

Cladding Oxidation

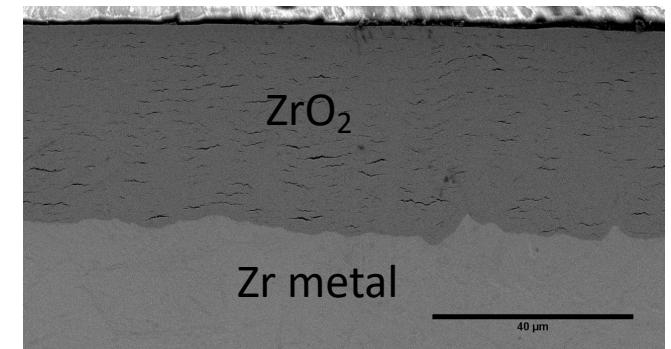
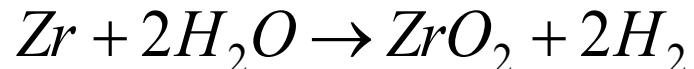
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Last time

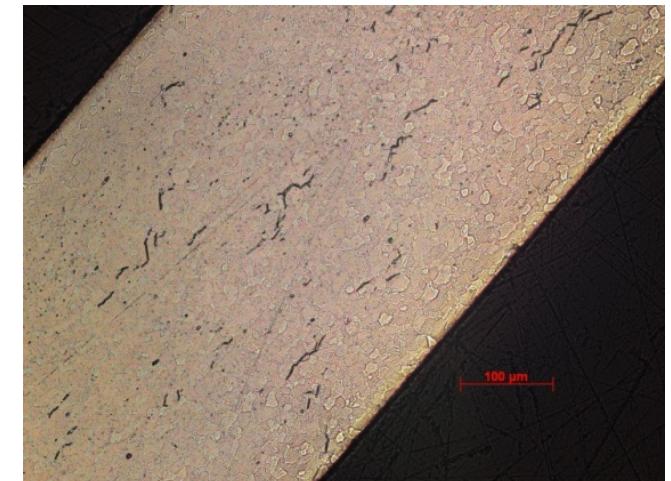
- Growth and creep are the major mechanisms for dimensional instability in zirconium alloy cladding
- Growth results from the clustering of interstitials on prismatic planes
- Creep occurs in three stages: (1) creep down from water pressure; (2) creep out from fuel column; (3) fuel column axial stress
- Under irradiation, zirconium experiences irradiation induced hardening due to interstitial loops
- Dislocation channels form that don't have loops, resulting in localized deformation
- Other phenomena:
 - Fatigue; SCC; PCMI; PCCI

Zirconium Oxidation

- Corrosion of zirconium is one of the largest concerns for LWR fuel operation



- Zirconium interacts with water to make zirconia and hydrogen
- Both the oxide layer and the hydrogen adversely impact cladding performance



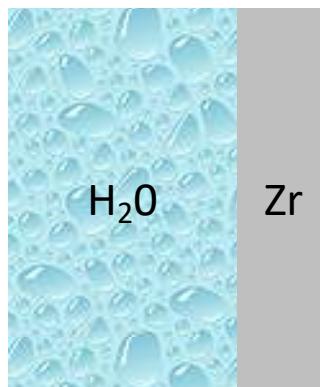
Corrosion

- 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 $Zr + 2H_2O \rightarrow ZrO_2 + 2H_2$
 - Electric current
- 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

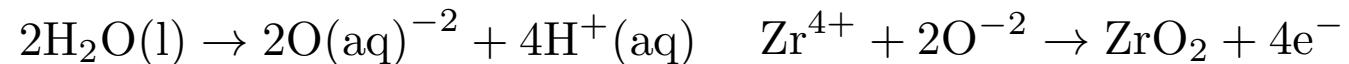
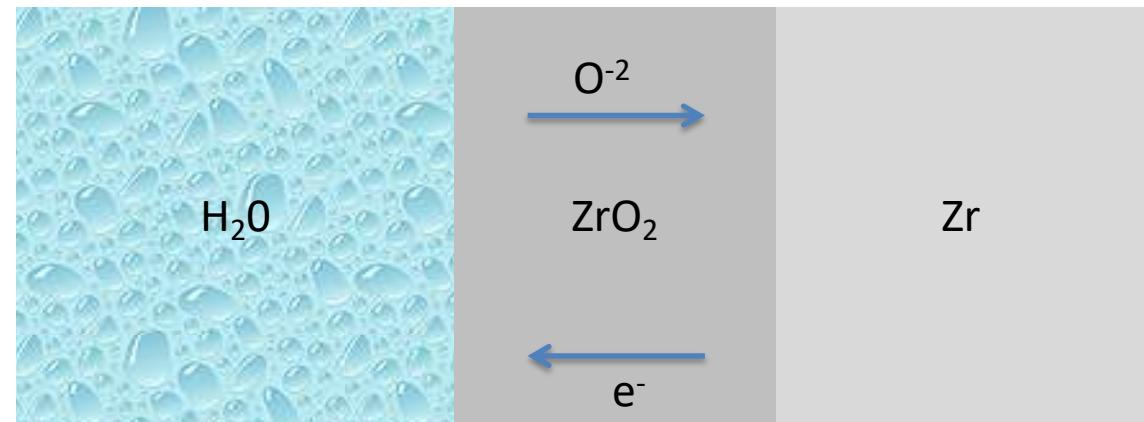
Corrosion

