PennState College of Engineering

NucE 497: Reactor Fuel Performance

Lecture 33: Hydride formation

April 3rd, 2017

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Most material taken from slides by Processor Motta

Today we will discuss hydride formation in the cladding

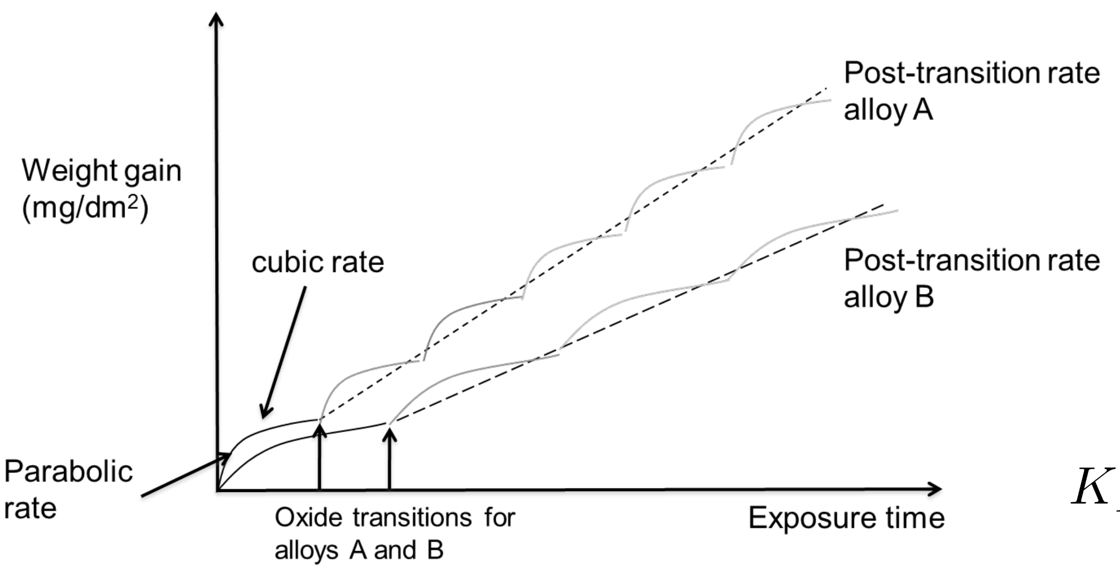
- Module 1: Fuel basics
- Module 2: Heat transport
- Module 3: Mechanical behavior
- Module 4: Materials issues in the fuel
- Module 5: Materials issues in the cladding
    - Zirconium alloys and fabrication
    - Cladding creep and growth
    - Mechanical behavior
    - **Oxidation**
    - **Hydride formation**
    - CRUD formation
- Module 6: Accidents, used fuel, and fuel cycle

Here is some review from last time

- Which step of oxidation is the slowest (the rate limiting step)
  a) Dissolution of water
  b) Transport of the oxygen atoms through the oxide layer
  c) Reaction of O ions with Zr to form ZrO_2
  d) Reduction of hydrogen ions by electrons at coolant
- What is NOT a negative effect of oxidation on cladding performance
  a) Creates hydrogen atoms that form brittle hydrides
  b) Reduces the thermal conductivity
  c) Replaces metal with a brittle oxide
  d) Reduces fission rate by absorbing neutrons

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

$$\delta^\star\,(\mu\mathrm{m}) = 5.1 \exp\frac{-550}{T}$$

Critical time for transition is defined as

$$t^\star\,(\mathrm{d}) = 6.62\times10^{-7}\exp\frac{11949}{T}$$

After transition, oxide thickness is

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

$$K_L\left(\frac{\mu\mathrm{m}}{\mathrm{d}}\right) = 7.48\times10^{6}\exp\frac{-12500}{T}$$

