Nuclear Fuel Performance

NE-533

Spring 2025

Housekeeping

- Last module!
- Planned final exam on last day of classes, April 22
- Will cover what we can until then

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

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

- 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
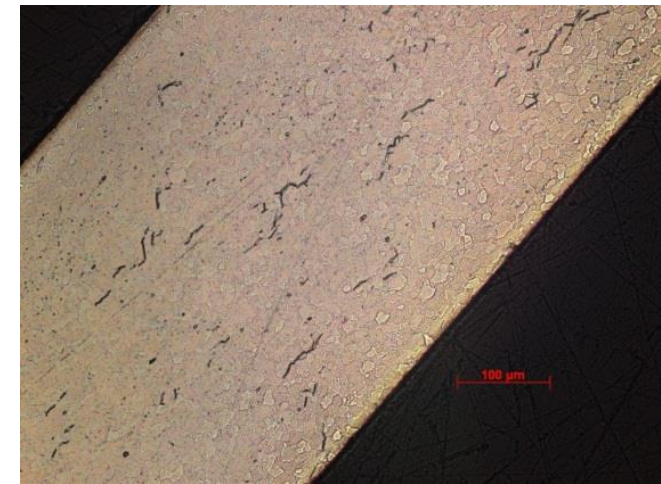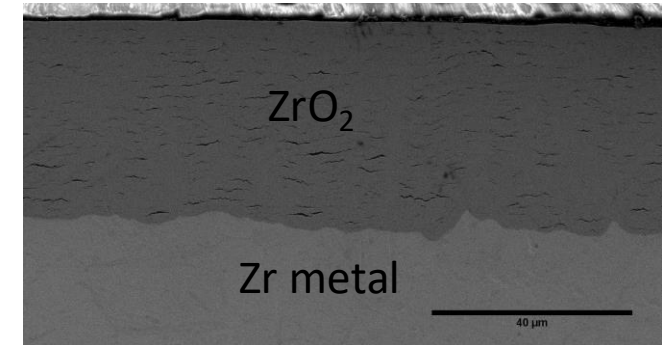
Corrosion

- 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

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

- 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
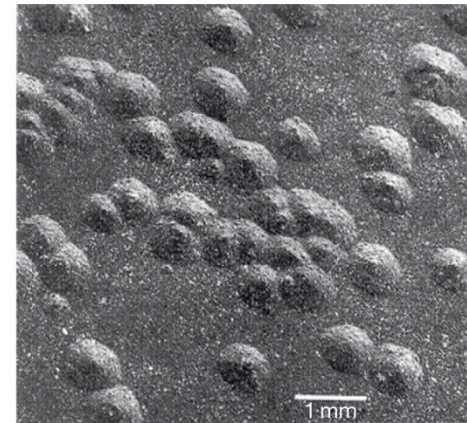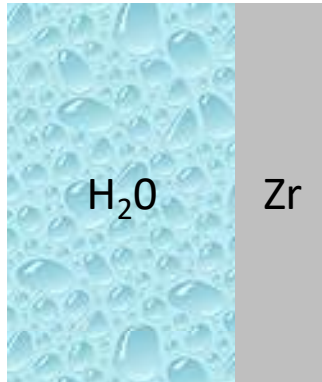
Corrosion

- 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
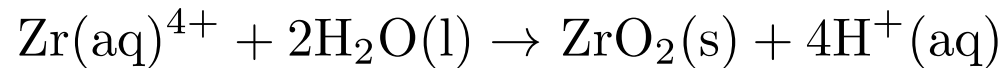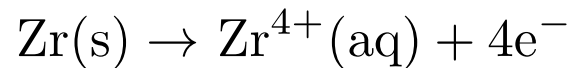
Corrosion Types in LWRs

- 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
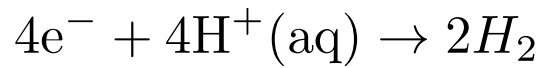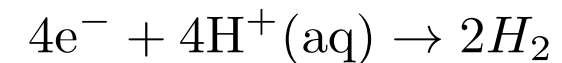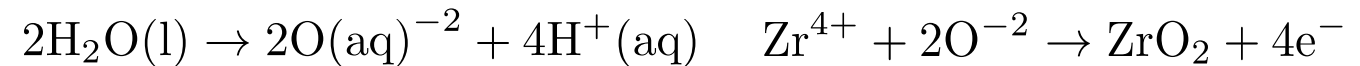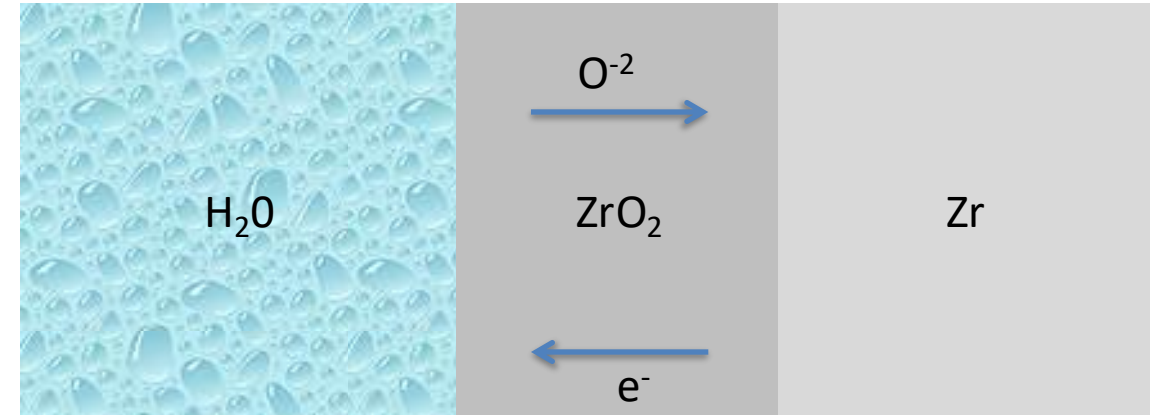
Formation of Oxide Layer

