# Nuclear Fuel Performance

NE-533

Spring 2022

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

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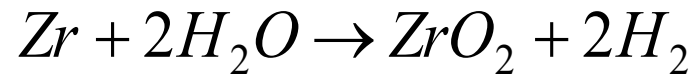
- Zirconium interacts with water to make zirconia and hydrogen
- Both the oxide layer and the hydrogen adversely impact cladding performance

ZrO₂

Zr metal

40 µm

100 µm
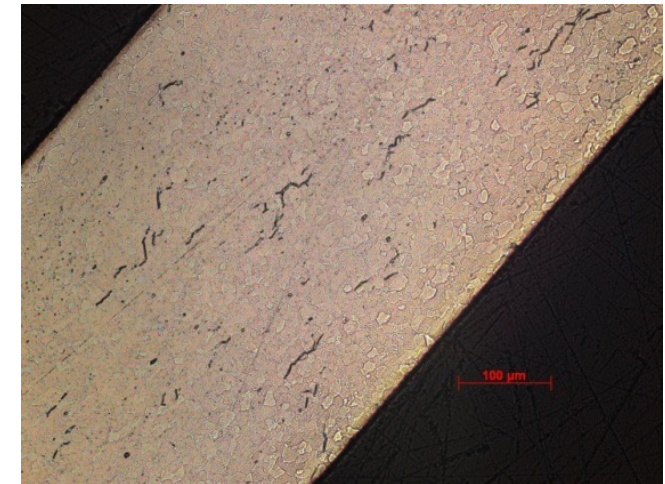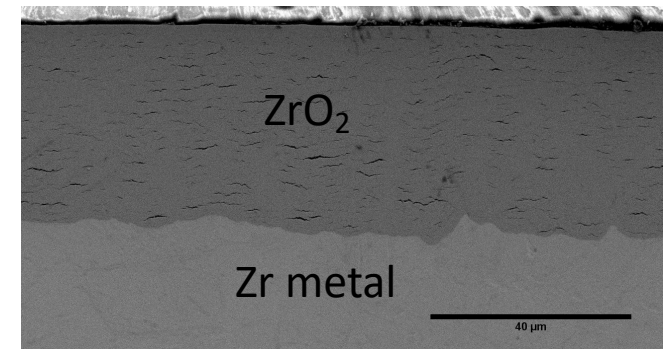
Corrosion

- 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
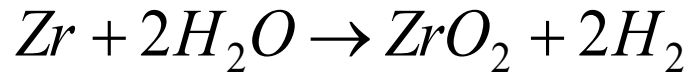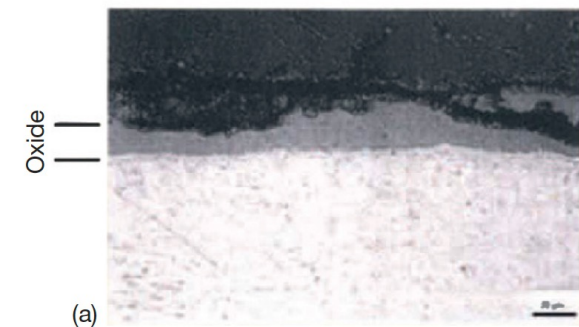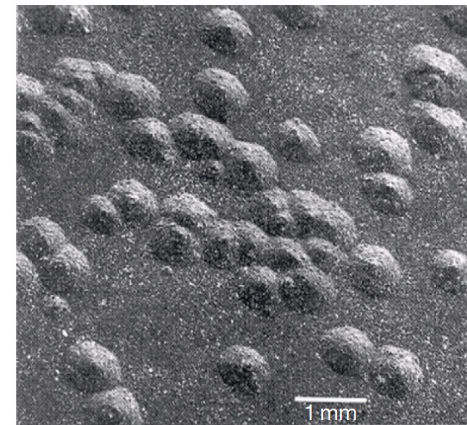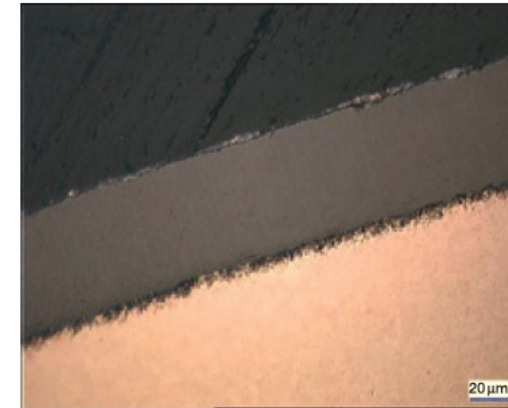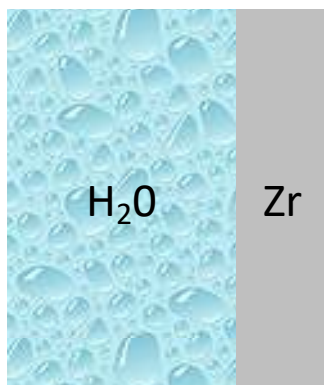
Corrosion

- 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
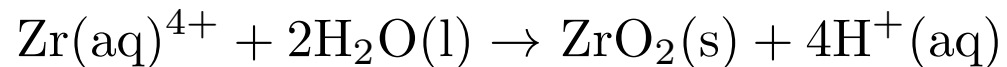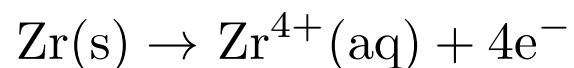
Corrosion Types in LWRs