- 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

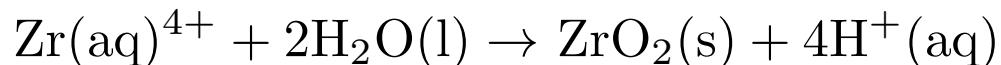
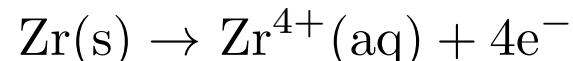
Formation of Oxide Layer



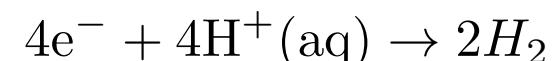
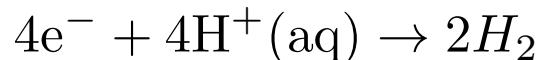
After Oxide Formation



Oxidation reaction:



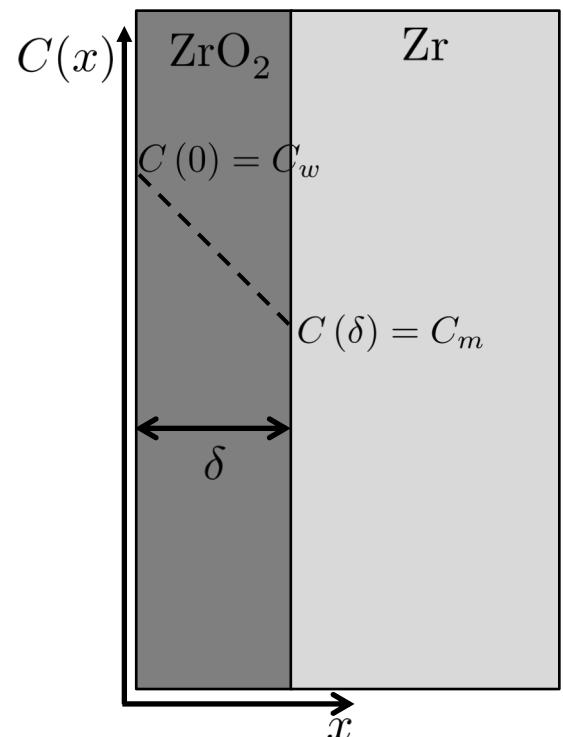
Reduction reaction:



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

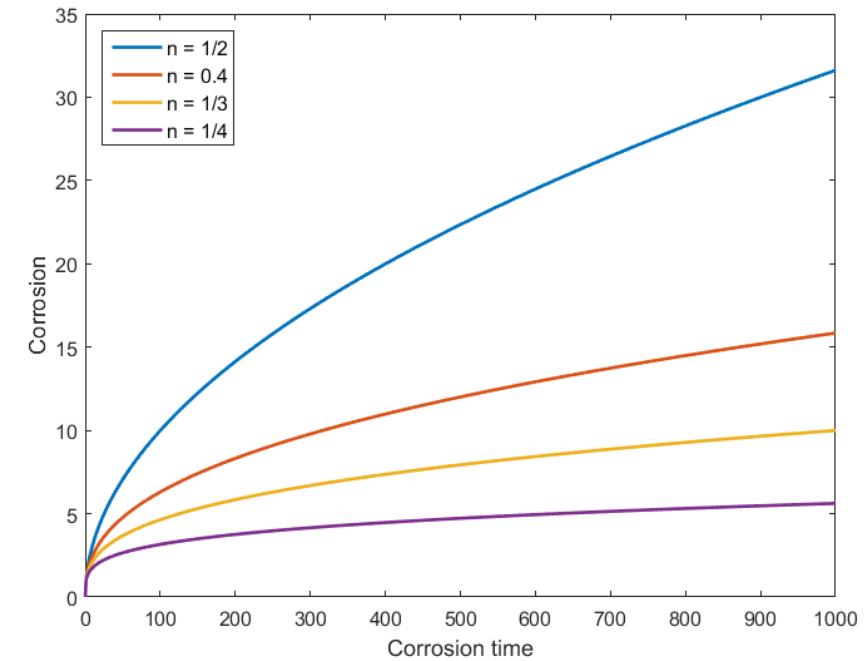
- Because the rate limiting steps are diffusion, we can model the oxidation rate using diffusion
- Assumptions:
 - Transport of O species is rate-limiting
 - Transport of charged species by diffusion only
 - Homogeneous oxide layer
 - No sources/sinks of ions in oxide
 - All oxygen is used to create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