After Oxide Formation

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

Oxidation reaction:

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

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

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

Reduction reaction:

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

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

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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

$$\frac{\delta^2}{2} = K^2\, t \rightarrow \delta = K\, t^{1/2}$$

$C(x)$ ZrO_2 Zr

$C(0) = C_w$

$C(\delta) = C_m$

δ

x
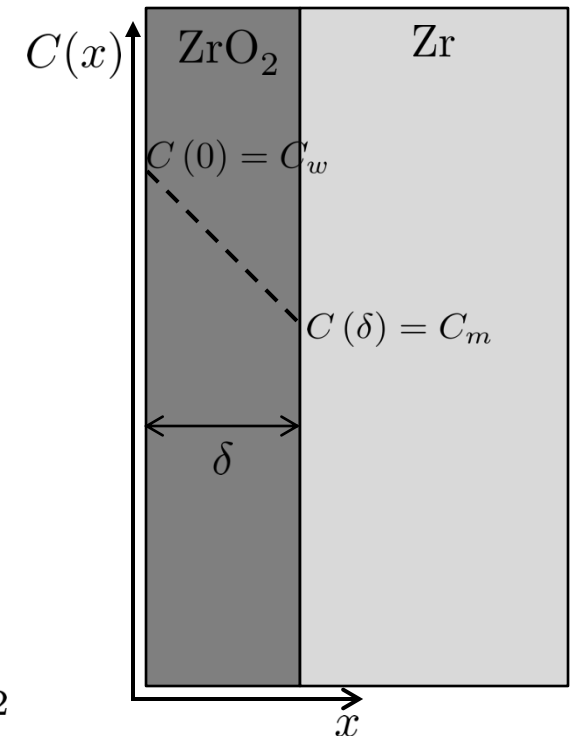
Observed kinetics are slower than parabolic

- Parabolic kinetics
  - Diffusion of species across the oxide
- Sub-parabolic kinetics
  - Additional ions, dopants, or defects 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
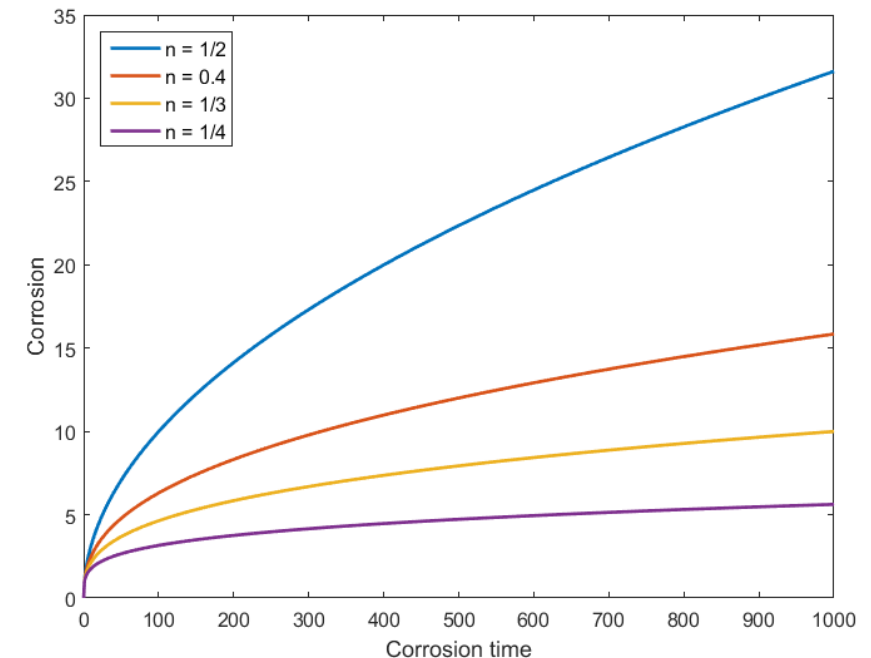
Corrosion Quantified