- 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
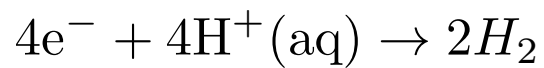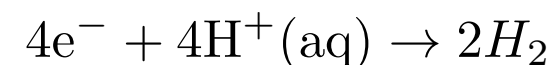

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Formation of Oxide Layer

H_2O | Zr

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

H_2O | O^{-2} / ZrO_2 / e^- | Zr

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

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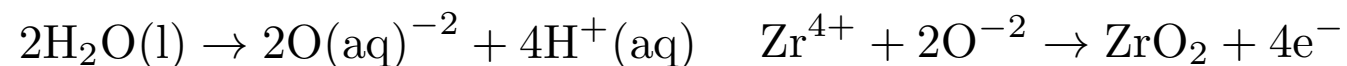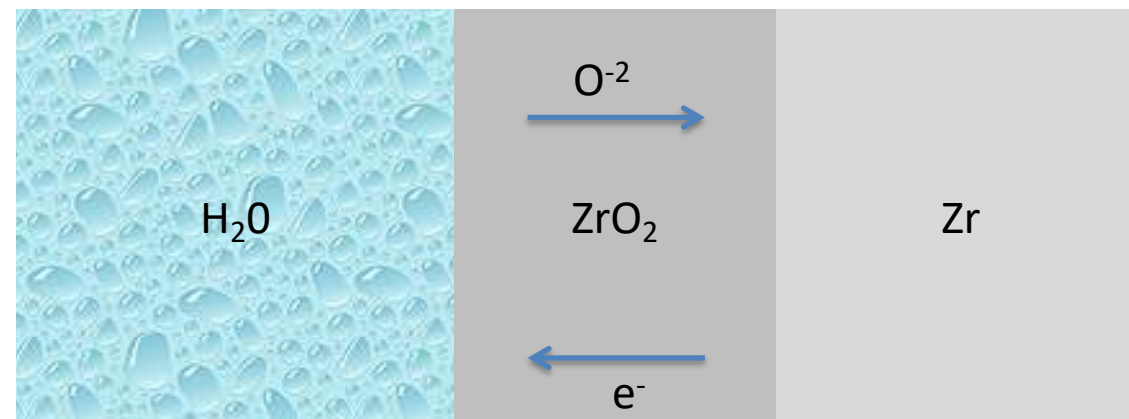
1. Dissociation of water at oxide/water interface
2. Absorption of oxygen into oxide layer
3. Diffusion of oxygen through oxide layer
4. Reaction of oxygen with zirconium
5. Diffusion of electrons through oxide layer
6. Reduction of hydrogen

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

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

$C(x)$ $\mathrm{ZrO_2}$ Zr

$C(0) = C_w$

$C(\delta) = C_m$

δ

x
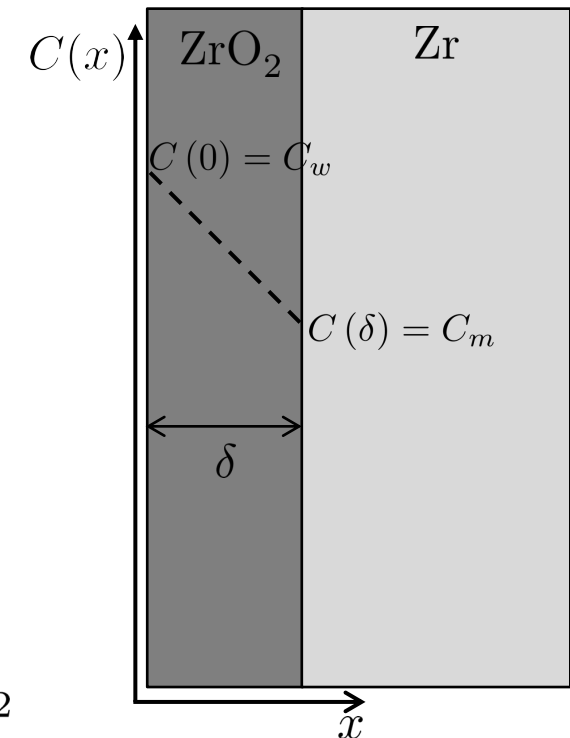
Observed kinetics are slower than parabolic

- Parabolic kinetics
  - Diffusion of species across the oxide
- Sub-parabolic kinetics
  - Additional ions 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
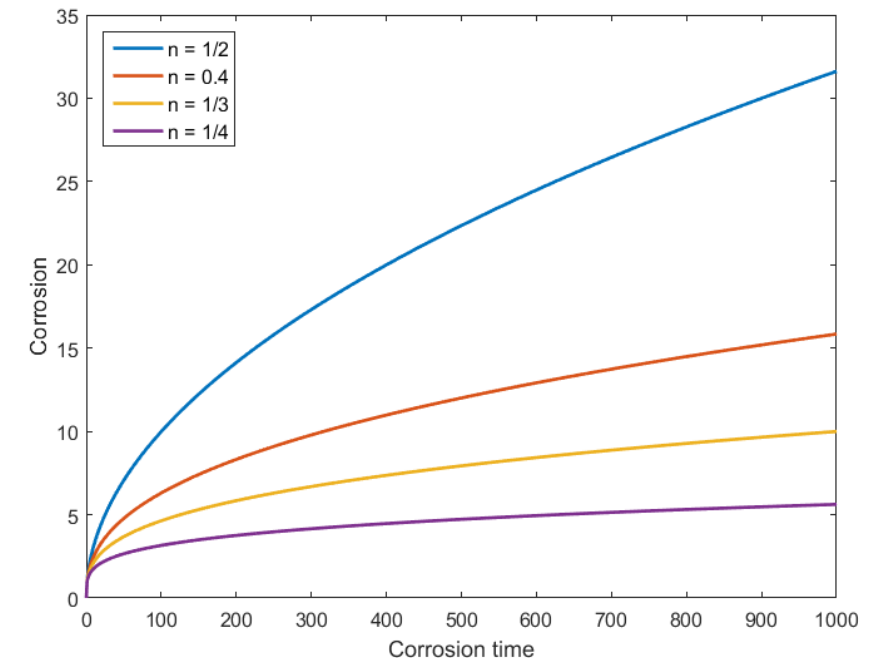
Corrosion Quantified