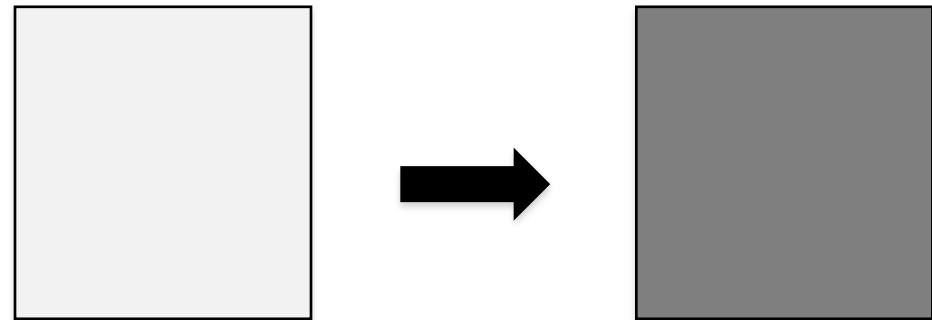


Corrosion Quantified

- Corrosion is measured by sample weight gain
- Oxidation of alloys is measured experimentally using the weight gain in mg/dm^2
- Oxide forms by incorporating oxygen in the metal structure causing an increase in weight

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

Dividing by the surface enables comparison between samples



Original coupon:
Weight m_1
Surface S

corroded coupon:
Weight $m_2 > m_1$
Surface S

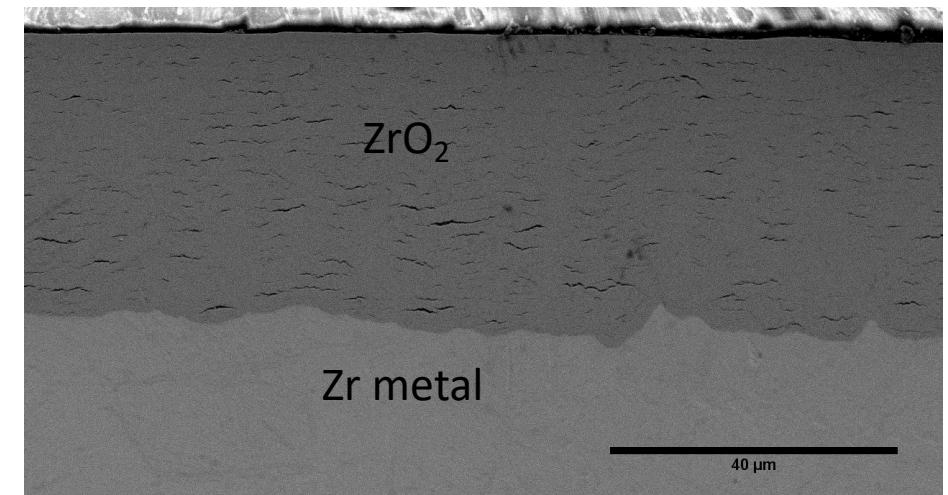
Approximation weight gain – oxide thickness for Zr:

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

Pilling-Bedworth ratio : PBR

- The ratio of oxide thickness to metal thickness is called the Pilling-Bedworth ratio (PBR)
- $\text{PBR} < 1$: the oxide coating layer is thin, likely broken and provides no protective effect (for example magnesium)
- $\text{PBR} > 2$: the oxide coating chips off and provides no protective effect (example iron)
- $1 < \text{PBR} < 2$: 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