- 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

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

Dividing by the surface enables comparison between samples

<u>Original coupon</u>:
Weight m_1
Surface S

<u>corroded coupon</u>:
Weight $m_2 > m_1$
Surface S
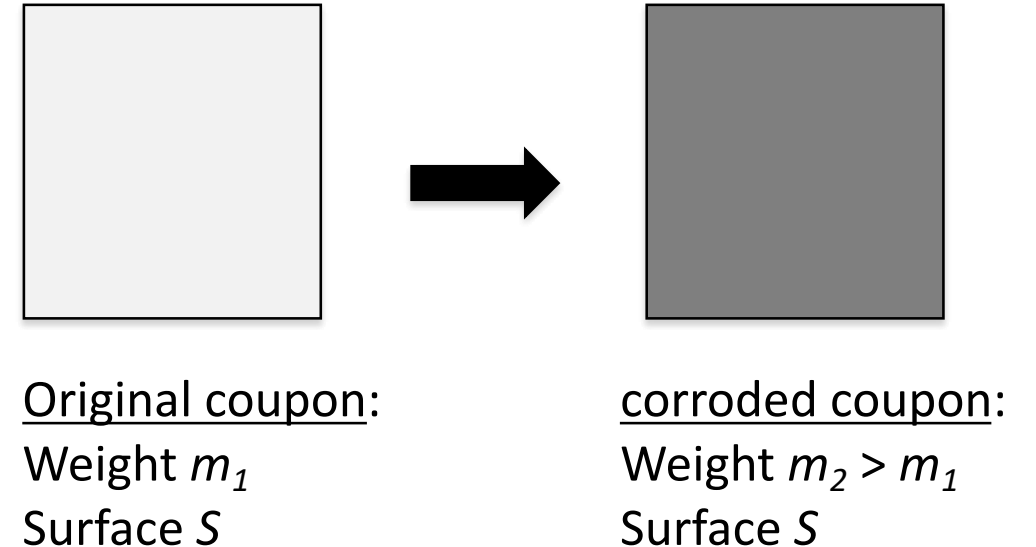
Approximation weight gain – oxide thickness for Zr:

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

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

$$R_{PB} = \frac{V_{oxide}}{V_{metal}} = \frac{M_{oxide} \cdot \rho_{metal}}{n \cdot M_{metal} \cdot \rho_{oxide}}$$
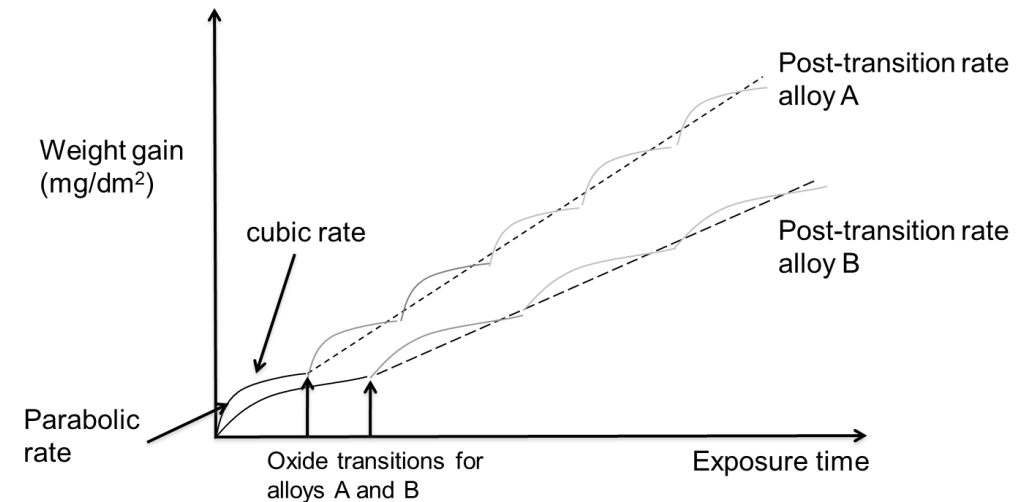
ZrO$_2$

Zr metal

40 µm

12
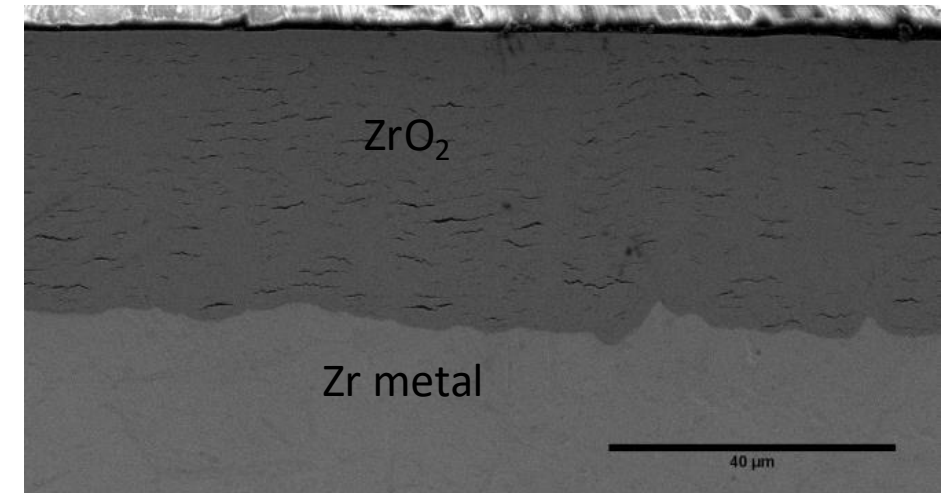
Corrosion Rate

- 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 $\delta^\star\,(\mu\mathrm{m}) = 5.1\exp\dfrac{-550}{T}$
- Critical time for transition is defined as

