# Nuclear Fuel Performance

NE-533

Spring 2023

Last Time

- Pellet-clad interaction (PCI) takes two forms
  - Pellet-clad chemical interaction, PCCI (bonding occurs)
  - Pellet-clad mechanical interaction, PCMI (pellet pushes and drags cladding)
- In order for SCC to initiate and propagate in any material, four conditions are simultaneously required:
  - A corrosive environment, a susceptible material, sufficient stress, and sufficient time
- Two types of mitigation strategies to limit PCI failures

CLADDING OXIDATION

Zirconium Oxidation

- Corrosion of zirconium due to the water coolant is one of the largest concerns for LWR fuel operation
- Corrosion of zirconium alloys in an aqueous environment is principally related to the oxidation of the zirconium by the oxygen in the coolant, dissolved or produced by radiolysis of water

$$Zr + 2H_2O \rightarrow ZrO_2 + 2H_2$$
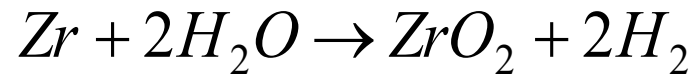
- Zirconium interacts with water to make zirconia and hydrogen
- Both the oxide layer and the hydrogen adversely impact cladding performance

ZrO$_2$

Zr metal

40 µm

100 µm
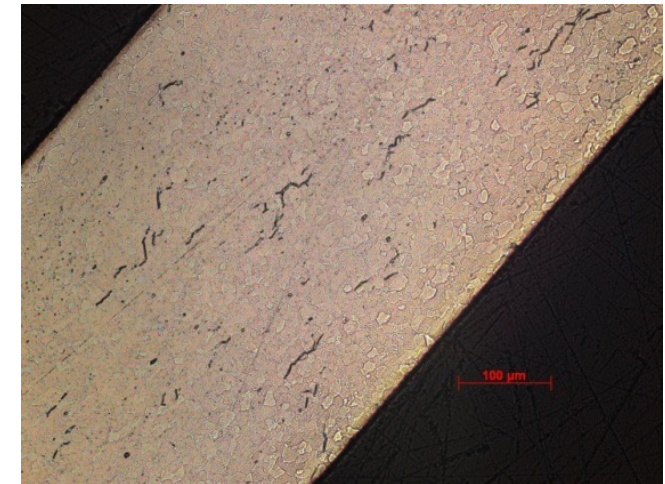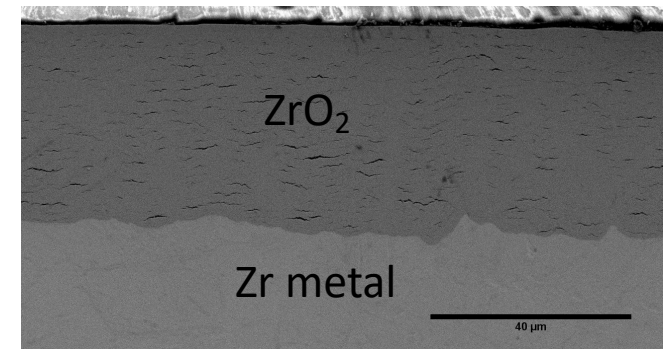
Corrosion

- Corrosion is the degradation of a material and its properties under the action of the surrounding environment by chemical and/or electrochemical reaction
- Corrosion reactions require the following:
  - Oxidant
  - Electric current

