j_i$ is the free oxygen flux in the metal.

As the oxidation process continues, microcracks developed in the oxide scale created by the volume differential with respect to the Zr metal start to grow. The transformation of the tetragonal phase into the monoclinic one results in an additional expansion of ~3% at 0 K, as given by their respective specific volumes of 0.139 and 0.143 nm$^3$ [4]. Eventually, these in-grown cracks form a network, which ultimately results in fragmentation of the oxide scale, giving rise to Stage 2 growth.

2.4. Stage 2: breakaway growth of the ZrO2 layer

Our critical assumption for Stage 2 growth is that free oxygen from the environment side becomes immediately available on the ZrO2/ZrO interface (at $y = s_1$) via transport through the microcrack network. At the point of spall, it is assumed that the entire oxide
layer has become monoclinic, and the mass balance system of
equations is solved again for the metal phase replacing the
boundary condition for the oxygen concentration in the oxide
metal interface with \( c_0(s_1, t) = C_0 \). As the oxide layer thickness
increases during Stage 2, it is assumed that the cracks grow while
maintaining the concentration of oxygen fixed at \( C_0 \) at the interface.
This availability of free oxygen accelerates oxide layer growth,
leading to breakaway behavior.

In terms of the model, the drift-diffusion equation need not be
solved any longer for Zone III. Instead, only eqs. (9) and (10) need be
considered with the updated dynamic boundary conditions:

\[
  \frac{\partial c_0}{\partial t}(s_1, t > t_{1-2}) = C_0
\]

where \( t_{1-2} \) is the time at which transition into Stage 2 occurs.
Equation (4) then becomes:

\[
  \frac{\partial s_1}{\partial t} = \frac{C_0 V}{2P e_T}
\]

(12)

where \( v \) is the velocity of the viscous flow of water through the
clad wall. Again, we note that this is the model assumed for
pure Zr, which is known to break down at less than two microns in
thickness. This does not appear to be the case, however, for the
oxide scale in more advanced Zr alloys, which is seen to reconsti-
tute cyclically.

2.5. Calculating the temperature gradients

As eqs. (8)–(10) show, \( T(y) \) and \( \frac{q_y}{g_T} \) are essential inputs to the
kinetic model. Calculation of the temperature gradients requires
that the temperature field be defined at every \( (y, t) \) point of the
finite difference mesh. For this, it is assumed that under steady
state reactor operation, the heat flux flowing from the fuel side
through the clad out to the coolant side is constant. The heat flux \( q_0 \)
can be obtained from Fourier’s law at \( t = 0 \) assuming a linear
temperature gradient in one dimension:

\[
  q_0 = -\kappa_1 \frac{dT}{dy} = \frac{T_0^0 - T_0^0}{L}
\]

(13)

where \( \kappa_1 \) is the thermal conductivity of the Zr metal (zone I), and \( T_0^0 \)
and \( T_0^0 \) are the initial temperatures at the inner and outer positions
of the clad, respectively. Further, it is assumed that \( T_c \) is constant in
time (set by the coolant temperature), while the inner temperature
\( T_L \) is allowed to vary as the cladding oxidizes and the overall ther-
mal conductivity changes. As the oxide and suboxide layers build
up, the temperature gradients in each one can be obtained from the
following conservation law:

\[
  q_0 = \kappa_1 \frac{T_L - T_2}{S_2 - S_1} + \kappa_{II} \frac{T_2 - T_1}{S_2 - S_1} = \kappa_{II} \frac{T_1 - T_0^0}{S_1}
\]

(14)

where \( \kappa_{II} \) and \( \kappa_{III} \) are the thermal conductivities of ZrO and ZrO₂,
and \( T_1 \) and \( T_2 \) are the temperature at the ZrO₂/ZrO (\( s_1 \)) and ZrO/Zr (\( s_2 \))
interfaces, respectively. Combining eqs. (13) and (14):

\[
  T_1 = T_0^0 + \frac{q_0 S_1}{\kappa_{II}}
\]

(15)

\[
  T_2 = T_1 + \frac{q_0 (S_2 - S_1)}{\kappa_{II}}
\]

(16)

from which all thermal gradients can be calculated as a function of
time by updating the temperature field via the thickness variables
\( s_1(t) \) and \( s_2(t) \). Equations (15) and (16) show that the interface
temperatures \( T_1 \) and \( T_2 \) are proportional to the thickness of the corresponding layers, while \( T_1 \) is expected to rise as \( s_2 \) grows and
the second term on the r.h.s. of eq. (17) becomes increasingly
smaller.

2.6. Determining the transition time from Stage 1 to Stage 2

2.6.1. Stress buildup

The two main sources of stress during the growth of the oxide layer
are thermal and growth stresses. Thermal stresses develop from
differential thermal expansion between the oxide and metal layers. Assuming a biaxial stress state, when the oxide phase can be
considered much thinner than the metallic substrate, the
(compressive) hoop stress in the oxide scale is:

\[
  \sigma_{ox}^{\text{th}} = \frac{E_{ox}}{1 - \nu_{ox}} \int_{T_i}^{T_f} \frac{\Delta \alpha(T)dT}{T_c}
\]

(18)

where \( E_{ox} \) and \( \nu_{ox} \) are, respectively, the Young’s modulus
and the Poisson ratio of the oxide. \( \Delta \alpha(T) \) is the differential thermal
expansion:

\[
  \Delta \alpha(T) = \alpha_{ox}(T) - \alpha_{m}(T)
\]

The sign of the thermal stresses depends on the conditions in the
oxide scale. The thermal expansion coefficient is in most cases
much higher for metals than it is for oxides. For nominal conditions,
when the metal substrate is subjected to higher temperatures than
the oxide scale, the metal expands by an amount that cannot be
matched by the oxide scale at the oxide/metal interface. This would
result in local tensile stresses on the oxide layer.