- 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
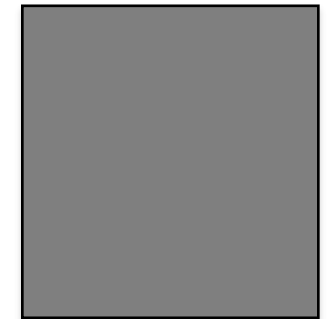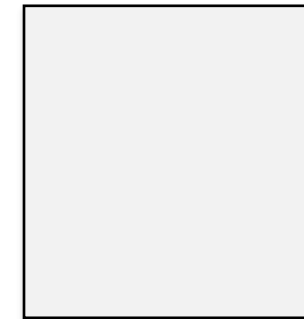
Original coupon:
Weight m_1
Surface S

corroded coupon:
Weight $m_2 > m_1$
Surface S

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

Dividing by the surface enables comparison between samples

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 of future use

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

ZrO_2

Zr metal

40 µm
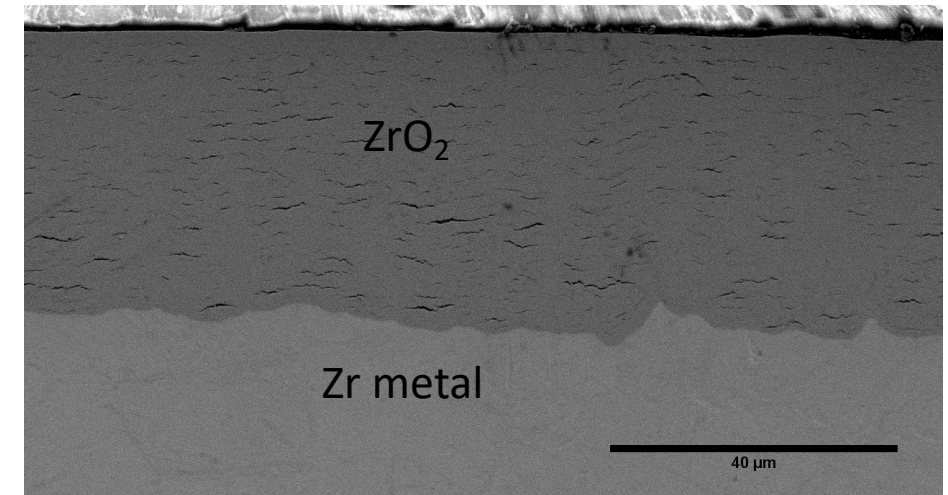
Example

- 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
  - $S = 0.28*0.28 = 0.0784$ 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
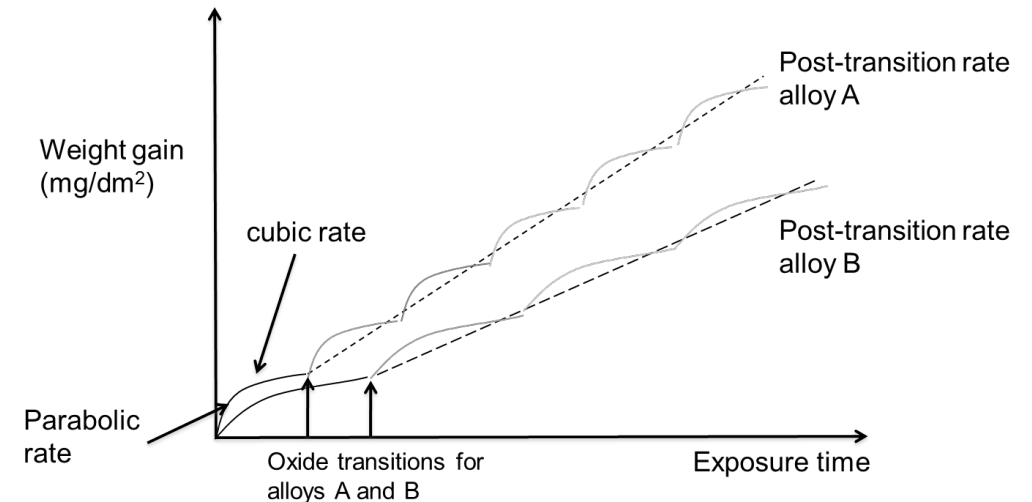 - $d = W/14.7 = 91.96/14.7 = 6.3$ microns thick after 200 days

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

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

Weight gain (mg/dm²)

cubic rate

Parabolic rate

Oxide transitions for alloys A and B

Post-transition rate alloy A

Post-transition rate alloy B

Exposure time

After transition, oxide thickness is

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

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

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
  - $\delta\,(\mu\mathrm{m}) = \delta^\star + K_L\left(t - t^\star\right)$
 - δ = 2.19 + 0.0333*(200 – 63.76) = 6.73 microns