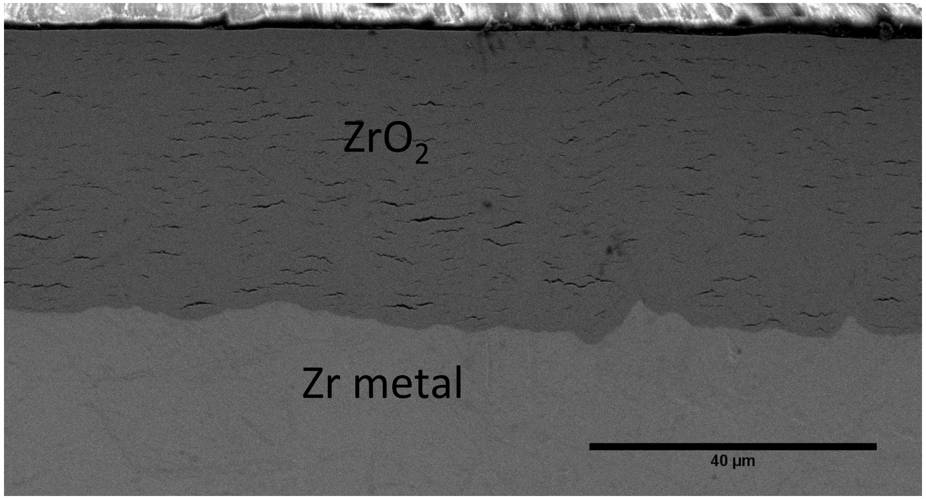
* Constants given apply to ZIRLO

Now let's work a problem

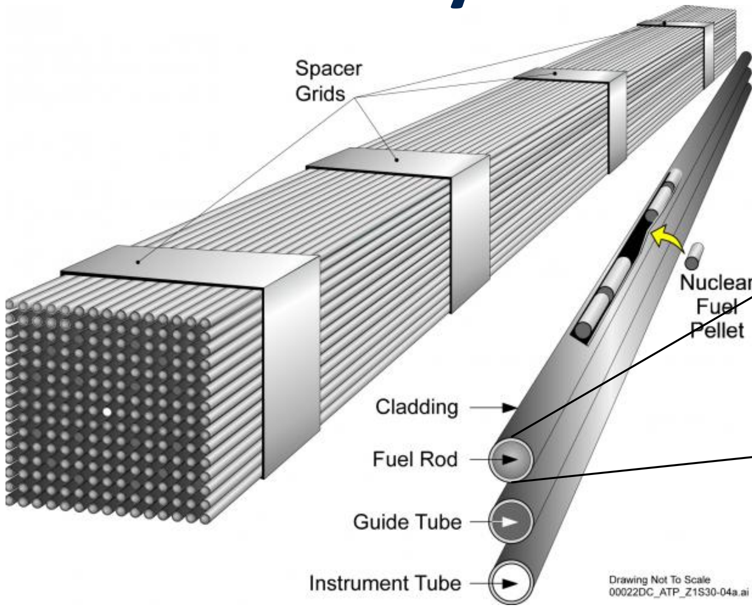
- Estimate the oxide thickness on a ZIRLO sample at 650 K after 200 days exposed to water.
- First, we have to determine if the oxide has gone through transition
  - $t^\star\,(\mathrm{d}) = 6.62\times 10^{-7}\exp\frac{11949}{T}$
  - t* = 6.62e-7*exp(11949/650 k) = 63.76 days
  - So, the sample is past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

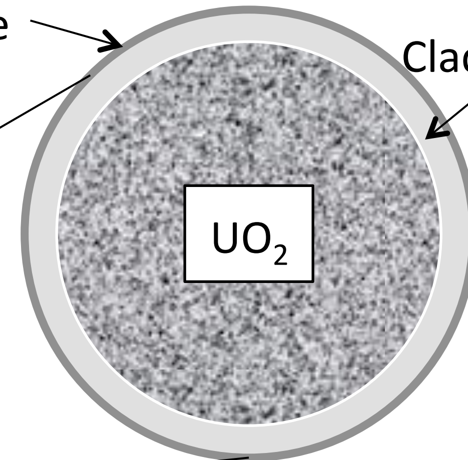
Note that the thickness of ZrO2 is wider than the corresponding thickness of Zr

- The ratio of oxide thickness to metal thickness is called the Pilling-Bedford ratio (PBR)
  - PBR = 1.56



Corrosion of zirconium so damaging in large part due to hydride formation

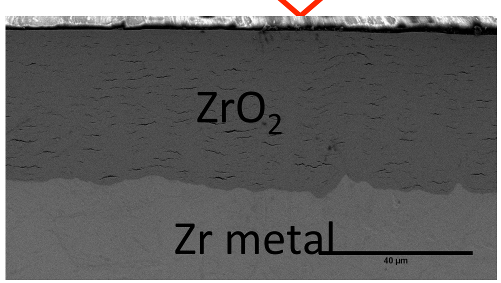


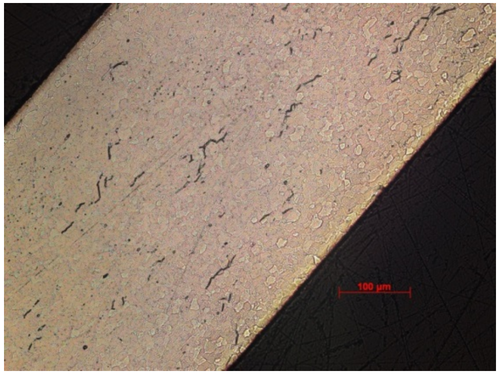


Corrosion reaction:

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

Hydrogen pick-up





Some of the hydrogen atoms produced by oxidation enter the cladding and form a hydride phase