Compressive thermal stresses can appear upon cooling to room
temperature of the clad, and can be responsible for oxide scale
failure. However, under operating conditions, the main (and second-
) source of stresses are growth stresses due to internal oxida-
tion. Growth stresses are mostly in-plane compressive, and they
might reach important levels (up to few GPa [27,56,73]). To calcu-
late their magnitude, we follow the ideas of Birks et al. [33]. If the
oxide scale at the metal/oxide interface grows by consumption of
the metallic substrate, the change of specific volume between the
consumed phase and the created one would engender a volume
eigenstrain (inelastic strain). The parameter associated with this
phenomenon is the Pilling-Bedworth ratio (PBR, introduced above).
If oxidation proceeds isotropically, the tangential strain due to oxide
growth is approximately:

\[
  \varepsilon_{ox}^T = \frac{1}{3} (\text{PBR} - 1)
\]

The stress state due to this strain is compressive and bi-axial:

\[
  \sigma_{ox}^T = -\frac{E_{ox}}{3(1 - \nu_{ox})} \varepsilon_{ox}^T = -\frac{E_{ox}(\text{PBR} - 1)}{3(1 - \nu_{ox})}
\]

These stresses develop mainly at the oxide/metal interface
during the initial stages of oxide formation. Subsequent oxide scale

\footnote{The hoop stress is equal to the axial stress, \( \sigma_0 - \sigma_2 \) (cylindrical coordinates).}
growth is usually considered to occur without significant stress generation or deformation, as the new oxide formed can be accommodated on top of the existing layer. Thus, growth stresses maintain the oxide near the interface under compression by a constant amount independent of the oxide scale thickness. We note however that in reality oxide growth is highly anisotropic [54] and thus the above assumptions result in an overestimation of the stresses as given by eq. (19).

Next, we provide a criterion to establish under which conditions the growth of the oxide layer leads to uniform fragmentation and the loss of the protective layer.

2.6.2. Failure criterion

For compressive stresses there are two routes for spalling. The first one, involves the nucleation and growth of a wedge crack, and occurs preferentially for strong interfaces and weak oxide scales; the second is by buckling, which is preferred for weak interfaces and strong oxide scales.

Protective oxide layers display brittle characteristics at low temperatures. Hence, in the temperature range of interest for LWR operation one can apply Griffith’s theory to calculate \( t_{1-2} \). A flaw that develops in the oxide layer will continue to grow under a stress \( \sigma_{\text{ox}} \) if its strain energy release \( G \) exceeds the critical energy release rate \( G^* \) of the oxide [33,74]:

\[
G_{\text{ox}} > G^*
\]

where \( G = K^2 / E_{\text{ox}} \), and \( K \) is the stress intensity factor:

\[
K = Y \sigma \sqrt{\pi a}
\]

where \( a \) is the flaw size and \( Y \) is a geometric parameter whose value is close to unity for a small crack embedded in a two-dimensional solid. \( G^* \) can be equated to a surface energy \( \gamma \), which results in the following criteria for fracture:

\[
\frac{\sigma^2}{Y^2 \pi a} > \frac{G}{E_{\text{ox}}}
\]

The final criterion in usable form furnishes the critical oxide scale thickness \( s^* \) at the onset of fragmentation:

\[
s^* > \frac{9\gamma(1 - \mu^2)}{E_{\text{ox}}(\text{PRB} - 1)^2 Y^2 \pi \epsilon}
\]

In this work we use eq. (22) to extract the value of \( \gamma \) assuming the lower end of the commonly cited values between one and two microns for \( s^* \) [21,77–79]. For the parameters listed in Table 1, a value of \( \epsilon = 10^{-4} \) is obtained, suggestig that fragmentation in ZrO\(_2\) can be triggered by very small cracks. For its part, the time \( t_{1-2} \) is directly obtained from the \( s_1(t) \) relation as \( s_1(t_{1-2}) = s^* \).

2.7. Numerical solution procedure

Solution of the above system of coupled PDEs by the finite difference method requires that eqs. (8)–(10) be discretized in space and time. Here, we partition time and space into finite grids as follows:

\[
t^j = \frac{i \delta t, j = 0, 1, 2, \ldots, N}
\]

and

\[
y_j = j \delta y, i = 0, 1, \ldots, M
\]

where the conventional notation of using superscripts to represent time (\( t^j \)) and subscripts to represent space (\( y_j \)) has been used. For uniform grids, \( \delta t \) and \( \delta y \) are simply:

\[
\delta t = t / N
\]

and

\[
\delta y = L / M
\]

with \( N \) and \( M \) representing the size of the grid, and \( t \) the total simulated time.

Adopting a scheme where time derivatives are replaced by forward differences, and space derivatives by central differences (known as ‘FTCS’ scheme), the discretized form of the drift-diffusion equation for the most general case, represented by eq. (10) (Zone iii) reads:

\[
\frac{c^{j+1}_i - c^j_i}{\delta t} = D_\text{III}(T_j) \left\{ \frac{c^{j+1}_{i+1} - 2c^j_i + c^{j+1}_{i-1}}{\delta y^2} + \frac{U_\text{III}}{kT_j} \frac{dT}{dy} \frac{2}{\delta y} \right\} \\
+ \left\{ \frac{\rho \lambda_0}{2kT_j} \exp \left[ - \frac{s_1 - y_j}{\lambda} \right] \left( c^{j+1}_{i+1} - \frac{2\delta y}{\lambda} c^j_i - c^{j+1}_{i-1} \right) \\
- c^{j+1}_{i+1} + c^{j+1}_{i-1} \right\}
\]

which can be written in explicit form as:

\[
c^{j+1}_i = c^j_i + a^j_1(1 + a_1 + a_2 + a_3 + a_4) + c^j_i(1 - 2a_1 + a_5) + c^{j+1}_i(1 + a_1 + a_2 + a_3 + a_4)
\]

with

\[
q = \frac{E_{\text{ox}}(\text{PRB} - 1)}{9(1 - \rho_{\text{ox}})^2}
\]

(21)

The finalized criterion in usable form furnishes the critical oxide scale thickness \( s^* \) at the onset of fragmentation:
sources. First-principles electronic structure calculations have recently reached levels of accuracy and computational efficiency capable of providing diffusion coefficients in oxide structures. However, despite the potential of \textit{ab initio} methods, it remains exceedingly difficult to perform calculations where the parametric space is greater than one. For this reason we complement electronic structure calculations with experimental data where needed. A compilation of all parameters used here is given in Table 1. The specific values and source of origin for each type of parameter is discussed in the following subsections.