Other factors affecting corrosion

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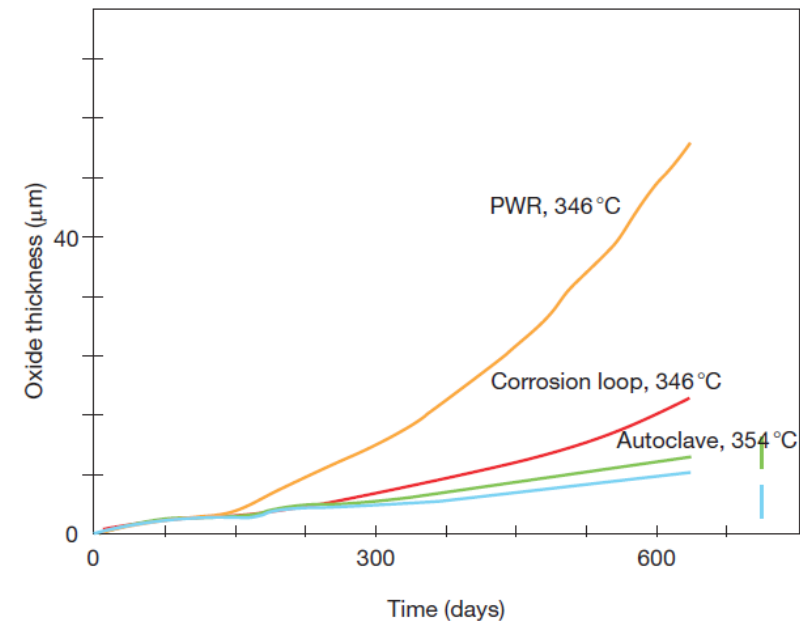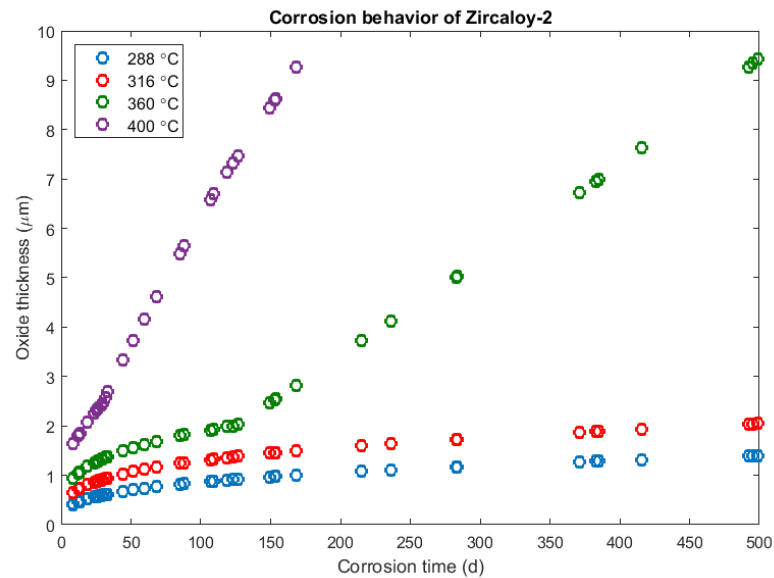
Impact of Corrosion

- 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
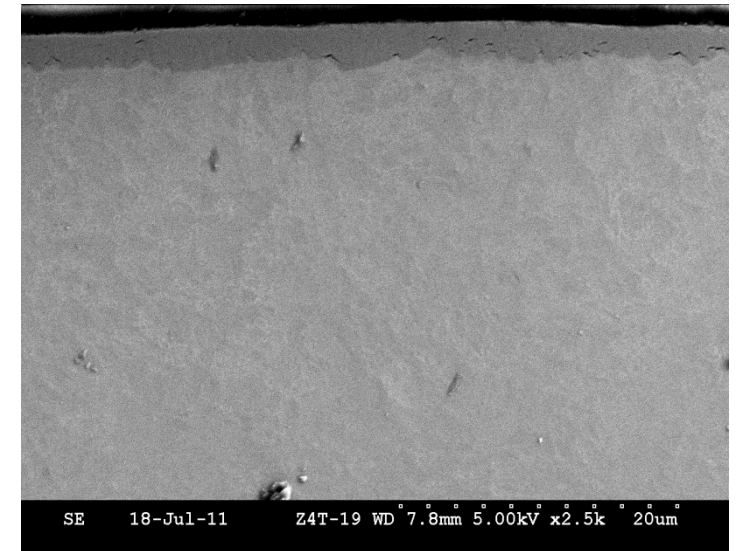
Corrosion Control