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

After transition, oxide thickness is

$$\delta\,(\mu\mathrm{m}) = \delta^\star + K_L\,(t - t^\star)$$

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

Other factors affecting corrosion

- Temperature:
  - Corrosion rate increases with temperature
- Irradiation: Radiation damage to the metal; Radiation damage to oxide
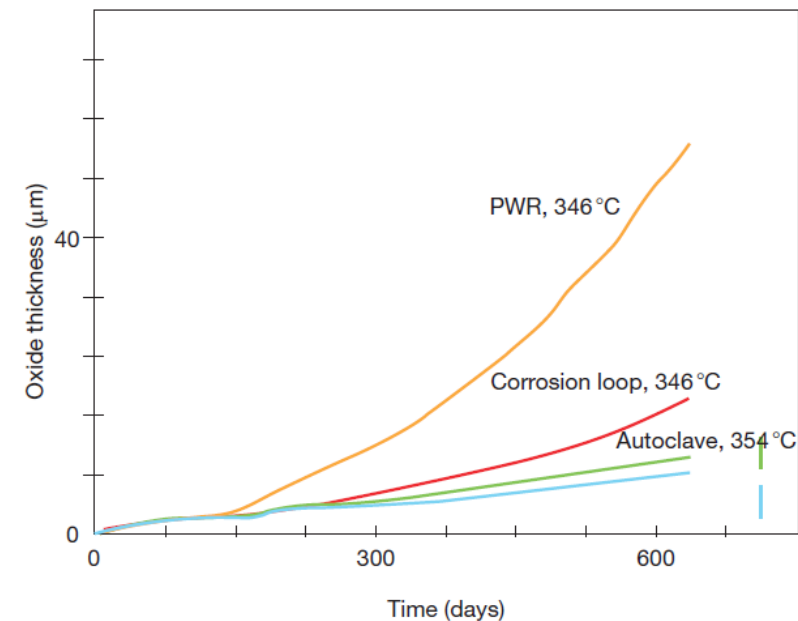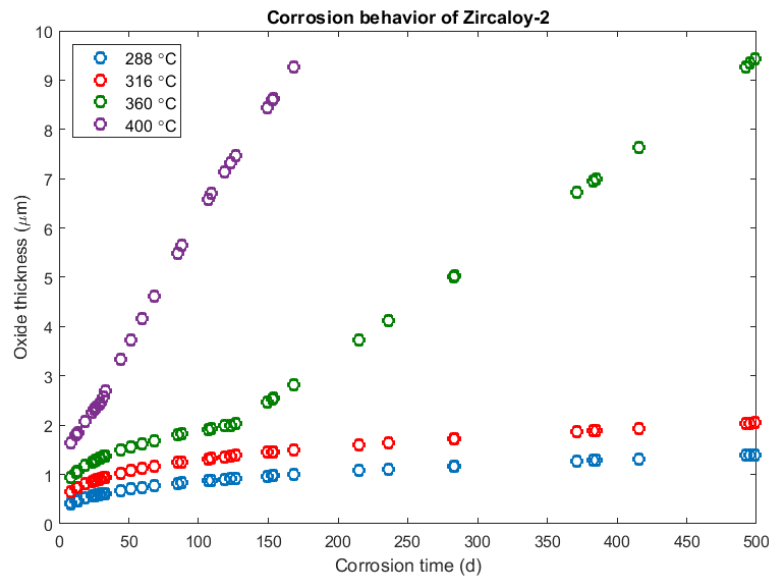
Impact of Corrosion

- The oxide layer has a low thermal conductivity, restricting heat transport
  - For Zircaloy, k = 22 W/(mK)
  - For ZrO_2, k = 1.7 – 2.7 W/(mK)
- The oxide layer is much more brittle than the zircaloy
  - Zircaloy metal is removed as brittle oxide is added to the material
- Oxidation produces hydrogen that can enter the cladding and form brittle hydrides

SE   18-Jul-11   Z4T-19 WD 7.8mm 5.00kV x2.5k   20um
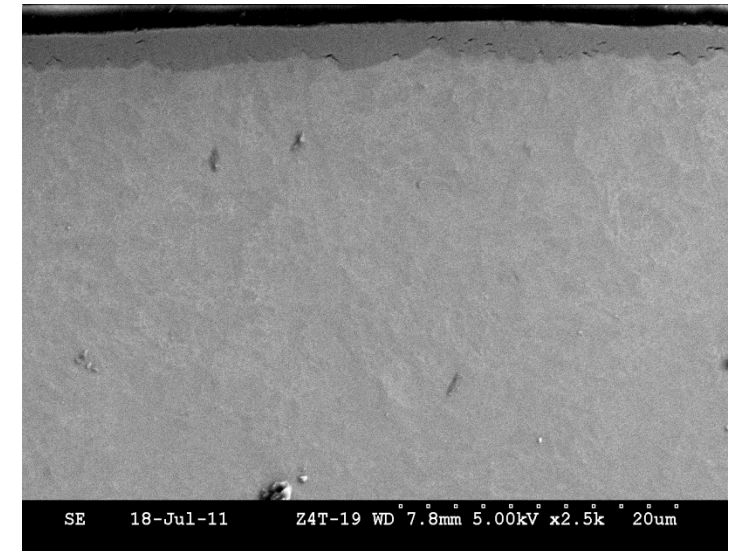
Corrosion Control