### 2.8. Model parameterization

The parameterization of the above kinetic model is an essential step in assuring the physical fidelity of the calculations. In terms of Stages 1 and 2, the key parameters are the diffusivities of free oxygen in metallic Zr, in the \( \delta \) suboxide, and in monoclinic zirconia, as well as thermal conductivities and elastic properties. A comprehensive data set satisfying the model needs is lacking, however, and here we draw from available experimental as well as numerical sources. First-principles electronic structure calculations have

<table>
<thead>
<tr>
<th>Property</th>
<th>Symbol</th>
<th>( \alpha )-Zr (Zone I)</th>
<th>ZrO (Zone II)</th>
<th>ZrO(_2) (Zone III)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diffusivity prefactor [m s(^{-1})]</td>
<td>( D_y )</td>
<td>( 6.61 \times 10^{-6} )</td>
<td>( 1.26 \times 10^{-11} )</td>
<td>( 9.00 \times 10^{-8} )</td>
</tr>
<tr>
<td>Activation energy [eV]</td>
<td>( U )</td>
<td>1.9</td>
<td>1.24</td>
<td>1.24</td>
</tr>
<tr>
<td>Thermal conductivity [W m(^{-1}) K(^{-1})]</td>
<td>( \kappa )</td>
<td>( 8.5272 \pm 0.0820 \times 10^{-7}T + 2.53259 \times 10^{-11}T^2 + 2.9918 \times 10^{-15}T^3 )</td>
<td>( \frac{\kappa_1 + \kappa_3}{2} \times 1700T^{-1} \times 10^{-16} )</td>
<td>( \frac{\kappa_1 + \kappa_3}{2} \times 1700T^{-1} \times 10^{-16} )</td>
</tr>
<tr>
<td>Charge Density [C m(^{-2})]</td>
<td>( \rho_0 )</td>
<td>N/A</td>
<td>662.0</td>
<td>662.0</td>
</tr>
<tr>
<td>Charge [C]</td>
<td>( q_i )</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>Permittivity constant [C(^2) m(^{-1})]</td>
<td>( \varepsilon )</td>
<td>N/A</td>
<td>3.26 \times 10^{-19}</td>
<td>3.26 \times 10^{-19}</td>
</tr>
<tr>
<td>Young’s modulus [GPa]</td>
<td>( E )</td>
<td>N/A</td>
<td>236</td>
<td>236</td>
</tr>
<tr>
<td>Poisson ratio</td>
<td>( \gamma )</td>
<td>N/A</td>
<td>0.25</td>
<td>0.25</td>
</tr>
<tr>
<td>Surface energy [J m(^{-2})]</td>
<td>( \gamma_s )</td>
<td>N/A</td>
<td>1.2</td>
<td>1.2</td>
</tr>
</tbody>
</table>

\*With a factor of 0.86 applied if during Stage 2.

Where \( T, y, \delta_1, \) and \( \delta_2 \) are all evaluated at time \( i \) and location \( j \). The numerical stability of the explicit FTCS scheme can be assessed by means of a Neumann’s analysis, which, for a purely parabolic problem is simply:

\[
a_1 \leq \frac{1}{2}
\]

This can be used as guidance when \( a_1 > a_2, a_3 \). For the general case given by eq. (24), we derive in Appendix B the stability criteria including all the terms given in the equation:

\[
\frac{\kappa}{D_\text{III}} \left( \frac{a_2}{a_3} \frac{\kappa}{\kappa_\text{III}} + \frac{\kappa(a_1 + \rho_3)}{\kappa_\text{III}} \right) \frac{\partial T}{\partial T} < \frac{2kT}{D_\text{III}} \frac{\partial y}{\partial y}
\]

For the explicit form of eqs. (8) and (9), we simply make \( a_2 = a_3 = a_4 = a_5 = 0 \) and replace \( D_\text{III}, U_\text{III}, \) and \( (\partial T/\partial y)_{\text{III}} \) with their respective counterparts for Zones I and II in eq. (24). The discrete update steps for \( s_1 \) and \( s_2 \) (eq. (4) and (5)) for Stage I growth are:

\[
s_1^{i+1} = s_1^i + \frac{D_\text{III} (T_{M-1} \delta_1 - s_2^i - s_1^i) \delta y}{2 \rho_2 \delta y}
\]

\[
s_2^{i+1} = s_2^i + \frac{D_\text{III} (T_{M-1} s_1^i - s_2^i - s_1^i) \delta y}{\rho_2 \delta y}
\]

where the index \( (M - 1) \) indicates the spatial point immediately before the corresponding interface. A schematic flow diagram of the integrated numerical model employed here is given in Fig. 2.

### 2.8.1. Oxygen diffusivity in \( \alpha \)-Zr

In principle, the diffusion coefficient of oxygen in hcp Zr depends both on \( T \) and \( z \). As noted above, the temperature dependence is intrinsically captured in the Arrhenius expression. However, the dependence on \( z \) has not been established to our knowledge and thus we resort to experimental measurements where the oxygen concentration is intrinsically captured in the final value of the parameters.

Since the first experimental measurements by Pemsl [80], several studies have focused on oxygen diffusion in Zr, Ritchie and Atrens [81] have provided an excellent compilation of all the experimental data up to 1977. For temperatures in the range 290–650 °C, they give following expression:

Fig. 2. Flow diagram of the numerical procedure employed here.
\[ D_i(T) = 6.61 \times 10^{-6} \exp \left( \frac{1.9}{kT} \right) \text{[m}^2\cdot\text{s}^{-1}] \]

as the best fit to all the data. Here the activation energy is given in units of eV (per atom, equivalent to 44,000 cal per mole). Diffusion in this case is associated with jumps of oxygen interstitials in the basal plane. Above 400°C they note that some authors have measured a different expression that yields higher diffusivities, attributable to diffusion along grain boundaries [82]:

\[ D_{III}(T) = 1.55 \times 10^{-10} \exp \left( \frac{1.0}{kT} \right) \text{[m}^2\cdot\text{s}^{-1}] \]

Subsequent experiments have attempted to revise the measurements provided by Ritchie and Atrens, with similar values obtained [83].