- 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 the 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
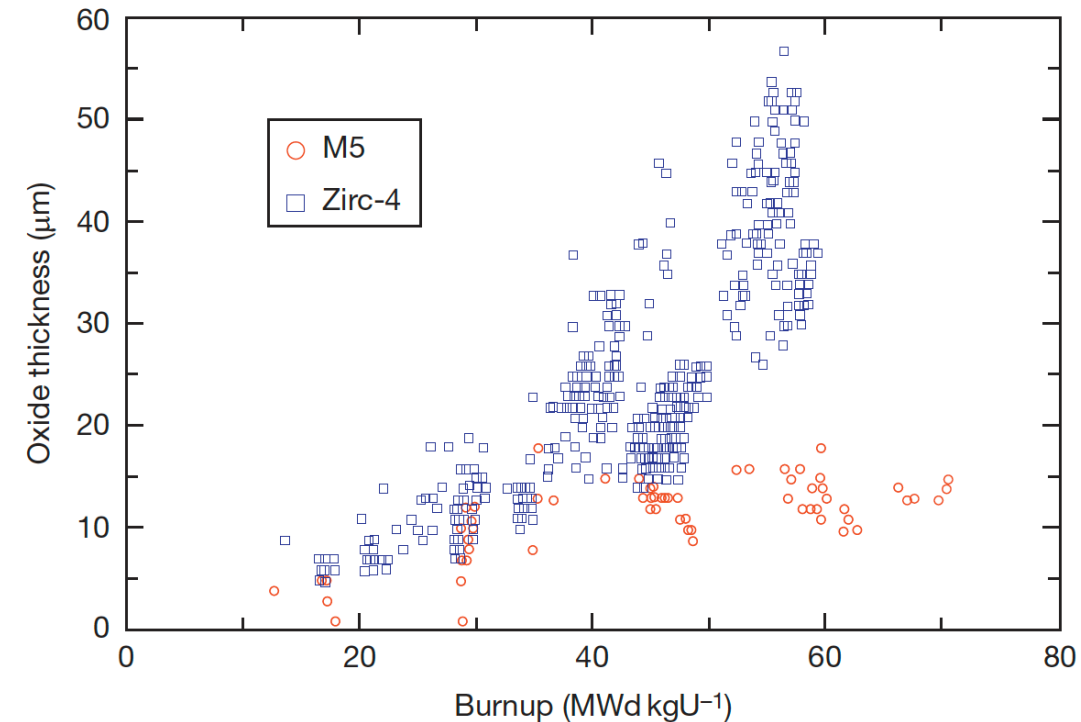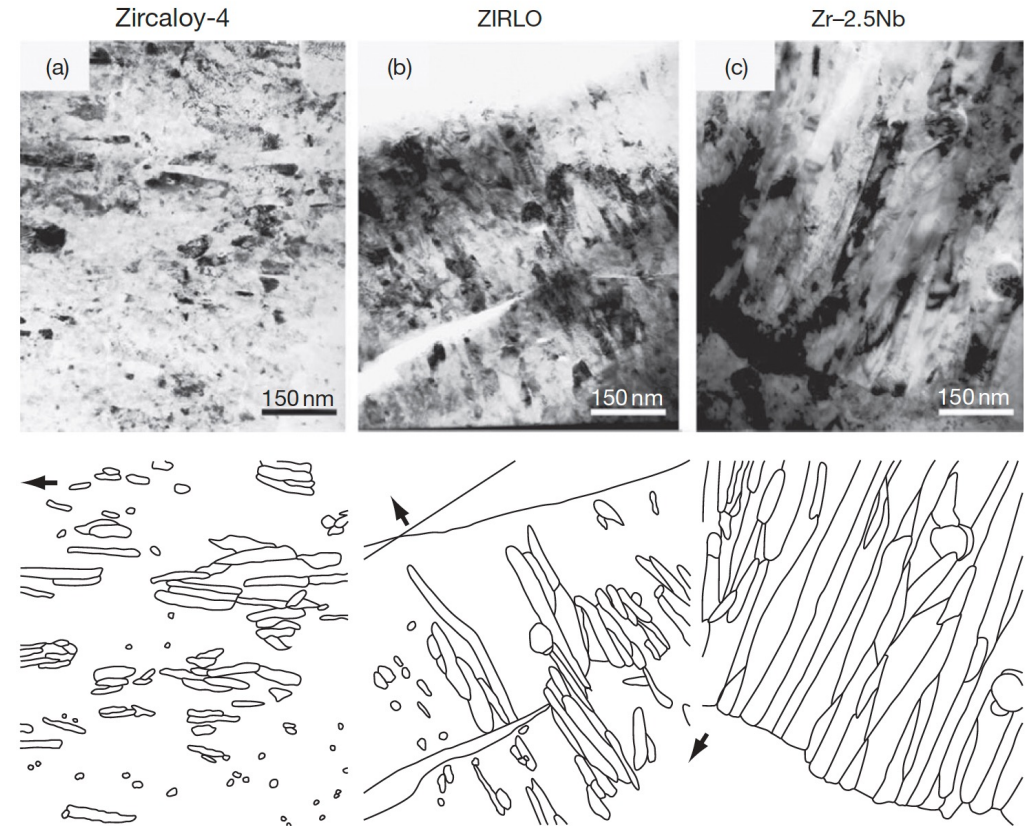
Corrosion Control

- 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
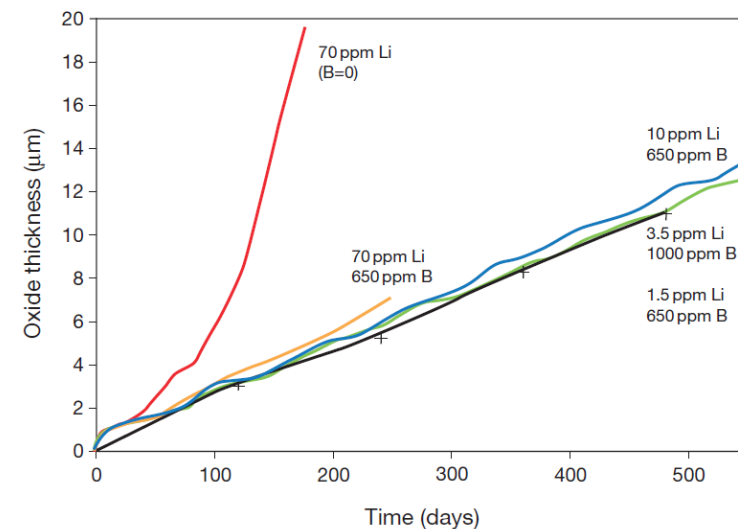
Corrosion Layer