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

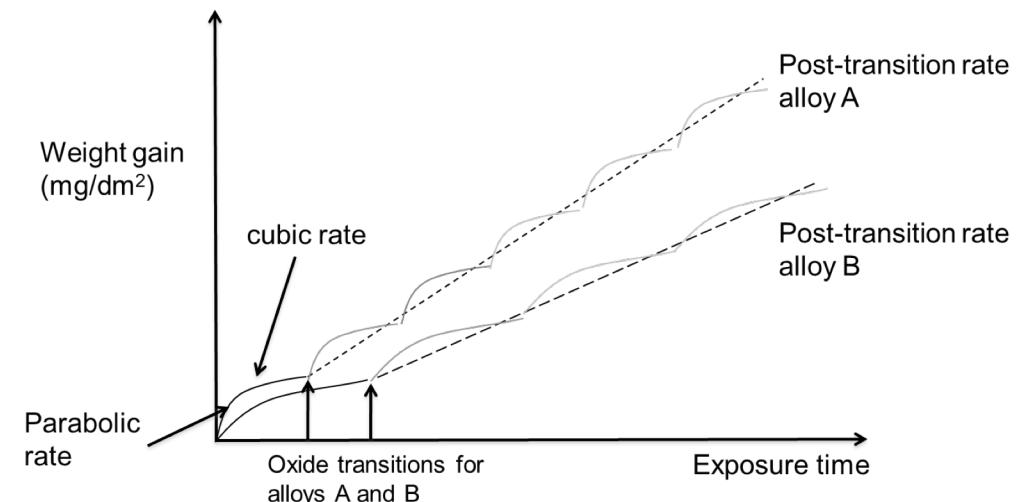


Example

- 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
 - $S = 0.28 \times 0.28 \text{ dm}^2$
 - $dM = 300 \text{ mg} - 307.21 \text{ mg}$
- Then we calculate the weight gain per area
 - $W = dM/S = (307.21 - 300)/0.28^2 = 91.96 \text{ mg/dm}^2$
- Last estimate the thickness
 - $d = W/14.7 = 91.96/14.7 = 6.3 \text{ microns thick after 200 days}$

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 $\delta^* \text{ } (\mu\text{m}) = 5.1 \exp \frac{-550}{T}$
- Critical time for transition is defined as $t^* \text{ (d)} = 6.62 \times 10^{-7} \exp \frac{11949}{T}$



After transition, oxide thickness is

$$\delta \text{ } (\mu\text{m}) = \delta^* + K_L (t - t^*)$$

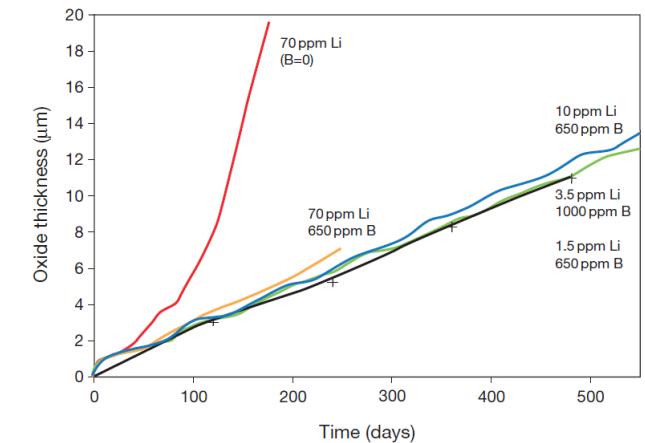
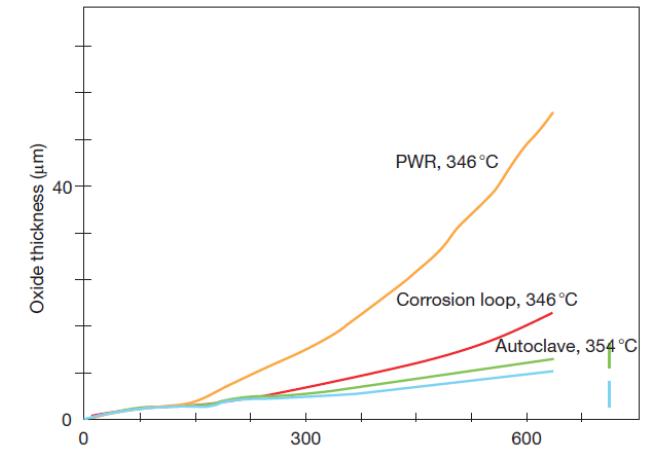
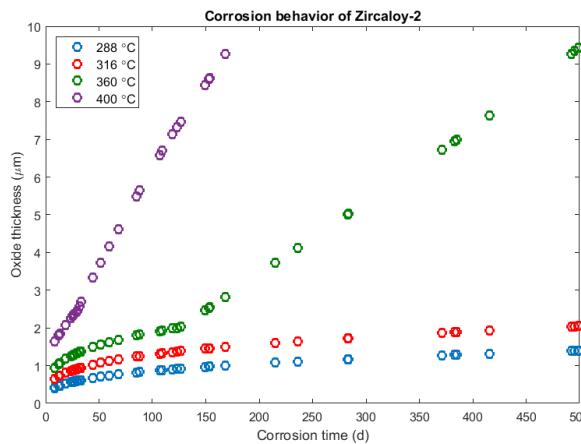
$$K_L \left(\frac{\mu\text{m}}{\text{d}} \right) = 7.48 \times 10^6 \exp \frac{-12500}{T}$$