The various values for \( U_i \) measured experimentally are consistent with recent density functional theory calculations of interstitial oxygen migration, where migration energies of approximately 1.0 eV are reported [66] (albeit with a relatively high degree of hysteresis, where migration energies of approximately 0.8 eV are reported [66]).

Our approach here is to estimate the diffusivity of oxygen by way of a vacancy mechanism, and hence it is quite slow. ZrO is a saturated line compound, we assume that diffusion proceeds by way of a vacancy mechanism, and hence it is quite slow. ZrO is a saturated line compound, we assume that diffusion proceeds by way of a vacancy mechanism, and hence it is quite slow. ZrO is a saturated line compound, we assume that diffusion proceeds by way of a vacancy mechanism, and hence it is quite slow. ZrO is a saturated line compound, we assume that diffusion proceeds by way of a vacancy mechanism, and hence it is quite slow.

2.8.2. Oxygen diffusivity in monoclinic ZrO₂

Measurements of oxygen diffusivity in monoclinic zirconia date back to the late 1960s, with the early work of Smeltzer and collaborators at high temperatures (\( > 1000^\circ\text{C} \)) [84,85]. A representative diffusivity coefficient extracted from their data is \( D_{III}(T) = 9.73 \times 10^{-7} \exp \left(-2.42 \frac{kT}{R} \right) \), while Keneshea and Douglass [86] find \( D_{III}(T) = 2.34 \times 10^{-8} \exp \left(-1.86 \frac{kT}{R} \right) \), both in \( \text{m}^2\cdot\text{s}^{-1} \) when the energies are given in eV. It appears that the measured diffusivities are relatively “fast”, indicating oxygen diffusion pathways through dislocations and/or grain boundaries. As noted by Cox and Pemsler [87], however, lattice diffusion takes place with a significantly lower activation energy, \(<1.5\text{ eV}, which makes lattice diffusion as important as defect-mediated diffusion at temperatures below 600°C. This is possibly due to a reduced vacancy formation energy. Cox and Pemsler’s measurements, however, were made in the 400–585°C temperature range, while the earlier work by Smith was done in the 380–386°C range [82] and also shows a reduced activation energy (1.24 eV). For this reason, in this work, we use Smith’s diffusivities as given by the expression:

\[ D_{III}(T) = 9.00 \times 10^{-8} \exp \left(-1.24 \frac{kT}{R} \right) \text{[m}^2\cdot\text{s}^{-1}] \]

2.8.3. Oxygen diffusivity in ZrO

The \( \delta' \) suboxide is a relatively new phase and we currently do not have any sources of data for oxygen diffusivity in ZrO. Because ZrO is a saturated line compound, we assume that diffusion proceeds by way of a vacancy mechanism, and hence it is quite slow. Our approach here is to estimate the diffusivity of oxygen by matching the thickness of the ZrO layer (equal to \( s_2-s_1 \) in our model) to experimentally-measured values, which range between approximately 60 and 120 nm [45–47]. Matching \( D_{III} \) in eq. (9) to yield a thickness of 65 nm results in a value of \( D_{III} = 1.46 \times 10^{-22} \text{m}^2\cdot\text{s}^{-1} \) at 600 K, which is the number used here. The reason why the oxygen diffusivity in the ZrO layer is so low is unknown to us at this point. It is known that for strong line compounds, with a very small concentration of oxygen vacancies, anion diffusion can be exceedingly low. This is a clear gap in our physical understanding of the Zr-O system, and little more than speculating can be done at this point until reliable atomistic calculations are performed to study and quantify the diffusion mechanism of oxygen in this \( \delta' \) phase.

2.8.4. Thermal conductivities

Fink and Leibowitz [88] have proposed a correlation for the thermal conductivity of Zr based on a statistical analysis of experimental measurements from 1951 to 1995. The recommended equation for \( k_1 \) the thermal conductivity of zirconium in units of [W m\(^{-1}\) K\(^{-1}\)] from 298 through 2000 K is:

\[ k_1 = 8.8527 + 7.0820 \times 10^{-3} T + 2.5329 \times 10^{-6} T^2 + 2.9918 \times 10^2 T^{-1} \]

For its part, ZrO₂ is an excellent insulator and displays very low values of \( k_{III} \). Most of the experimental measurements, however, have been done at high temperatures in yttria or calcia-stabilized zirconia. According to Klemens [89], the temperature dependence of the thermal conductivity is well described by:

\[ k_{III}(T) = 1700 T^{-1} [\text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}] \]

During Stage 1, however, as the oxide layer grows and develops an intrinsic pore network, the thermal conductivity gradually deteriorates from its fully-dense value given by the above expression. To reflect this, we use the corrections to \( k_{III} \) developed by Nait-Ali et al. [90] for porous zirconia:

\[ k_{III}(T, f) = k_{III}(T) \left( 1 - \frac{3f}{2 + f} \right) \]

where \( f \) is the pore volume fraction. Further, assuming values of \( f \approx 0.14 \) during the onset of spall [91], we adopt a linear time dependence for \( f \) between \( t = 0 \) and \( f = f_{1700} \) from zero to its maximum value of 0.14. Once the oxide layer fails, the coolant permeates through the pores and equalizes the temperature across the entire layer.

As above, we do not know of any data for the thermal conductivity in ZrO, and as a first-order approximation, here we simply take \( k_1 \) as the average between \( k_1 \) and \( k_{III} \).