$$Zr + 2H_2O \rightarrow ZrO_2 + 2H_2$$

- A corrosion reaction is composed of an oxidation reaction and a reduction reaction
- During corrosion at a particular spot on the surface of the object, oxidation takes place, and that spot behaves as an anode
- The electrons released at this anodic spot move through the metal and go to another spot and reduce H, which behaves as a cathode
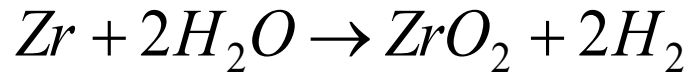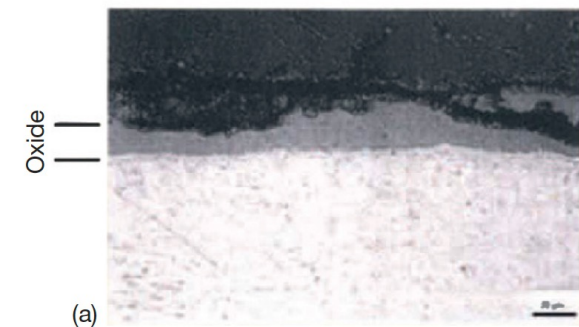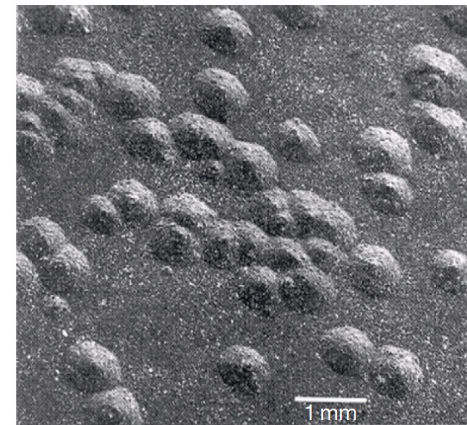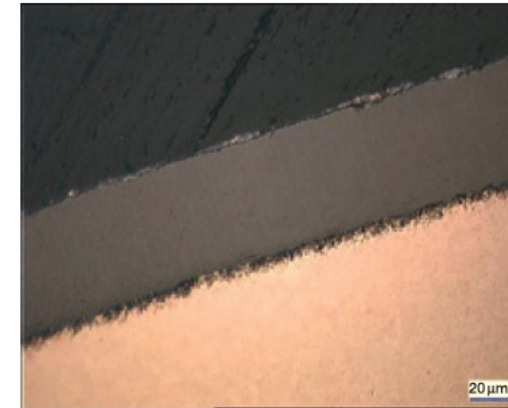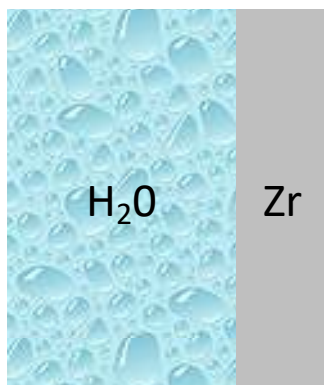
Corrosion

- Corrosion reaction rates are determined by thermodynamics and kinetics
- Thermodynamics tell us whether a material may corrode
  - Measure voltage difference between anodic and cathodic sites
- Kinetics tell us how quickly a material will corrode
  - Measure net current between anodic and cathodic sites
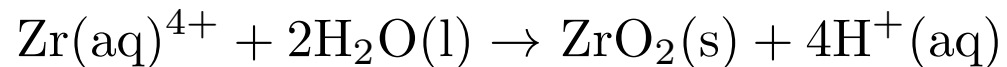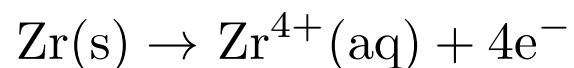
Corrosion Types in LWRs

- Several types of corrosion morphologies have been observed in nuclear reactors and in autoclave experiments, of which the most important are: 1) uniform, 2) nodular, and 3) shadow

- Uniform: The formation of a thin uniform layer of zirconium dioxide on the surface of a zirconium alloy component

- Nodular : The formation of local, small, circular zirconium oxide blisters

- Shadow: The formation of local corrosion regions that mirror the shape (suggestive of a shadow) of other nearby noble reactor core components
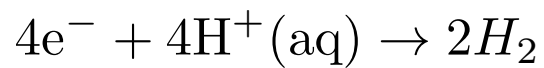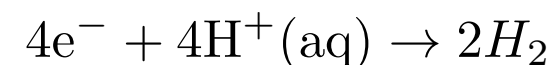
Formation of Oxide Layer

Oxidation reaction:

$$Zr(s) \rightarrow Zr^{4+}(aq) + 4e^-$$

$$Zr(aq)^{4+} + 2H_2O(l) \rightarrow ZrO_2(s) + 4H^+(aq)$$

Reduction reaction:

$$4e^- + 4H^+(aq) \rightarrow 2H_2$$

After Oxide Formation

$$2H_2O(l) \rightarrow 2O(aq)^{-2} + 4H^+(aq) \qquad Zr^{4+} + 2O^{-2} \rightarrow ZrO_2 + 4e^-$$