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
 - $t^* \text{ (d)} = 6.62 \times 10^{-7} \exp \frac{11949}{T}$
 - $t^* = 6.62e-7 \exp(11949/650) \text{ k} = 63.76 \text{ days}$
 - So, the sample is past transition, so we need to use the linear fit
- Next, we calculate the oxide thickness at transition
 - $\delta^* \text{ (\mu m)} = 5.1 \exp \frac{-550}{T}$
 - $\delta^* = 5.1 \exp(-550/650) = 2.19 \text{ microns}$
- Now, we can compute the final oxide thickness
 - $K_L \left(\frac{\mu\text{m}}{\text{d}} \right) = 7.48 \times 10^6 \exp \frac{-12500}{T}$
 - $K_L = 7.48e6 \exp(-12500/650) = 0.0333$
 - $\delta \text{ (\mu m)} = \delta^* + K_L (t - t^*)$
 - $\delta = 2.19 + 0.0333 * (200 - 63.76) = 6.73 \text{ microns}$

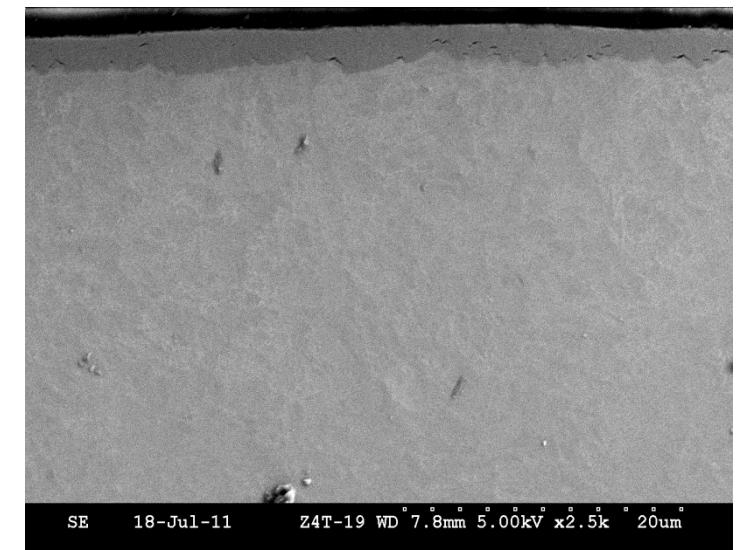
Other factors affecting corrosion

- Irradiation: Radiation damage to the metal;
Radiation damage to oxide
- Water chemistry: Coolant additions are
added to control neutronics, corrosion, and
hydrogen pick-up
- Temperature:
 - Corrosion rate increases
with temperature



Impact of Corrosion

- The oxide layer has a low thermal conductivity, restricting heat transport
 - For Zircaloy, $k = 22 \text{ W}/(\text{mK})$
 - For ZrO_2 , $k = 1.7 - 2.7 \text{ W}/(\text{mK})$
- 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



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

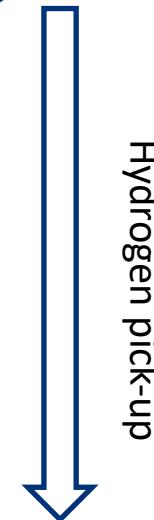
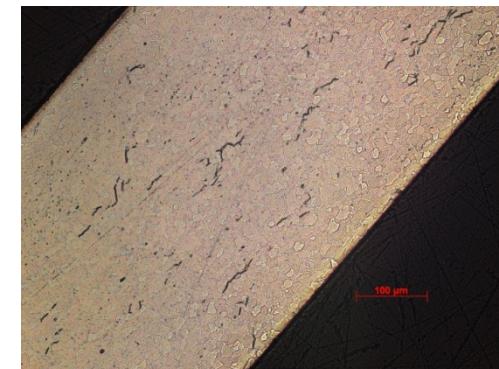
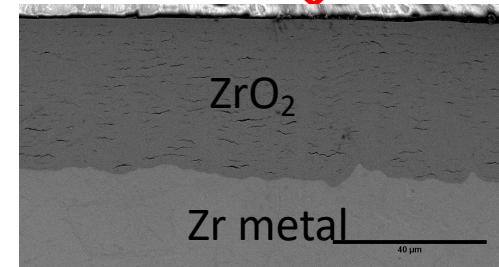
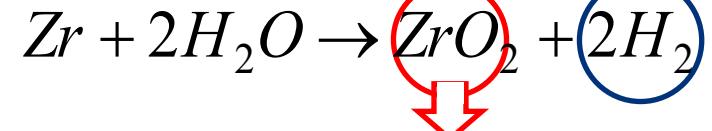
Hydride Formation

- Corrosion of zirconium 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
- 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
 - $J_H = 2 f J_O$

Corrosion reaction:



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_{ZrO_2} is 5.68 g/cm³, of which $32/(91+32) = 0.26 = 26\%$ is O, thus 1.47 g/cm³ of O
 - A 1 micron oxide layer corresponds to a weight gain of 14.7 mg/dm² and thus with an 80 micron layer, weight gain = $14.7 \times 80 = 1176 \text{ mg/dm}^2$
 - This mass corresponds to $1.176 N_A / 16$ atoms of oxygen = $4.42 \times 10^{22} \text{ atoms/dm}^2$
 - $f = 15\%$, so the ingress of hydrogen will be $0.15 \times 2 \times 4.42 \times 10^{22} = 1.33 \times 10^{22} \text{ atoms of hydrogen/dm}^2$, 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 $600 - 80/\text{PBR} = 600 - 80/1.56 = 549 \text{ microns}$
 - The volume of zirconium is $549 \times 10^{-4} (\text{cm})^3 \times 10 \times 10 = 5.49 \text{ cm}^3$
 - $\rho_{\text{Zr}} = 6.5 \text{ g/cm}^3$, so the total mass of Zr is $6.5 \times 5.49 = 35.7 \text{ g}$.
 - Thus the hydrogen concentration is $0.022/35.7 = 6.18 \times 10^{-4} = 618 \text{ wt. ppm}$, 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

$$C_H^{clad} [\text{wt.ppm}] = \frac{m_H}{m_{Zr}} = \frac{2fm_O}{m_{Zr}} = \frac{2f \times \delta \times \rho_{oxide} \times f_{ZrO_2}^O \times M_H / M_O}{\left(t - \frac{\delta}{PBR} \right) \times \rho_{metal}} \times 10^6$$

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

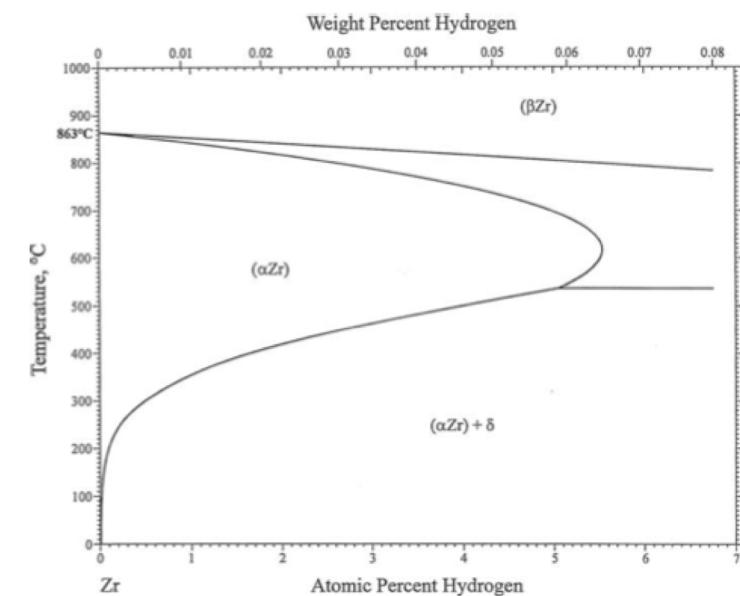
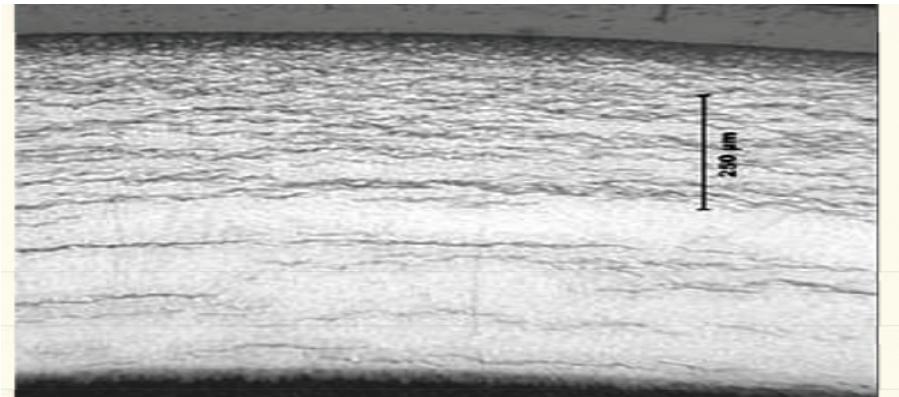
t cladding thickness

Hydrogen Diffusion

- The diffusion coefficient of H in Zr is $D_{Zr}^H = D_o^H \exp(-E_m^H / k_B T)$
 $E_m^H = 0.47 eV$ $D_o^H = 7 \times 10^{-3} \text{ cm}^2 / \text{s}$
- 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?
 - $D_{Zr}^H = 7 \times 10^{-3} \times \exp(-0.47 / (k_B * (355 + 273.15))) = 1.19 \times 10^{-6} \text{ cm}^2/\text{s}$,
 - $t = 0.06^2 / (4 * 1.19 \times 10^{-6}) \text{ cm}^2/\text{s} = 756.3 \text{ s} = 12 \text{ min}$,
 - So, the hydrogen atoms have plenty of time to move through the entire clad