2.8.5. Electrical properties

The constants involved with the electro-migration terms in eqs. (6) are the charge of oxygen anions, \( q_i \), the charge density at the oxide interface, \( \rho_0 \), the absolute permittivity of ZrO₂, \( \varepsilon \), and the decay constant, \( \lambda \). We use a value of \( \varepsilon = 3.26 \times 10^{-25} \text{C}^2\text{eV}^{-1} \) from various measurements [92,93]. The charge of O\(^{2-}\) is simply \( q_i = -3.20 \times 10^{-19} \text{C} \), while \( \rho_0 \) is used as a fitting parameter. We find a value of \( \rho_0 = 662.0 \text{C} \cdot \text{m}^{-2} \) satisfactory for pure Zr under the conditions studied here. It is difficult to assess whether this is a reasonable number due to a lack of dedicated measurements in nuclear-grade Zr, although it is larger than measurements of charge densities at oxide interfaces in metal/semiconductor junctions involving Zr [94,95]. Finally, we simply make \( \lambda = dy \).

2.8.6. Mechanical properties

Very little work is reported in literature on the elastic properties of pure monoclinic zirconia. Elastic constants have been derived by several authors using lattice vibration models for tetragonal zirconia [96]. In monoclinic single crystals, Chan et al. [97] have done measurements up to 1000°C using ultrasonic velocity measurements by Brillouin scattering. Yeung et al. [88] have compiled the different values published in the literature and report a value of \( E_{\text{eq}} = 236 \text{GPa} \) between 300 and 600°C for monoclinic zirconia. This is what is used in eqs. (18)–(22) above.
For Poisson’s ratio we simply use a value of \( \nu_{\text{ox}} = 0.25 \) as given in commercial databases [89], while the surface energy of monoclinic zirconia has been measured at \( \gamma = 1.2 \) J m\(^{-2} \) [52,100]. Equation (22) can then be used to estimate either \( \varepsilon^* \) or \( \varepsilon \) from knowledge of one or the other.

### 2.9. Physical dimensions and boundary conditions

The final set of parameters needed to run the model defines the physical dimensions and boundary conditions of the model. The clad thickness \( L \), and the inner and outer clad temperatures \( T_0 \) and \( T_L \) (at \( t = 0 \)) are nominal values in LWR.

The value of \( C_0 \) can vary among several LWR concepts, as the oxygen partial pressure in water depends on temperature, pressure, and water chemistry. Values for pressurized water reactors (PWR), boiling water reactors (BWR), water-water energetic reactors (VVER), and heavy water CANDU reactors are provided by Billot et al. [101]. However, in general, the amount of oxygen (and hydrogen) dissolved in water is relatively small in the temperature range explored here, and oxygen ions are made available by the reduction of water on the surface of the clad. For example, the value reported by Pemsler in his studies of water corrosion of Zr is of 0.54 g·cm\(^{-3} \) (or \( 1.69 \times 10^{28} \) m\(^{-3} \)) [80]. Here we fit the value of \( C_0 \) such that the model predicts a Stage 1→2 transition of 55 days\(^7\) consistent with the measurements by Motta et al. [45,102]. All these numbers are given in Table 2.

As well, for consistency with experiments, we have decided to use a constant value of \( \varepsilon^* = 1.27 \mu \text{m} \) [21], regardless of reactor type. From eq. (22), this choice results in a value of \( \varepsilon \approx 4 \times 10^{-6} \), much smaller than the value reported for other oxides [75]. Finally, the spatial and temporal mesh sizes, \( \delta y \) and \( \delta t \), are also given in the Table.

### 3. Results

As explained in Section 2.3, our model provides a spatio-temporal picture of the oxidation process in Stages 1 and 2. Next, we present our main results and a brief discussion about their relevance and validity.

#### 3.1. Pure Zr

We begin with the evolution of the inner clad temperature, \( T_i \), with time. Fig. 3 shows the variation of \( T_i \) with exposure time. As the figure shows, the variation is of only two degrees, which has a negligible impact on the temperature gradients that develop in each of the layers captured by the model. We emphasize that the total heat flux is conserved (as to mimic constant power conditions in a LWR), and \( T_i \) changes as a consequence of keeping the coolant temperature fixed at 600 K.

Fig. 4 is an alternative to the temperature profiles at 0, 20, and 60 days, calculated according to eqs. (15)–(17). After 55 days (breakaway oxidation), the temperature in the entire oxide layer equals with the coolant temperature due to water percolation through the crack network. Although the absolute temperature changes are small, gradient on the order of \( 10^6 \) K m\(^{-1} \) are seen to develop in the oxide scale, which is what is important for thermomigration. After breakaway, the absence of such gradients in the ZrO\(_2\) layer implies no effect on oxygen diffusion.

Next, we study the oxygen penetration inside the clad as a function of time. Fig. 5 shows the total oxygen concentration as a function of depth for two distinct time instants in Stage 1. These profiles result from solving the drift-diffusion equation (cf. eq. (8) through (10)) in each one of the three zones depicted in Fig. 1. Solid and dashed lines correspond to the oxygen concentration profile at 20 and 40 days of exposure, respectively. As the figure shows, mass continuity exists at the interfaces, marked by the dashed lines in each case. However, the profiles clearly show discontinuities in the mass fluxes, which results in net interface

\footnotesize

\( ^7 \) For pure Zr specimens.

---

### Table 2

Numerical parameters used in the model.

<table>
<thead>
<tr>
<th>( L ) [( \mu \text{m} )]</th>
<th>( T_0 ) [K]</th>
<th>( T_L ) [K]</th>
<th>( C_0 ) [m(^{-3} )]</th>
<th>( \rho_0 ) [m(^{-3} )]</th>
<th>( s^* ) [( \mu \text{m} )]</th>
<th>( \delta t ) [h]</th>
<th>( \delta y ) [( \mu \text{m} )]</th>
<th>( \lambda )</th>
</tr>
</thead>
<tbody>
<tr>
<td>600</td>
<td>600</td>
<td>660</td>
<td>1.56 \times 10^{28}</td>
<td>4.31 \times 10^{24}</td>
<td>1.27</td>
<td>0.011</td>
<td>0.058</td>
<td>( \delta y )</td>
</tr>
</tbody>
</table>

---

![Fig. 3](image-url) Variation of the temperature at \( \gamma = L \) (inner clad radius, fuel side) with exposure time. The temperature rises steadily during Stage 1 and then drops quickly after the failure of the oxide layer.