- The oxidation and hydrogen uptake of Zircaloy is of course determined by many factors
- The chemical and physical state of the material: composition, metallurgical condition, and surface condition
- Two different zirconium alloys employed in French PWRs, Zircaloy and Zr1% Nb (M5), display distinct corrosion behaviors
- The peak oxide layer thickness of Zircaloy-4 increases significantly with burnup, whereas that of Zr1%Nb shows a moderate increase
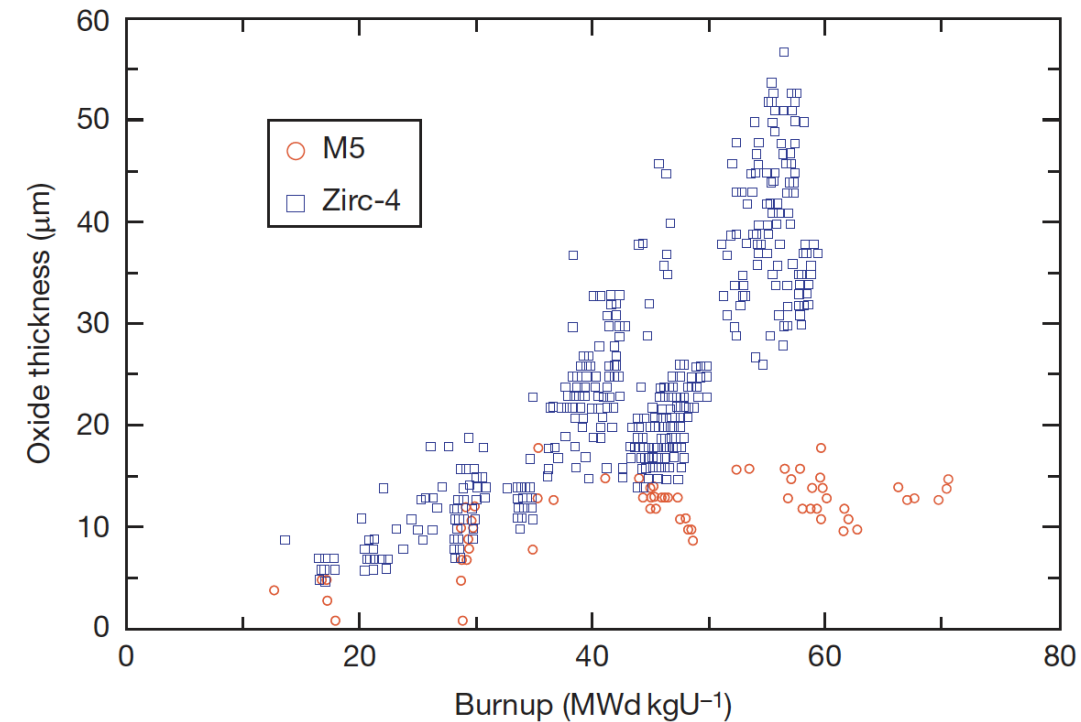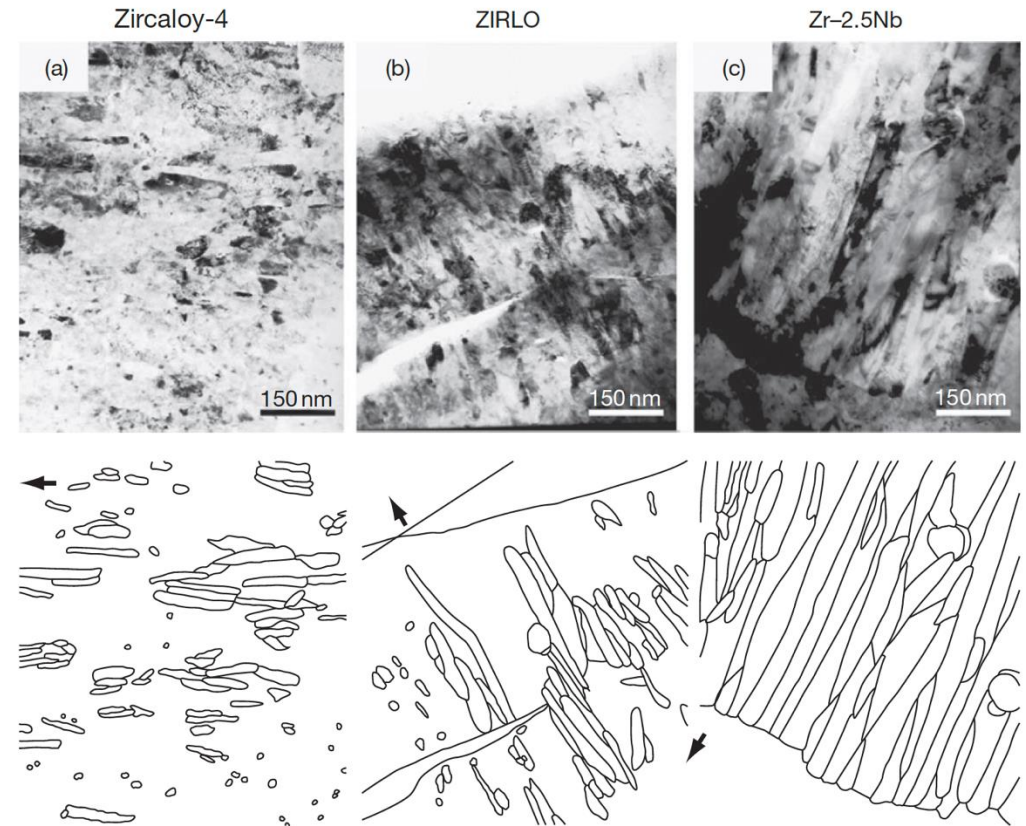
Corrosion Control