- 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 as well can increase the amount available to form hydrides, but this is minor
- The fraction of the produced hydrogen that enters the cladding is defined by the pickup fraction:

$$f_H = \frac{H_{absorbed}}{H_{generated}}$$

- Hydrogen is produced twice as fast as oxygen
  - $J_H = 2 f J_O$

ZrO$_2$

Zr metal

Hydrogen pick-up

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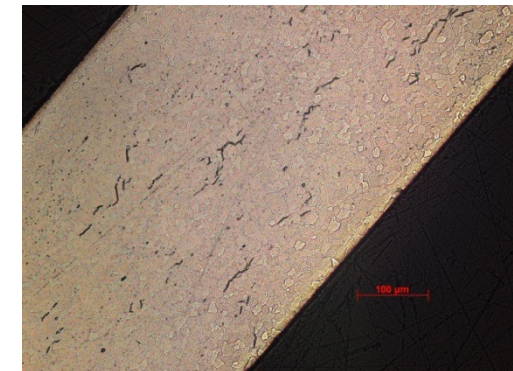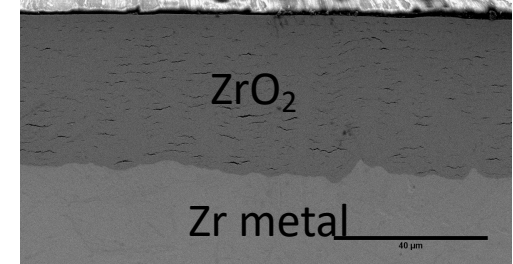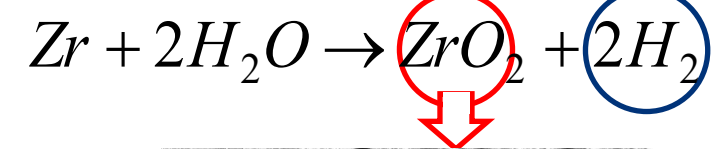
Given a thickness of oxide, how can we predict the hydrogen pickup?

- A cladding with an initial thickness of 600 microns that initially has 40 wt. ppm H undergoes corrosion to a total oxide thickness of 80 microns. What is the overall hydrogen content in wt. ppm if the hydrogen pickup fraction is 15%?
- First, we must determine the weight of H that has entered the cladding
  - ρ_{ZrO2} is 5.68 g/cm^3, of which 32/(91+32)= 0.26 = 26% is O, thus 1.47 g/cm^3 of O
  - A 1 micron oxide layer corresponds to a weight gain of 14.7 mg/dm^2 and thus with an 80 micron layer, weight gain = 14.7*80 = 1176 mg/dm^2
  - This mass corresponds to 1.176 N_A/16 atoms of oxygen = 4.42 x 10^{22} atoms/dm^2
  - f = 15%, so the ingress of hydrogen will be 0.15*2*4.42e22 = 1.33e22 atoms of hydrogen/dm^2, or 0.022 g of H.
- Now, we determine the fraction in wt. ppm in a 10 cm square cross section w/ PBR = 1.56
  - The uncorroded thickness is 600 – 80/PBR = 600 – 80/1.56=549 microns
  - The volume of zirconium is 549 x 10^{-4} (cm)*10*10 =5.49 cm^3
  - ρ_{Zr} = 6.5 g/cm^3, so the total mass of Zr is 6.5*5.49 =35.7 g.
- Thus the hydrogen concentration is 0.022/35.7 =6.18e-4= 618 wt. ppm, which, added to the original 40 wt. ppm, is 658 wt. ppm

We can estimate the hydrogen content in the cladding from the oxide thickness *δ* and the pickup fraction *f*

$$C_H^{clad}[wt.ppm] = \frac{m_H}{m_{Zr}} = \frac{2fm_O}{m_{Zr}} = \frac{2f \times \delta \times \rho_{oxide} \times f_{ZrO_2}^{O} \times M_H/M_O}{\left(t - \dfrac{\delta}{PBR}\right) \times \rho_{metal}} x10^6$$

C_H^{clad} concentration (wt ppm)