![Fig. 4](image-url) Temperature depth profiles at 0, 20, and 60 days. The graph shows the growth of the oxide layer(s) during each time interval. Also shown is the flat temperature profile.
motion. The shaded areas represent the stoichiometric oxygen concentration, which—as expected—jumps discontinuously at $s_1$ and $s_2$. Note that we have expressed oxygen concentrations normalized to the pure Zr atomic density, so that the ZrO$_2$ layer is characterized by a value of $2\rho_{Zr}$, as dictated by stoichiometry, whereas in the ZrO layer it has a value of one.

We also plot the corresponding oxygen depth profiles for two time instants during Stage 2 (at 60 and 70 days) in Fig. 6. After failure of the oxide scale (at 55 days), oxygen makes its way unimpeded to the ZrO$_2$/ZrO interface ($s_1$). For the purposes of oxygen diffusion, this effectively shifts the outer boundary of the clad from $y = 0$ to $y = s_1$, which is now exposed to a fixed oxygen concentration of $C_0$. After breakaway, then, the oxygen content in the ZrO layer suffers a transient—shown in the figure as a maximum in the concentration curves—driven by such an adjustment.

Tracking the positions of $s_1$ and $s_2$ as a function of time allows us to plot the growth of the oxide scale with time, Fig. 7. The value of $s_1$ represents the thickness of the ZrO$_2$ layer, while the value ($s_2 - s_1$) gives the thickness of the ZrO layer (fixed to approximately 65 nm in this study). Both curves display nonlinear behavior up to a thickness of $s^*$ (beginning of Stage 2). Solid and dashed black lines are visual guides representing growth scaling laws ($s(t) = at^b$) with $a$ and $b$ indicated in each case. The main results from these curves are: (i) Up to the breakaway point, the oxide scale grows as $s_1(t) = 0.33t^{0.34}$, where $s_1$ is expressed in microns when $t$ is in days. For its part, the ZrO/metal interface evolves as $s_2(t) = 0.33t^{0.35}$; (ii) the model has been calibrated such that Stage 2 starts when $s_1 = s^* = 1.27$ µm, which leads to a duration of approximately 55 days for Stage 1; (iii) the oxide scale grows linearly from that point onwards. Notwithstanding the large variability in experimental measurements found in the literature for a given material composition even under nominally equivalent conditions, we include the results from Motta et al. for pure Zr [102] based on which we have chosen the parameters $s^*$ and $s_1$.

It is also of interest to study the relative contribution of each of the terms that appear in eq. (10) for oxygen diffusion in the oxide. For this, we switch off each term one at a time and examine the $s_1$-vs-$t$ behavior during Stage 1. The results are shown in Fig. 8, which shows three curves, one for each scenario. First, we solve the diffusion equation just with the Fickian term. As expected, this gives
rise to an evolution that is best fit by a $\sim \sqrt{t}$ law. Second, we add electro-migration, which is seen to ‘bend’ the curve towards a $t^{1/3}$ evolution. Finally, adding thermo-migration results in only variations on the order of 2% in $s_1$ with respect to the previous case.

3.2. Sensitivity study of relevant parameters

Next, we carry out a sensitivity study of the model by considering its response to variations in key parameter models. Fig. 9 shows the impact on the growth law for ZrO$_2$ (in pure Zr) of variations of the oxygen concentration in the environment, $C_0$ (Fig. 9a), the oxygen diffusivity in the oxide, $D_{III}$ (Fig. 9b), and the charge imbalance at the metal/oxide interface, $\rho_0$ (Fig. 9c). As the plots show, changes of ±15% in these parameters result in variations of less than 5% in the values of $s_1$, suggesting that variations in model parameters are ‘muffled’ by the model itself.

While this analysis cannot be considered an exhaustive uncertainty quantification study, it can nonetheless help us understand the effect of uncertainties in some of the most important parameters entering the model, so that reasonable limits can be set to its applicability.

3.3. Effect of alloy composition

Another important aspect to consider is the impact of alloy composition on the model predictions. Motta et al. have provided an excellent compendium of the qualitative effects of alloy composition on Zr oxidation [102], while Bell et al. have recently discussed the issue using electronic structure arguments [71]. However, gathering complete data sets for different Zr-based alloys is as challenging as it is for pure Zr. Our approach to study chemical composition effects is to choose alloys for which the oxygen diffusivity has been accurately measured (both in the metal and the oxide). As well, we assess the existence of a charge gradient based on the measured time exponents in the experimental literature. Based on these criteria, we have chosen Zircaloy-4 (nominal composition: Zr-1.5Sn-0.2Fe-0.1Cr) [103,104] and Zr-2.5Nb [105] as the subjects of our study. Fig. 10 shows the comparison between the three systems, with the corresponding time exponents given for each case. When plotted in normalized scale, there is virtually no distinction between pure Zr and Zircaloy-4, with both exponents being very similar. Conversely, Zr-2.5Nb displays a quadratic behavior, as established experimentally. From the point of view of our model, this is simply indicative of the role played by electro-migration, which is qualitatively identical for Zr and Zircaloy-4, and nonexistent for Zr-2.5Nb. Their failure thicknesses and transition times are all different and are given in Table 3 along with the value of the oxygen diffusion coefficients and the rest of the fitting parameters.

4. Discussion of results

The results shown in the previous section reveal the potential of our methodology, which uses a three-layer spatio-temporal description of the oxidation process in Zr, to model oxygen corrosion kinetics in nuclear environments. Our approach is based on a Stefan interface tracking model to represent the motion of the two interfaces representing the three layers. These layers are tied together via mass conservation boundary conditions, for which drift-diffusion equations must be solved simultaneously.