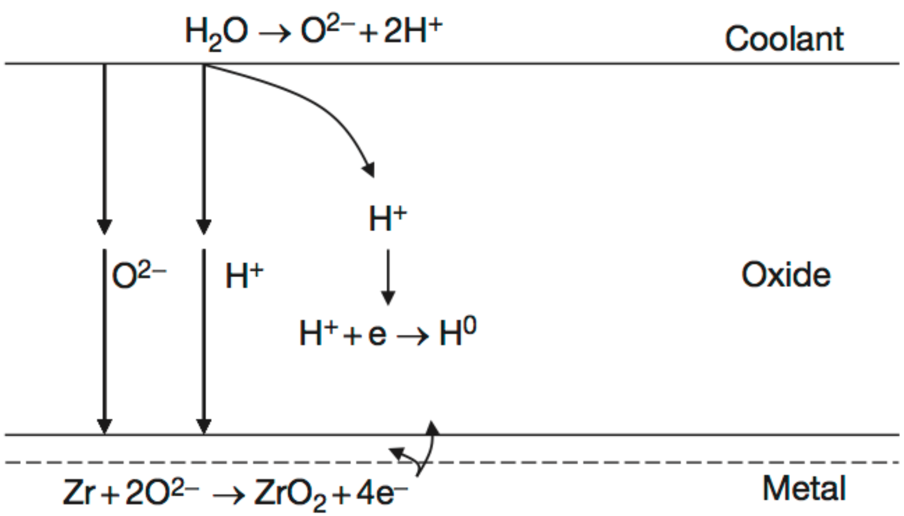


Figure 1 Schematic presentation of the corrosion of the zirconium alloys. Corrosion of zirconium alloys in nuclear power plants; TECDOC-684; International Atomic Energy Agency, Vienna, Austria, Jan 1993.

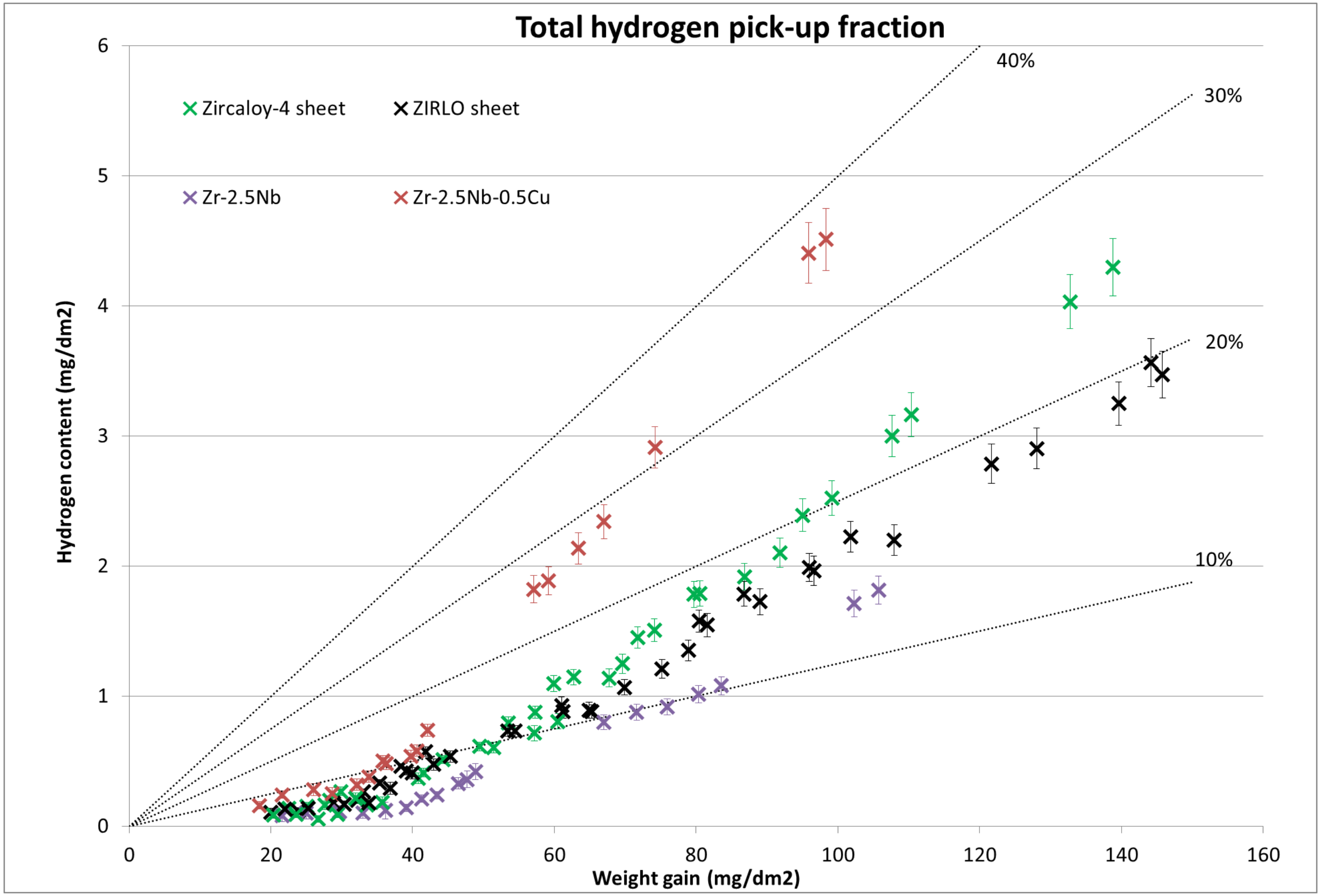
Taken from *Allen et al., Comprehensive Nuclear Materials (2012), 5, 49-68.*