- Water Chemistry
  - The dissolved oxygen and hydrogen play a major role in the corrosion process, but other dissolved species must also be taken into account
  - To control the pH of the coolant at slightly alkaline conditions, LiOH is added and H3BO3 (boric acid) is added for reactivity control in PWRs
  - Impurities (Cl, F) and coolant-borne species (Cu, Ni, etc.) must be considered
- Temperature and irradiation also have an effect on the corrosion behavior, but are governed by engineering constraints
- CRUD (Chalk River Unidentified Deposit) can accelerate corrosion
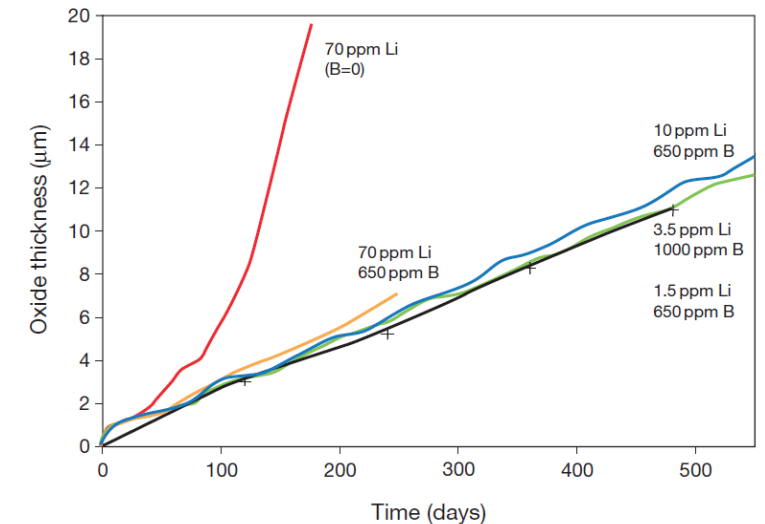
Corrosion Layer

- Uniform corrosion is a passivating event since a protective layer of zirconium oxide is formed as a result of the reaction with the O2 ions or the OH radicals
- The oxide layer is microcrystalline, initially equiaxed, later growing into columnar grains that are formed in a dense packing, of which the mean crystallite size increases as the oxide thickens

Corrosion Summary

- Corrosion is the environmental degradation of materials
- Cladding oxidizes, forming ZrO_2
- The limiting step for oxidation is the oxygen transport through the oxide layer
  - It begins being controlled by diffusion
  - Then, a protective layer forms that slows oxidation
  - Once transition occurs, it loses its protectiveness and speeds up again
- Oxidation hurts cladding performance by
  - Restricting heat transport
  - Converting zircaloy into a brittle oxide

Hydride Formation

Corrosion reaction:

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

- Corrosion of zirconium is so damaging in large part due to hydride formation
- Some of the hydrogen atoms produced by oxidation enter the cladding and form a hydride phase
- Other sources of H can increase the amount available to form hydrides, but this is minor
- Hydrogen pickup causes hydrogen embrittlement, loss of fracture toughness, delayed hydride cracking, accelerated corrosion, and accelerated irradiation growth

ZrO_2

Zr metal
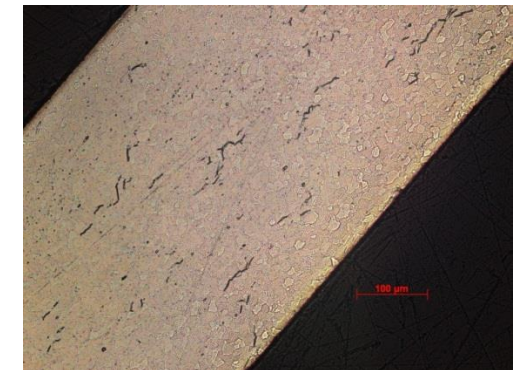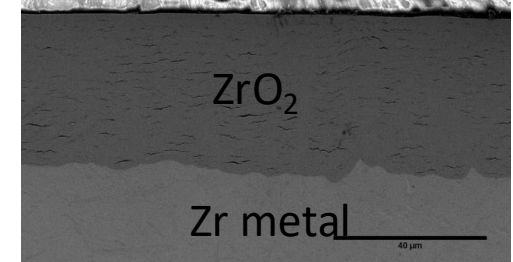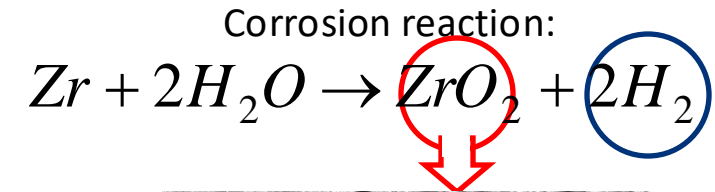
Hydrogen pick-up

Hydrogen Diffusion

- The diffusion coefficient of H in Zr is

$$D_{Zr}^H = D_o^H \exp(-E_m^H / k_B T)$$

$$E_m^H = 0.47 eV \quad D_o^H = 7 x 10^{-3} cm^2 / s$$

- The characteristic time required for hydrogen to diffuse through the entire cladding is

$$t = \frac{L^2}{4D_{Zr}^H}$$

- What is the characteristic time for cladding at 355°C (average cladding temperature) that is 0.06 cm thick?
  - D^H_{Zr} = 7x10^{-3}*exp(-0.47/(k_B*(355+273.15))) = 1.19e-6 cm^2/s,
  - t = 0.06^2/(4*1.19e-6) cm^2/s =756.3 s =12 min,
 - So, the hydrogen atoms have plenty of time to move through the entire clad