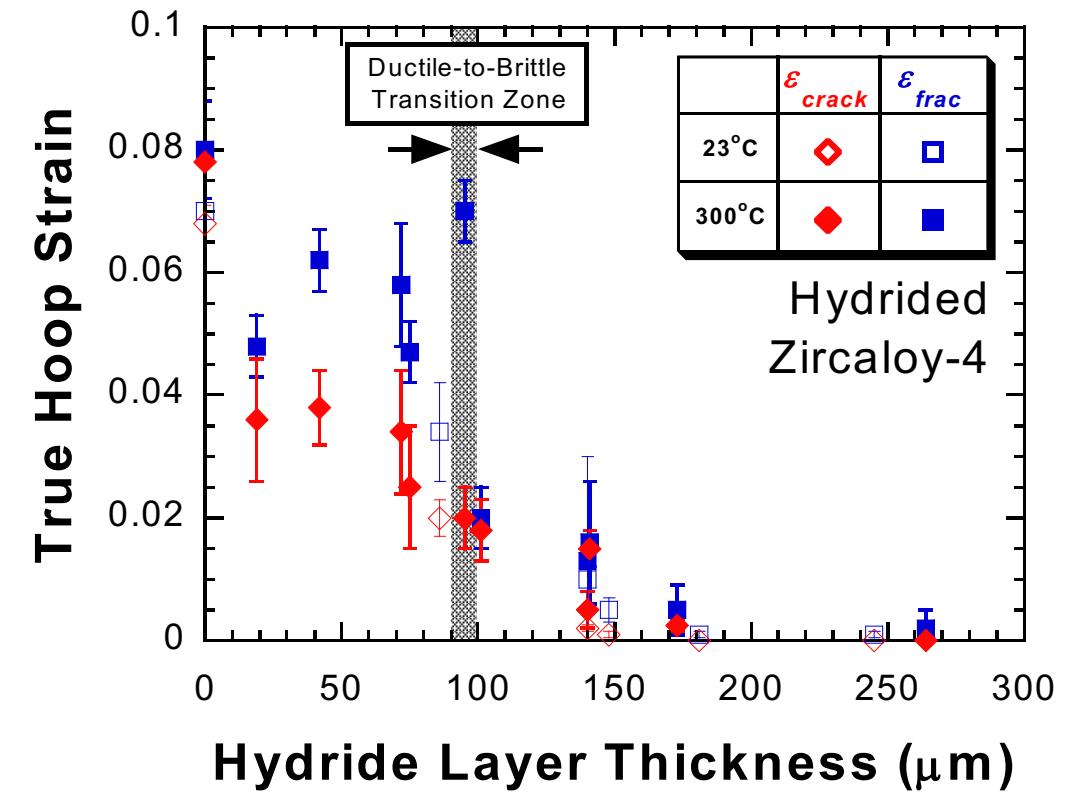
Hydriding

- 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



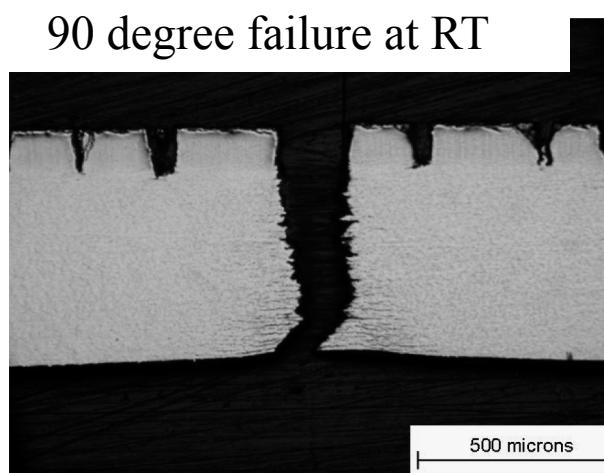
Effect of Hydrides

- 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

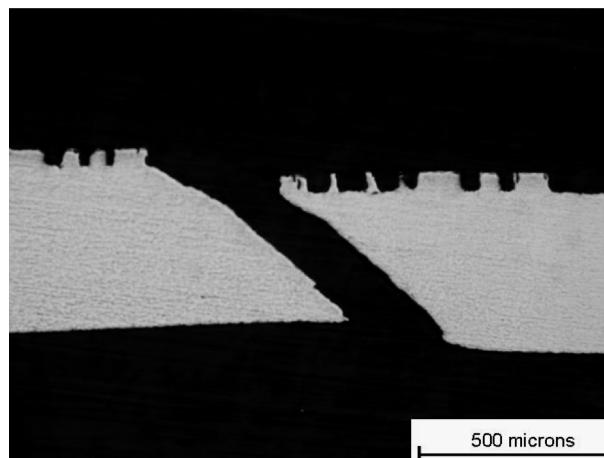


Blister failure examples

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

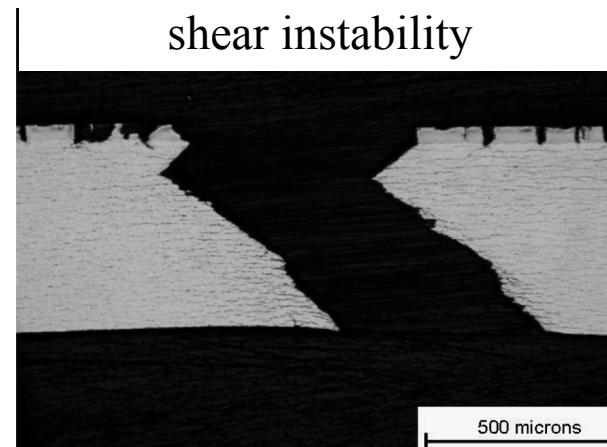


**53 µm Blister
Broken at 300 °C
M025**