ρ_{oxide} oxide density

ρ_{Zr} Zr metal density

$f_{ZrO_2}^{O}$ Fraction of oxygen in ZrO2 mass

PBR Pilling-Bedworth Ratio

M_H moelcular mass of H

M_O molecular mass of O

t cladding thickness

# Hydrogen Diffusion

- The diffusion coefficient of H in Zr is

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

$$E_m^H = 0.47 eV \qquad D_o^H = 7x10^{-3} cm^2 / s$$

- 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
- 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
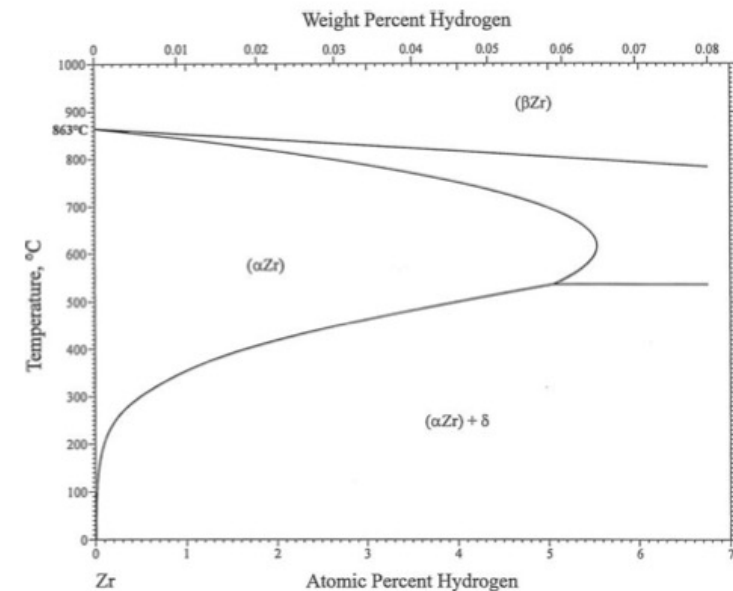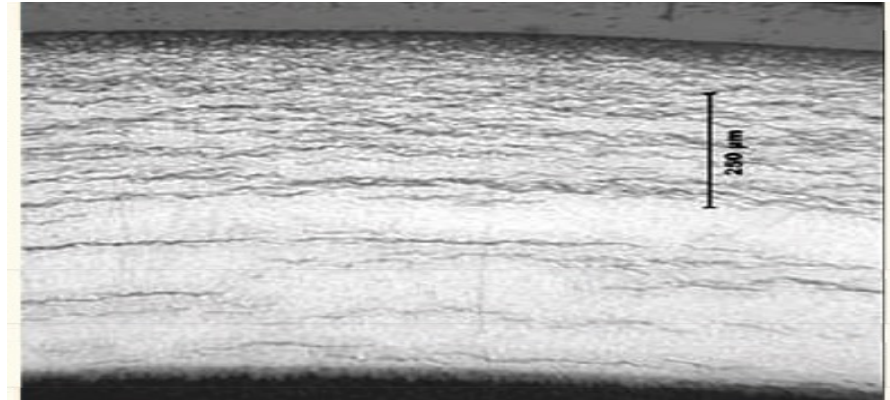
Effect of Hydrides

- 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

- Blisters have an elliptic shape, are more localized on the tube external surface and are deeper, usually covering half of the cladding thickness
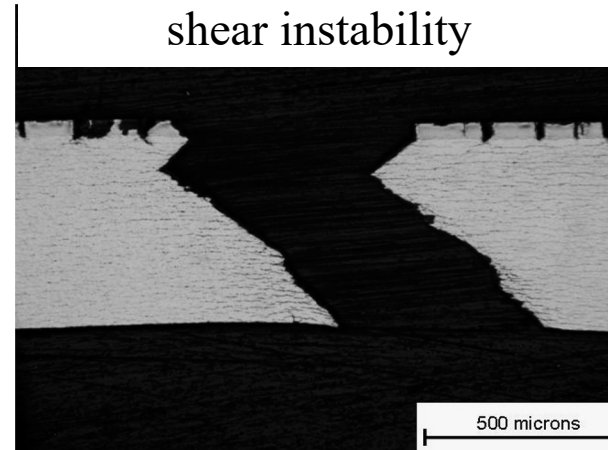
Hydrided Zircaloy-4
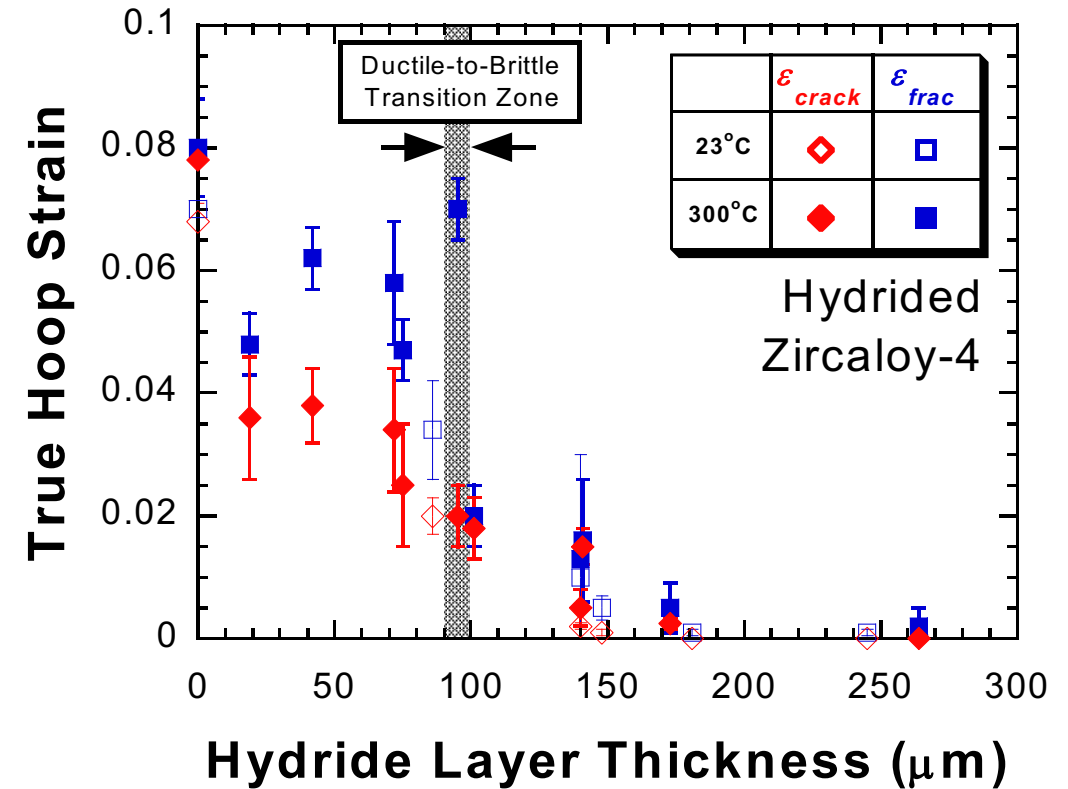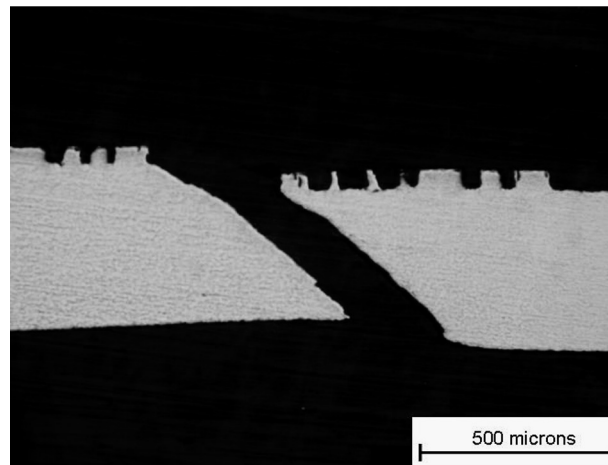
Blister failure examples