- 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
  - $J_H = 2 f J_O$

Normally Hydrogen pickup fraction is assumed constant but really it is not



f = 15% is a commonly used value

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
  - δ_{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 (see previous lecture), 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
  - 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
  - δ_{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

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

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

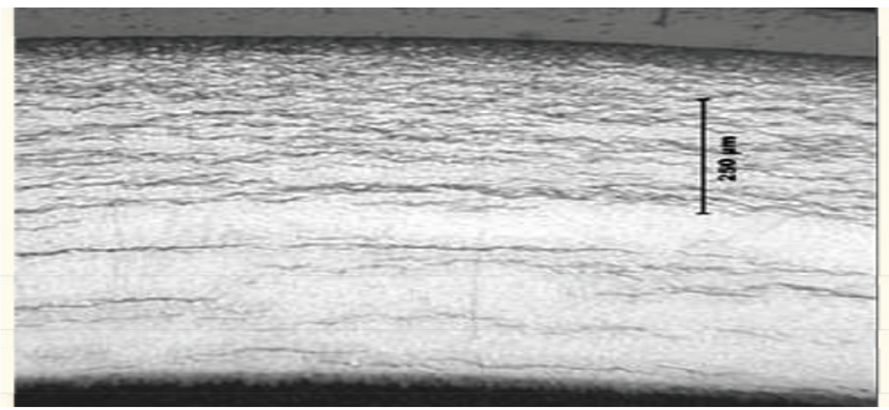
t cladding thickness

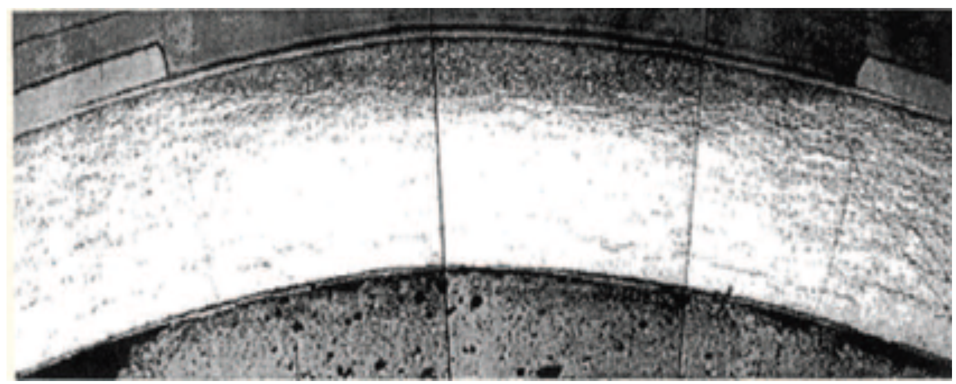
Hydrogen diffuses very quickly in zirconium, so that the hydrogen quickly spreads through the cladding

- 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} = 7e-3*exp(-0.47/(kb*(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 hydrogren atoms have plenty of time to move through the entire clad

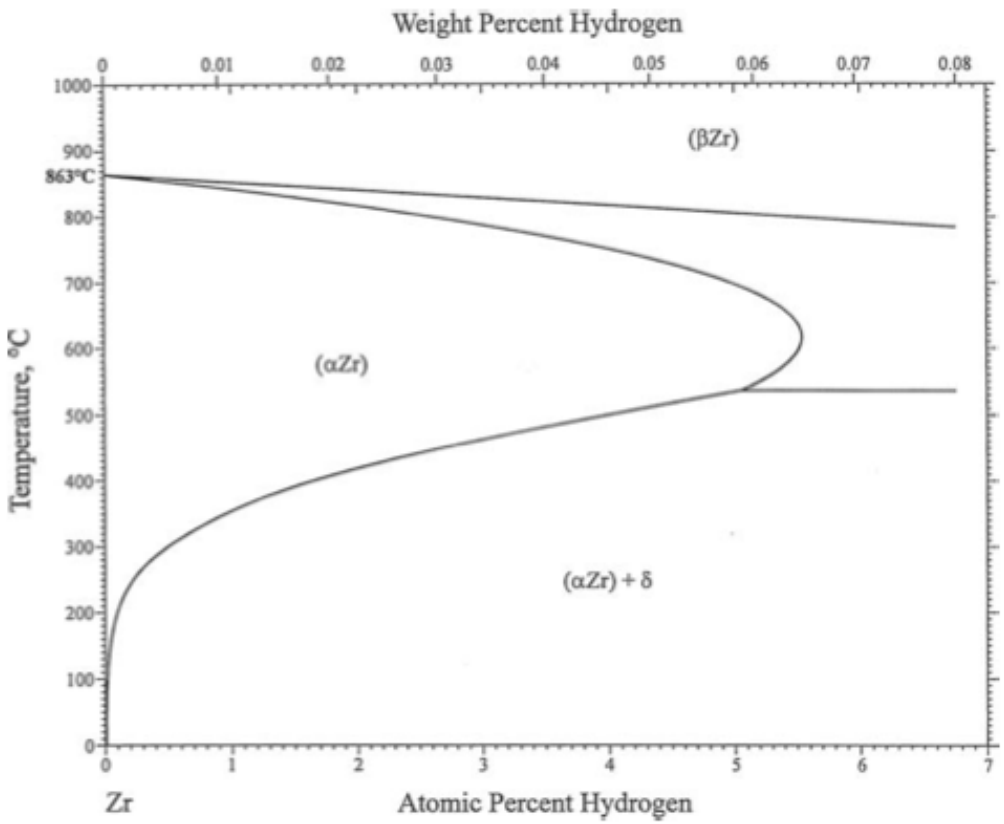
Hydride concentrations are not uniform, because they respond to temperature and stress gradients