$$4e^- + 4H^+(aq) \rightarrow 2H_2$$
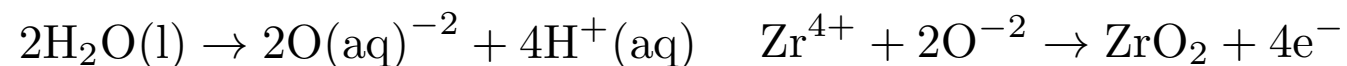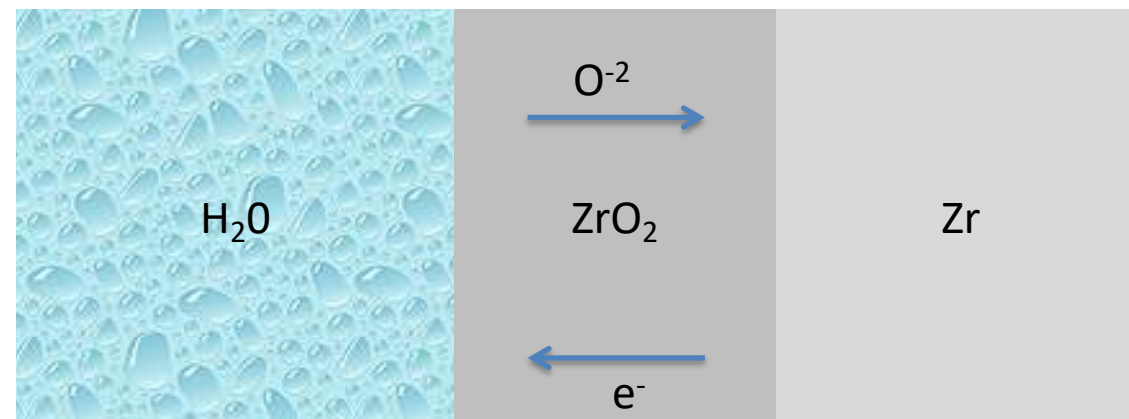
1. Dissociation of water at oxide/water interface
2. Absorption of oxygen into oxide layer
3. Diffusion of oxygen through oxide layer
4. Reaction of oxygen with zirconium
5. Diffusion of electrons through oxide layer
6. Reduction of hydrogen

Corrosion rate limited by diffusion

- Because the rate limiting steps are diffusion, we can model the oxidation rate using diffusion
- Assumptions:
  - Transport of O species is rate-limiting
  - Transport of charged species by diffusion only
  - Homogeneous oxide layer
  - No sources/sinks of ions in oxide
  - All oxygen is used to create oxide
  - No loss of oxide

$$\frac{\delta^2}{2} = K^2 t \rightarrow \delta = K t^{1/2}$$
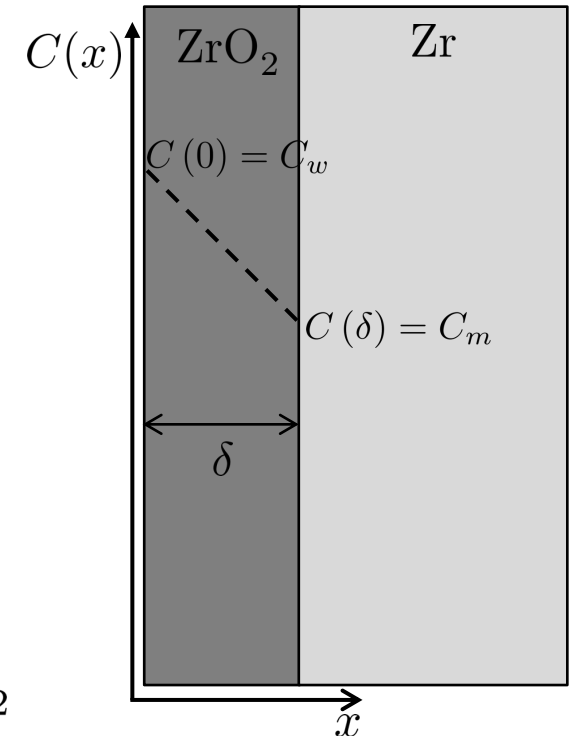
Observed kinetics are slower than parabolic