The spatial dependence in the model is only one-dimensional, along the depth direction, which simplifies the numerical treatment of the equation system. Although such a simplification disregards the formation of the oxide from a grain nucleation and growth process, which is known to be the operating mechanism in
Zr clad corrosion, the model contains features that are indirectly associated with a polycrystalline microstructure, such as the formation of a substoichiometric (tetragonal) oxide phase near the interface and fragmentation after a certain time. Another, perhaps less limiting, simplification is that O and Zr are the only chemical species considered here, when it is well known that hydrogen and water chemistry do have a strong impact on the oxidation kinetics, as does alloy composition in Zr alloys.

This capability to capture a multilayer representation of the oxidation process is one of the main features of the model. The literature is increasingly indicative of a situation in which ZrO is known to transition into Stage 2 oxidation at a critical scale thickness of 1-to-2 μm, while Zircaloy-4 is seen to fail around 2.5 μm. In both cases, Stage 1 is characterized by $t^{1/3}$ kinetics. We have used the parameters $C_0$ and $r_0$ to recover such behavior. Evidently, more than one combination of values for these two parameters can yield the desired results. We recognize this and cautiously note that the values employed here are not definitive, other than we have not let them fluctuate uncontrollably and have made sure that they stay within reasonable experimental limits. The main point is that, although electro-migration—induced by charge accumulation in a localized region near the oxide interface—can bend the standard diffusive curves $\sim t^{1/2}$ in both directions, only a suitable choice of parameters can furnish the experimentally-observed $t^{1/3}$ behavior. This has been known in the community for some time \cite{67,106}, and here we present a modeling effort showcasing precisely how to achieve that.

In terms of the numerics, the model is solved using an explicit second-order finite difference discretization, a very standard method of solving partial differential equations numerically. As it relates to the present calculations, the main difficulties were the timescale used, which is set on the one hand by the material constants employed (e.g. diffusivities, and dielectric constants), and on the other by numerical stability criteria that set limits on the value of the time increments that can be used. Because the the relationship between $\dot{\varepsilon}$ and $\dot{\gamma}$ (cf. Sec. 2.7) is material constant dependent, achieving time synchronicity across the different zones is not entirely trivial and an extra constraint must be added to the time step to ensure that the interfaces evolve on the same timescale.

Finally, our model does not explicitly capture irradiation effects. Multiple studies have shown that Stage 1 is only slightly affected by irradiation, with the major effect shown on Stage 2 kinetics \cite{53,107}. However, newer data suggests that higher dose rates significantly accelerate oxidation during the early stages of corrosion \cite{108}. As mentioned above, a model incorporating these effects is underway and will published in the future. Our emphasis so far has been on capturing the cubic growth kinetics for Stage 1 oxidation and develop a mechanical failure criterion that provides a physically based transition to Stage 2 kinetics. On a qualitative level, both of these goals have been attained, although much work remains to be done to fully understand the peculiarities of Zr oxidation in nuclear environments.

5. Conclusions

We end this paper with a list of the most important conclusions:

- We have developed a one-dimensional numerical model of oxide scale formation and growth in zirconium under nuclear reactor operating conditions. The model tracks the motion of interfaces governed by oxygen diffusion, which includes concentration driven transport, thermo-migration, and electro-migration.

### Table 3
Comparison of parameters for Zr, Zirc-4, and Zr-2.5Nb. The parameters for pure Zr are directly taken from Table 1. Data for Zircaloy-4 is taken from Refs. \cite{103,104}, while the parameters for Zr-2.5Nb are from Zhang et al. \cite{105}.

<table>
<thead>
<tr>
<th>Species</th>
<th>$s^*$ [μm]</th>
<th>$t_{1\rightarrow2}$ [days]</th>
<th>$D^f$ [m$^2$s$^{-1}$]</th>
<th>$U_0$ [eV]</th>
<th>$D^b$ [m$^2$s$^{-1}$]</th>
<th>$U_H$ [eV]</th>
<th>$C_0$ [$r_0^2$]</th>
<th>$r_0$ [C⋅m$^{-2}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr</td>
<td>1.27</td>
<td>40</td>
<td>$6.61 \times 10^{-6}$</td>
<td>1.9</td>
<td>$9.00 \times 10^{-8}$</td>
<td>1.24</td>
<td>0.36</td>
<td>662.0</td>
</tr>
<tr>
<td>Zirc-4</td>
<td>2.47</td>
<td>149</td>
<td>$3.92 \times 10^{-4}$</td>
<td>2.2</td>
<td>$2.76 \times 10^{-6}$</td>
<td>1.5</td>
<td>0.52</td>
<td>156.0</td>
</tr>
<tr>
<td>Zr-2.5Nb</td>
<td>2.41</td>
<td>112</td>
<td>$1.72 \times 10^{-5}$</td>
<td>1.9</td>
<td>$1.72 \times 10^{-5}$</td>
<td>1.9</td>
<td>142.22</td>
<td>0.0</td>
</tr>
</tbody>
</table>
• The model includes the formation of three layers: ZrO2 (outermost), ZrO (middle), and metallic Zr suboxides and solid-solutions (innermost). As well, certain aspects of the model reflect the existence of a substoichiometric tetragonal Zr near the ZrO2/ZrO oxide interface.

• A mechanical failure criterion based on oxide fragmentation and Pilling-Bedworth stresses has been derived to predict the transition from Stage 1 to Stage 2.

• The model is parameterized with both experimental and computational data, and it captures a full temperature dependence across the Zr clad.

• Our results show that cubic growth behavior can be predicted when electro-migration is considered, and a suitable choice of parameters is adopted. These parameters are fitted to reasonable values that yield the desired behavior.

• The sharp transition to breakaway growth in Stage 2 after oxide scale fragmentation occurs as a consequence of the accumulation of compressive stresses in the oxide/metal interface.

• A preliminary sensitivity analysis has been conducted, showing that changes of ±15% in key model parameters results in variations of less than 5% in the time-dependent kinetics of the oxide layer.