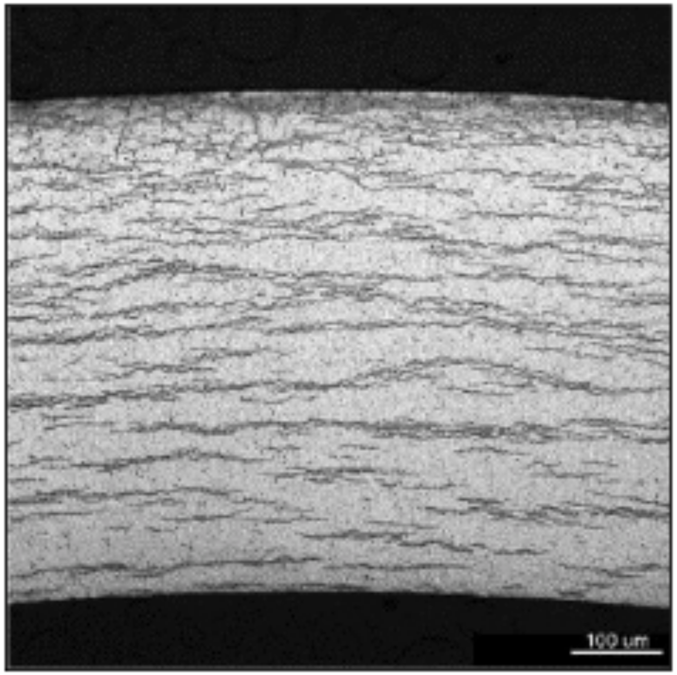
- Hydrogen tends to move toward lower temperature (Soret effect)
- It also moves to areas with tensile stress
- Where in the cladding has the lowest temperature?





Hydrogen has a low solubility in zirconium, so even small hydrogen concentrations result in hydrides