Hydriding

- Hydride concentrations are not uniform, because they respond to temperature and stress gradients
- Plate-type hydrides lead to stress concentrations, prefer matrix tensile stresses
- Hydrogen tends to move toward lower temperature (Soret effect)
- It also moves to areas with tensile stress
- Hydrogen has a low solubility in zirconium, so even small hydrogen concentrations result in hydrides
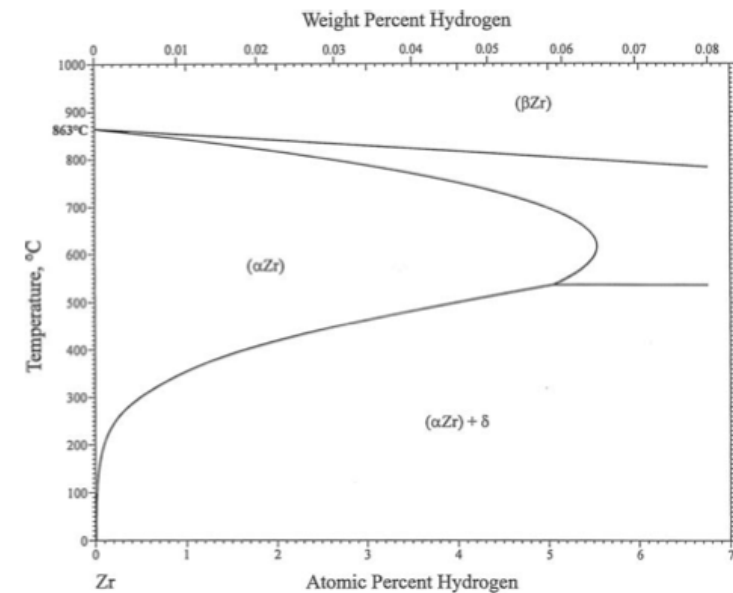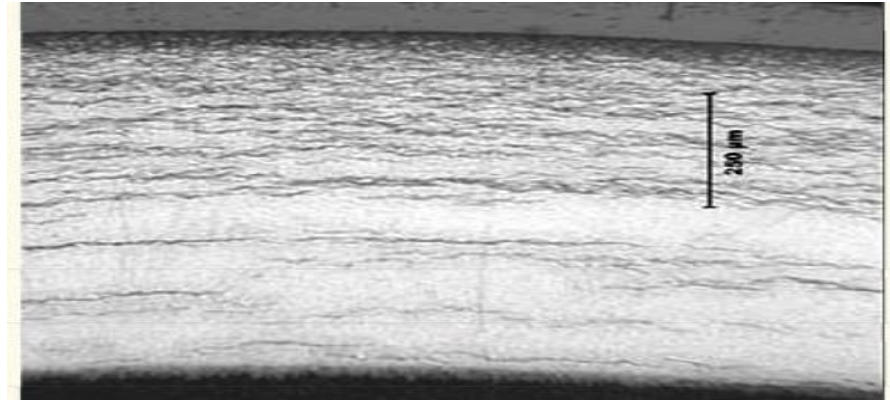
Effect of Hydrides

- The hydride rim is caused by the Soret effect and the temperature dependence of the solubility

- The hydride rim and blisters can cause a loss of ductility, leading to earlier failure

- Hydride rims are layers of uniform depth, that can reach 50–60 microns, and cover a wide area on the tube azimuthal and axial directions

- If hydride is localized, can form blisters

- Blisters have an elliptic shape, are more localized on the tube external surface and are deeper, usually covering half of the cladding thickness
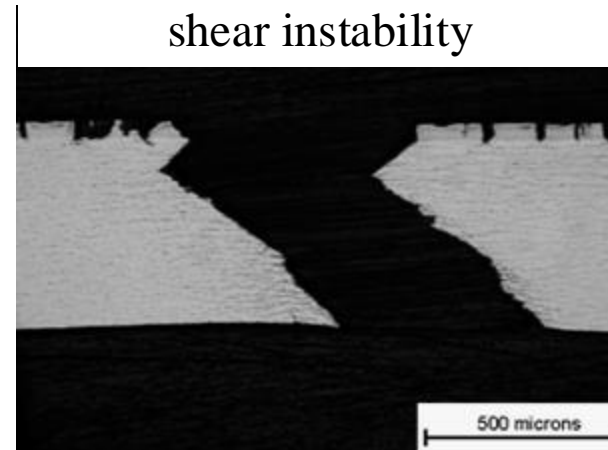