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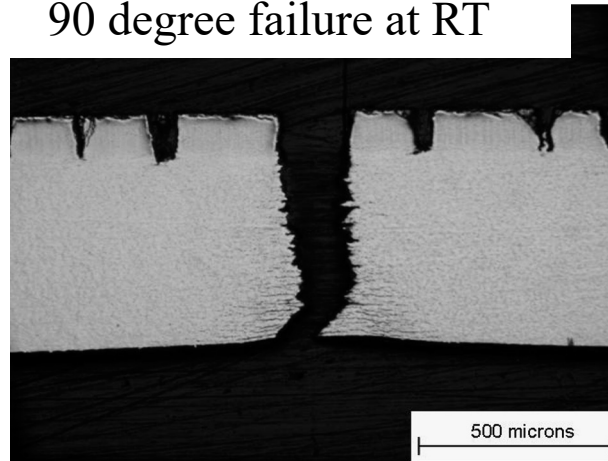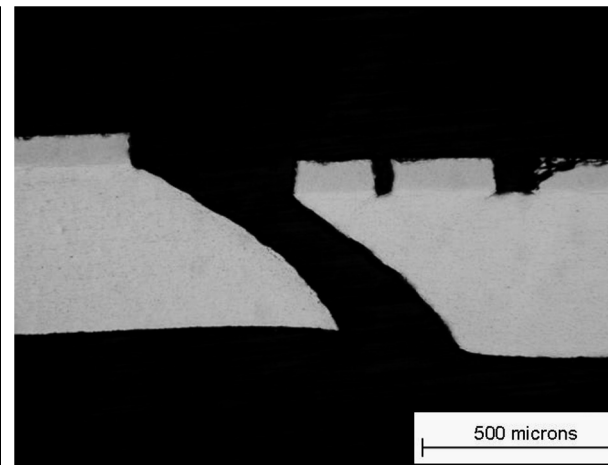
But in small blisters => shear instability

93 µm Blister Broken at 25 °C M020

40 µm Blister Broken at 25 °C M014

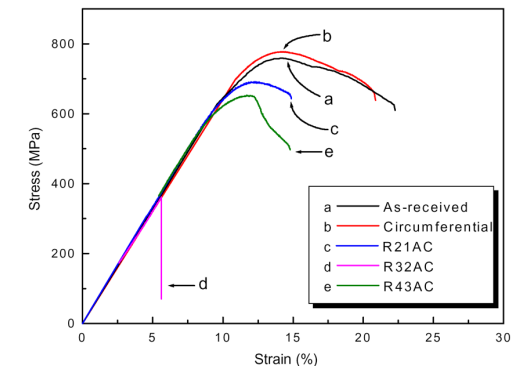53 µm Blister Broken at 300 °C M025

83 µm Blister Broken at 300 °C M023

At 300 C, 45 degree shear

Circumferential vs Radial Hydrides

- Under reactor conditions, hydride platelets precipitate circumferentially
- In used fuel after drying, the hydrides can reprecipitate with a radial orientation
- The hydrides reform in a radial direction due to the tensile hoop stress
- Radial hydrides provide easy crack paths and significantly decrease the ductility of the cladding

Delayed Hydride Cracking

- The theory of DHS is that the crack tip hydride grows as hydrogen migrates from hydrides in the bulk of the material to the crack tip
- The driving force for the diffusion of the hydrogen is the difference in the chemical potential of hydrogen between the bulk material and the crack tip hydride in response to hydrostatic stress
- An increasing hydrostatic tensile stress reduces the chemical potential of hydrogen in the hydride relative to the bulk
- This chemical potential difference causes hydrogen in solution to diffuse to the crack tip where it precipitates

Hydrides Summary

- Hydrogen released by oxidation enters the cladding
- It quickly diffuses throughout the cladding, but prefers low temperature
- Due to low solubility (that is a function of temperature), hydrides form
- Hydrides are brittle, and so reduce the ductility of the cladding
- Radial hydrides can form in used fuel after drying, and reduce the ductility much more than circumferential hydrides
- DHC is a phenomenon based upon increased solubility of hydrides in the high tensile stress around a crack tip