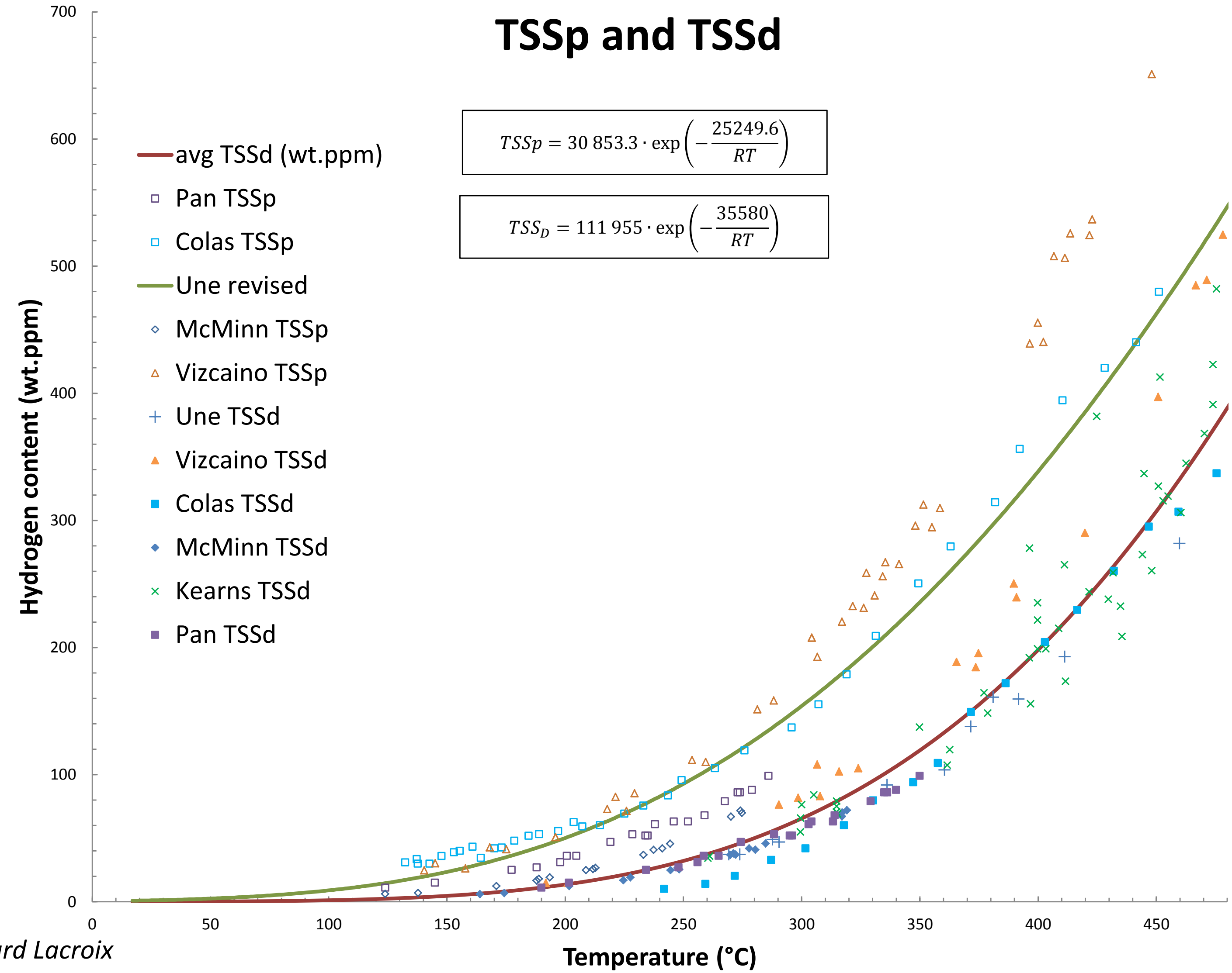




Hydrided fuel cladding

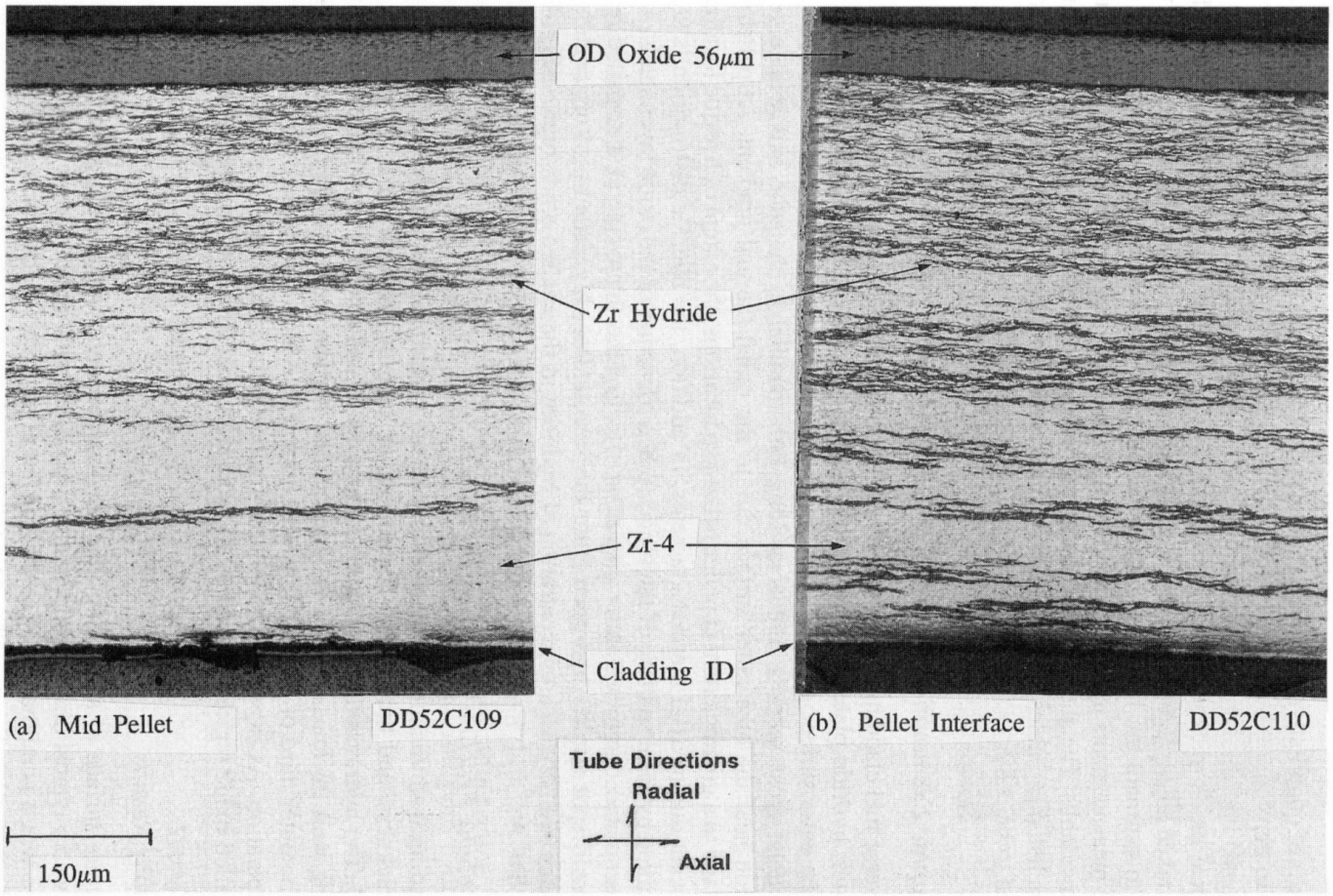
Daum et al. Penn State 2007

Hydrides dissolve during heating at a lower temperature than they precipitate during cooling



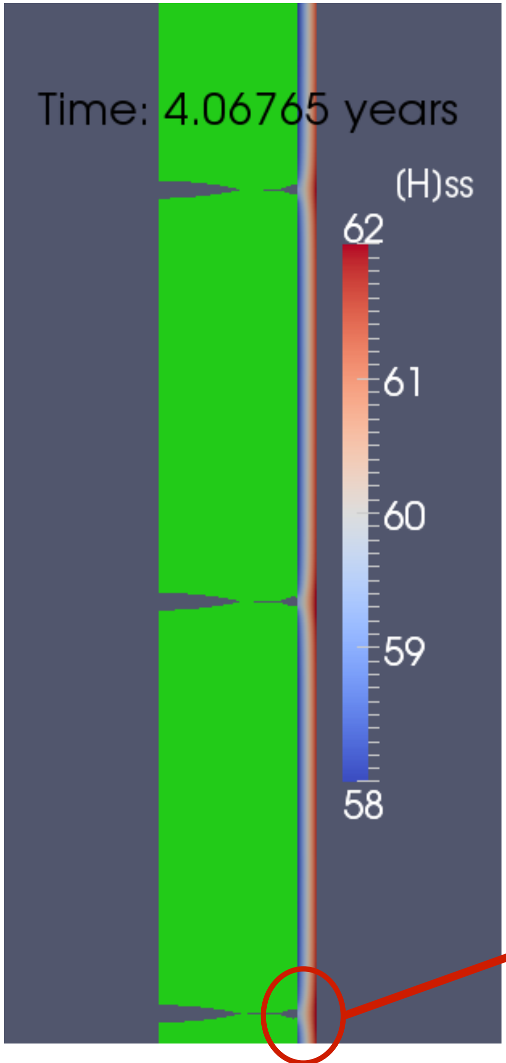
Plot from Evrard Lacroix