Hydrided
Zircaloy-4
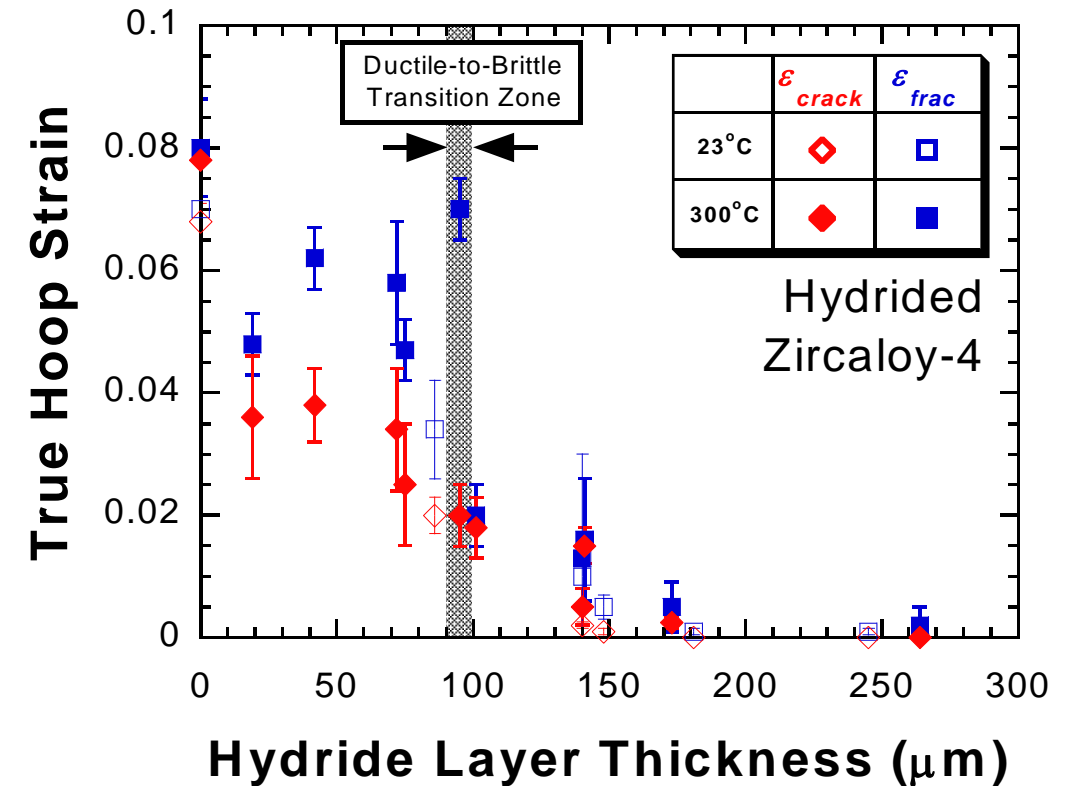
Blister failure examples

90 degree failure at RT
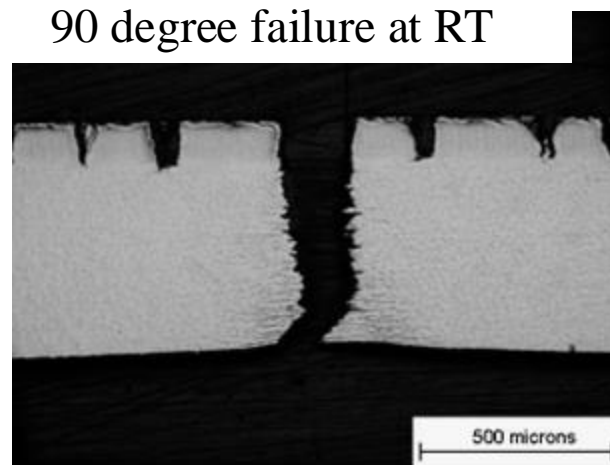
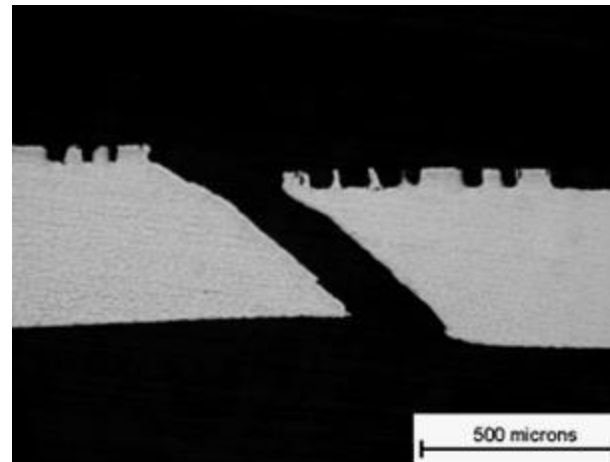But in small blisters => shear instability

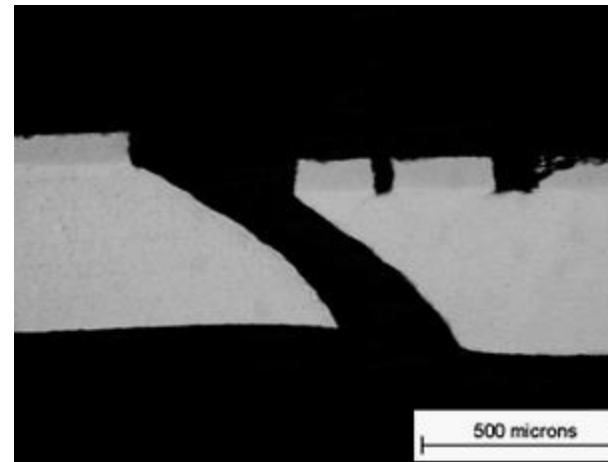**93 μm Blister Broken at 25 °C M020**

40 μm Blister Broken at 25 °C M014

53 μm Blister Broken at 300 °C M025

83 μm Blister Broken at 300 °C M023

At 300 C, 45 degree shear