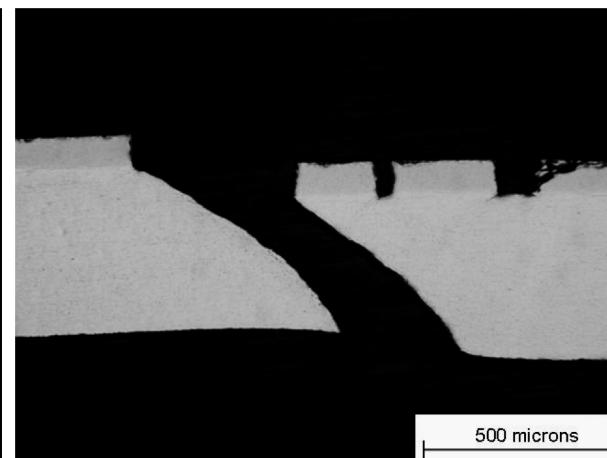


But in small blisters =>
shear instability

**40 µm Blister
Broken at 25 °C
M014**



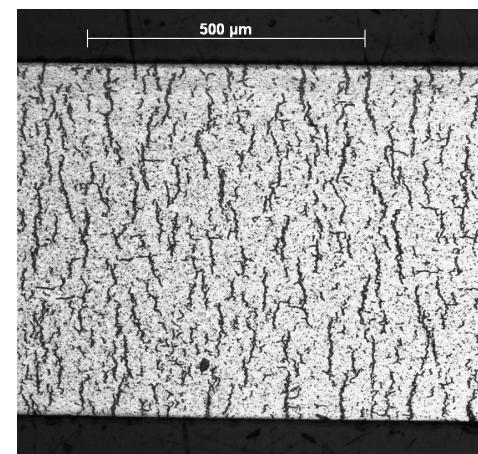
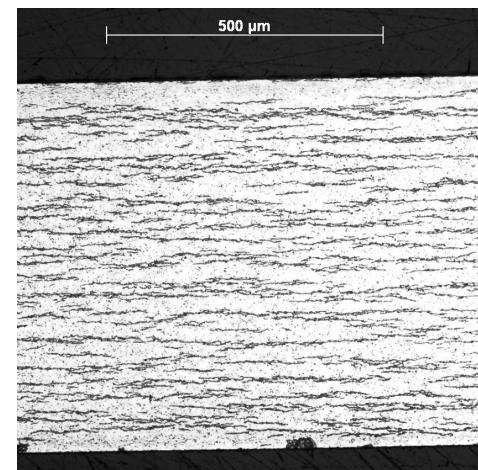
**83 µm Blister
Broken at 300 °C
M023**



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

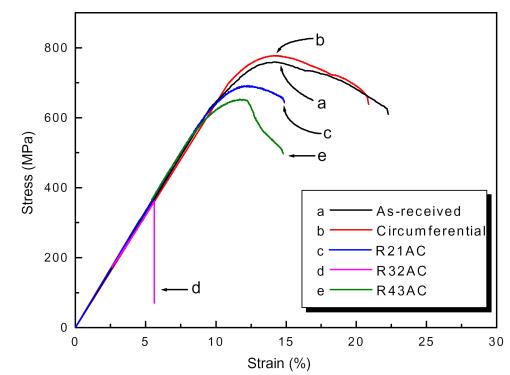


25 °C



At Yield Load

100 Microns



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