Acknowledgments

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Appendix A. Analytical justification for an exponentially-decaying charge density

The charge density in the vicinity of a chemical reaction site can be safely assumed to be maximum at the reaction site and to gradually decrease towards zero with distance from it (in the limit of an electro-neutral medium). Several works have suggested that charged species. Assuming first-order kinetics, this excess charge is consumed at a rate given by:

\[
\frac{d\rho}{dt} = -\alpha \rho
\]  

where \( \rho \) is the charge density and \( \alpha \) is a constant. As well, if the corrosion front is moving with a velocity \( v = \frac{dx}{dt} \), the time change of the charge density can also be expressed as:

\[
\frac{d\rho}{dt} = \frac{d\rho}{dx} \frac{dx}{dt} = v \frac{d\rho}{dx}
\]  

Combining eqs. (A.1) and (A.2) leads to:

\[
\frac{d\rho}{dx} = \frac{\alpha}{v} \rho
\]  

Although the velocity of the oxidation front changes with time, this change rate can be considered much slower than the local charge density variation. Consequently, the advancing reaction front is assumed to advance at a constant velocity \( v \) such that integration of eq. (A.3) results in:

\[
\rho(x) = \rho_0 \exp\left(-\frac{\alpha}{v} x\right)
\]  

where \( \rho_0 \) is the charge density at the moving interface, and the ratio \( \frac{\alpha}{v} \) is denoted by the constant \( \lambda \) in Section 2.3.

Appendix B. Stability criterion

The Neumann stability criterion for linear differential equations with periodic boundary conditions allows us to expand the solution in a finite Fourier series. Each Fourier mode, defined by its wave number \( \omega \), is tracked in time assuming a simple separable solution of the form:

\[ c_i(t) = b(t_i) e^{i\omega t} \]

such that eq. (24) transforms into:

\[
b^{i+1} \exp[i \omega t] = \left( a_1 + a_2 + a_3 + a_4 \right) b^i \exp[i(\omega + 1)t] + \left( 1 - 2a_1 + a_2 \right) b^i \exp[i(\omega - 1)t] + (a_1 + a_2 + a_3 + a_4) b^i \exp[i(\omega - 1)t] + (a_1 + a_2 + a_3 + a_4) b^i \exp[i(\omega - 1)t]
\]

\[ (B.1) \]

such decrease can take the form of an exponential decay \([109,110]\). Here, we derive an expression for the charge density that follows an exponential decay from simple kinetic considerations.

The accumulation of charge near a moving corrosion reaction front results from an imbalance between positively and negatively charged species. Assuming first-order kinetics, this excess charge is consumed at a rate given by:

\[
\frac{d\rho}{dt} = -\alpha \rho
\]  

where \( \rho \) is the charge density and \( \alpha \) is a constant. As well, if the corrosion front is moving with a velocity \( v = \frac{dx}{dt} \), the time change of the charge density can also be expressed as:

\[
\frac{d\rho}{dt} = \frac{d\rho}{dx} \frac{dx}{dt} = v \frac{d\rho}{dx}
\]  

Combining eqs. (A.1) and (A.2) leads to:

\[
\frac{d\rho}{dx} = \frac{\alpha}{v} \rho
\]  

Although the velocity of the oxidation front changes with time, this change rate can be considered much slower than the local charge density variation. Consequently, the advancing reaction front is assumed to advance at a constant velocity \( v \) such that integration of eq. (A.3) results in:

\[
\rho(x) = \rho_0 \exp\left(-\frac{\alpha}{v} x\right)
\]  

where \( \rho_0 \) is the charge density at the moving interface, and the ratio \( \frac{\alpha}{v} \) is denoted by the constant \( \lambda \) in Section 2.3.

\[ (B.1) \]

Von Neumann’s analysis applies to periodic systems where the coefficients \( a_1, a_2, a_3, a_4, \) and \( a_5 \) are constant in time and space. Strictly speaking, this is not satisfied in cases with varying temperature gradients, but it can generally be assumed to hold when the coefficients vary slowly. Operating with the above equation:

\[
b^{i+1} \exp[i \omega t] = \left( a_1 + a_2 + a_3 + a_4 \right) b^i \exp[i(\omega + 1)t] + \left( 1 - 2a_1 + a_2 \right) b^i \exp[i(\omega - 1)t] + (a_1 + a_2 + a_3 + a_4) b^i \exp[i(\omega - 1)t] + (a_1 + a_2 + a_3 + a_4) b^i \exp[i(\omega - 1)t]
\]

\[ (B.2) \]

\[ ^6 \text{Note that in this appendix we use } j \text{ and } k \text{ as the temporal and spatial indices, to distinguish them from the complex variable } i. \]
which can then simplified to:

\[
\frac{\dot{\xi}}{B_\varphi} = 1 - 2a_1 + a_2 + (a_1 + a_2 + a_3 + a_4) e^{(\text{h} \delta \varphi) + e^{(\text{h} \delta \varphi)}} \quad (B.3)
\]

Noting that:

\[
a^{(\text{h} \delta \varphi)} = \cos(\text{h} \delta \varphi) + i \sin(\text{h} \delta \varphi),
\]

we can rewrite (B.3) as:

\[
\frac{\dot{\xi}}{B_\varphi} = 1 - 2a_1 + a_2 + 2(a_1 + a_2 + a_3 + a_4) \cos(\text{h} \delta \varphi) \quad (B.4)
\]

The Neumann stability criterion is defined as:

\[
\frac{\dot{\xi}}{B_\varphi} \leq 1
\]

We consider the two extrema of trigonometric functions \(\text{h} \delta \varphi = 0\) and \(\text{h} \delta \varphi = \pi/2\). In the former case, the stability condition is simply:

\[
a_5 \leq 2a_1
\]

whereas for \(\text{h} \delta \varphi = \pi/2\) we have:

\[
a_5 \geq 2(a_2 + a_3 + a_4)
\]

The combination of both conditions results in:

\[
a_2 + a_3 + a_4 \leq 1 \quad (B.7)
\]

Substituting for the expressions of each coefficient from Section 2.7 and operating, we arrive at:

\[
\dot{\alpha} \leq \frac{2kT}{D(U \frac{dt}{dV} + (\frac{dU}{dV} - \frac{dV}{dU}))} \delta y
\]

which sets limits on the admissible values for \(\dot{\alpha}\) and \(\delta y\).

References