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

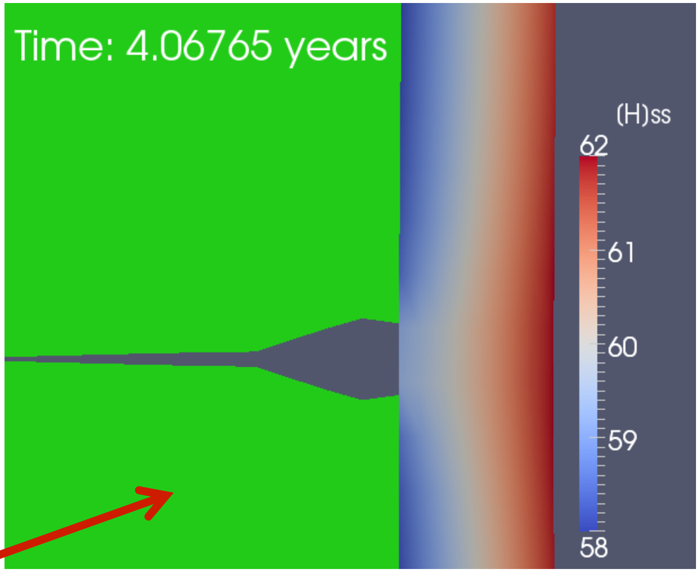


—*Etched appearance of zirconium hydride concentrations and orientation at mid-pellet and pellet-to-pellet interface location*

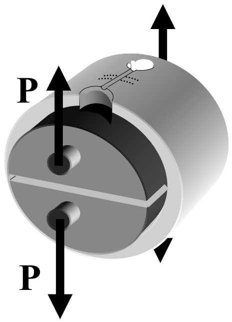
Hydrogen concentration varies between pellets, due to temperature gradients