- Parabolic kinetics
  - Diffusion of species across the oxide
- Sub-parabolic kinetics
  - Additional ions in oxide
  - Non-uniform electric field in oxide layer
- Once a nonhomogeneous electric field arises, the corrosion rate decreases to the sub-parabolic rate due to inhibition of transport of charged species
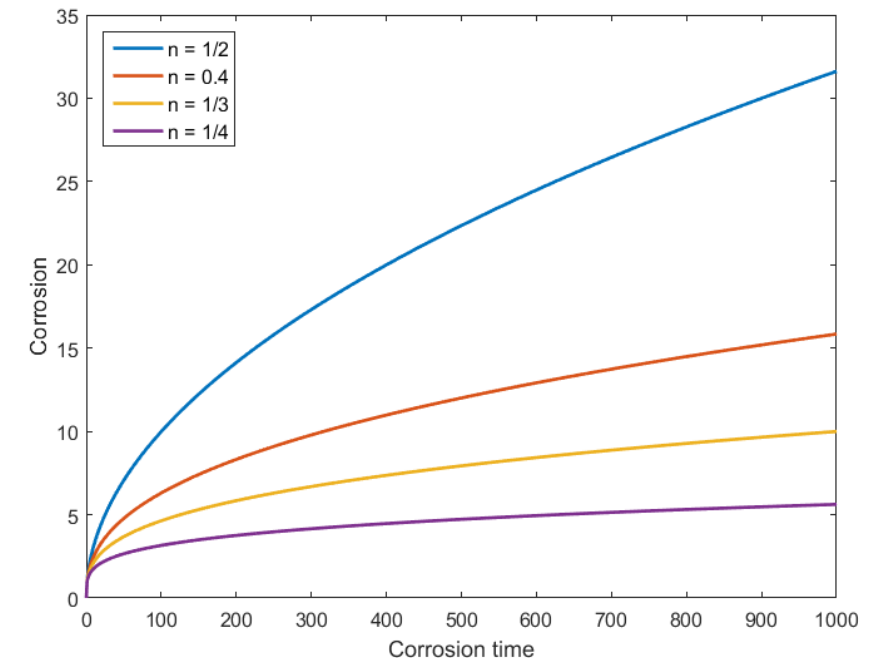
Corrosion Quantified

- Corrosion is measured by sample weight gain
- Oxidation of alloys is measured experimentally using the <u>weight gain</u> in mg/dm^2
- Oxide forms by incorporating oxygen in the metal structure causing an increase in weight
- 14.7 comes from density of O in ZrO2

<u>Original coupon</u>:
Weight m_1
Surface S
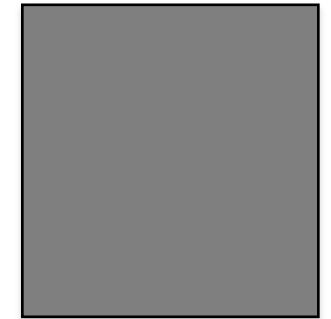
<u>corroded coupon</u>:
Weight $m_2 > m_1$
Surface S

$$W = (m_2 - m_1)/S$$

Dividing by the surface enables comparison between samples

<u>Approximation weight gain –
oxide thickness for Zr</u>:

$$\delta(\mu m) = \frac{w(mg/dm^2)}{14.7}$$

# Pilling-Bedworth ratio : PBR

- The ratio of the volume per unit of the metal oxide to the volume per unit of the corresponding metal is called the Pilling-Bedworth ratio (PBR)
- PBR < 1: the oxide coating layer is thin, likely broken and provides no protective effect (for example magnesium)
- PBR > 2: the oxide coating chips off and provides no protective effect (example iron)
- 1 < PBR < 2: the oxide coating is passivating and provides a protecting effect against further surface oxidation
- Passivation refers to a material becoming "passive," that is, less affected or corroded by the environment

$$R_{PB} = \frac{V_{oxide}}{V_{metal}} = \frac{M_{oxide} \cdot \rho_{metal}}{n \cdot M_{metal} \cdot \rho_{oxide}}$$

ZrO_2

Zr metal

40 µm
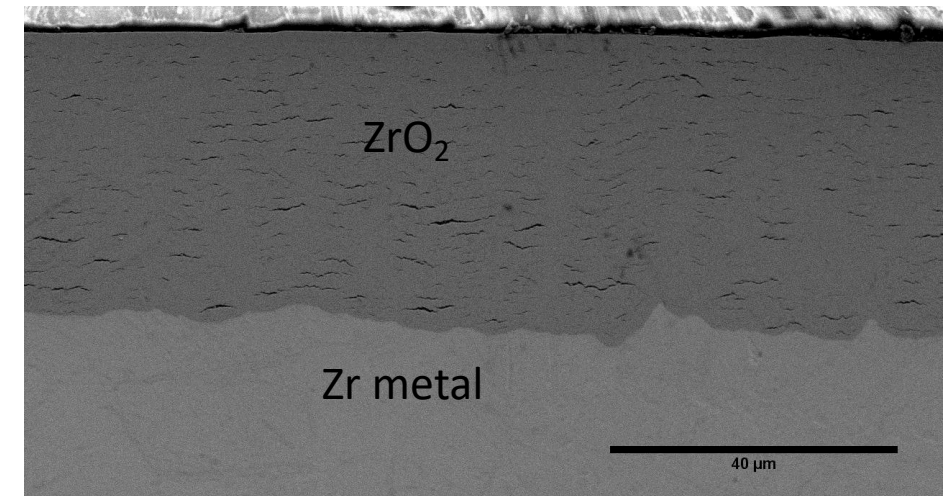
Example

- A corrosion coupon of ZIRLO measures 2.8 cm x 2.8 cm x 600 μm and has an initial mass of 3 g. After corrosion for 200 days, its final mass is 3.0721 g. What is the estimated oxide thickness?
- First, we need to convert the units (10 cm = 1 dm)
- Find area
  - $S = 0.28 \cdot 0.28 = 0.0784$ dm^2
- Find mass change
  - $dM = 307.21 - 300$ mg $= 7.21$ mg
- Then we calculate the weight gain per area
  - $W = dM/S = (7.21)/0.0784 = 91.96$ mg/dm^2
- Last estimate the thickness
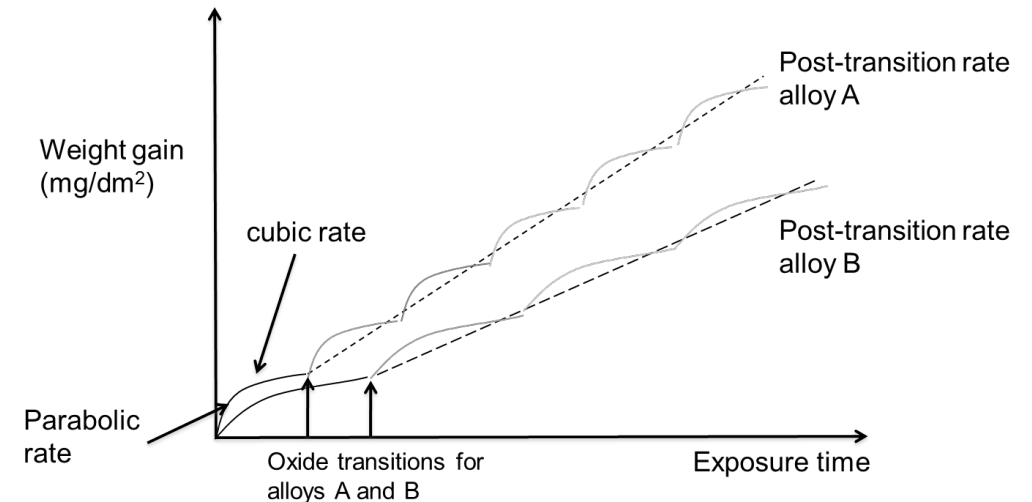 - $d = W/14.7 = 91.96/14.7 = 6.3$ microns thick after 200 days

Corrosion Rate

- Average weight gain of a sample follows linear kinetics
- The oxide reaches transition at different times in different points, but the average is linear
- Critical oxide thickness for transition is defined as $\delta^\star \left(\mu\mathrm{m} \right) = 5.1 \exp \dfrac{-550}{T}$
- Critical time for transition is defined as

$$t^\star \left(\mathrm{d} \right) = 6.62 \times 10^{-7} \exp \dfrac{11949}{T}$$

After transition, oxide thickness is
$$\delta \left(\mu\mathrm{m} \right) = \delta^\star + K_L \left(t - t^\star \right)$$

$$K_L \left(\dfrac{\mu\mathrm{m}}{\mathrm{d}} \right) = 7.48 \times 10^6 \exp \dfrac{-12500}{T}$$

Example

- Estimate the oxide thickness on a ZIRLO sample at 650 K after 200 days exposed to water.
- First, we have to determine if the oxide has gone through transition
  - $t^\star\,(\mathrm{d}) = 6.62 \times 10^{-7} \exp \dfrac{11949}{T}$
  - t* = 6.62e-7*exp(11949/650 k) = 63.76 days
  - So, the sample is past transition, so we need to use the linear fit
- Next, we calculate the oxide thickness at transition
  - $\delta^\star\,(\mu\mathrm{m}) = 5.1 \exp \dfrac{-550}{T}$
  - δ* = 5.1*exp(-550/650) = 2.19 microns
- Now, we can compute the final oxide thickness
  - $K_L \left(\dfrac{\mu\mathrm{m}}{\mathrm{d}} \right) = 7.48 \times 10^6 \exp \dfrac{-12500}{T}$
  - K_L = 7.48e6*exp(-12500/650) = 0.0333
  - $\delta\,(\mu\mathrm{m}) = \delta^\star + K_L\,(t - t^\star)$
  - δ = 2.19 + 0.0333*(200 – 63.76) = 6.73 microns