Hydrogen profile at the inter-pellet gap

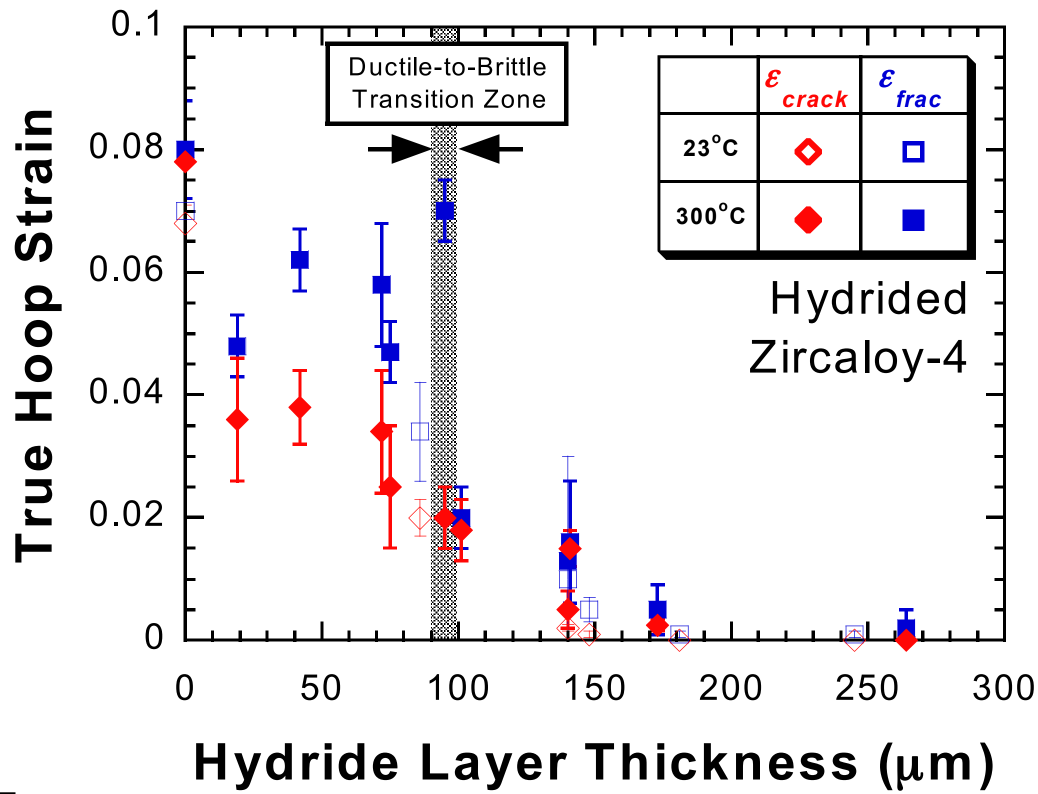


The hydride rim and blisters can cause a loss of ductility



The presence of a hydride rim or blister considerably decreases cladding ductility

⇒ Major influence in decreasing RIA resistance



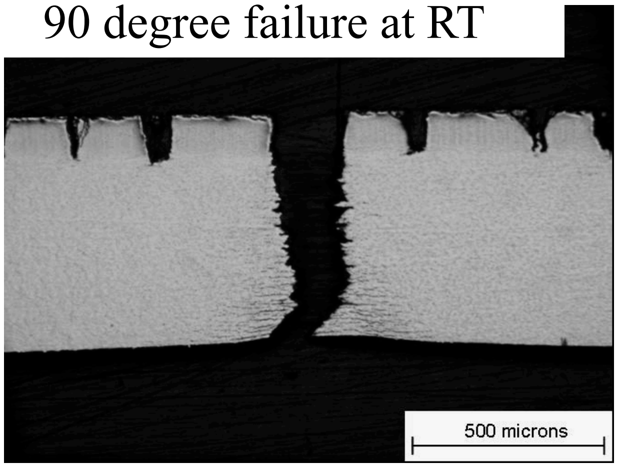
Daum, Bates, Koss Motta, 2003

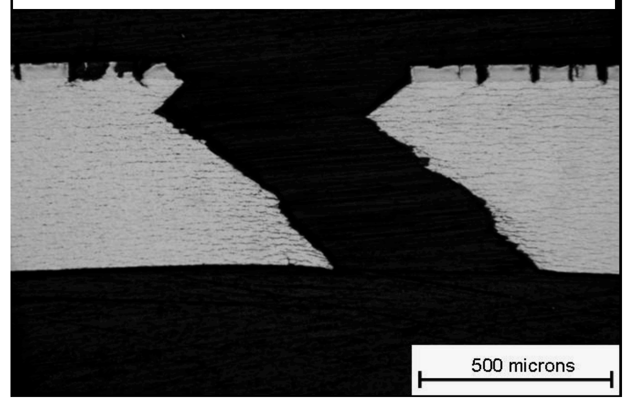
Here are some examples showing the impact of blisters on cladding failure

90 degree failure at RT

But in small blisters => shear instability

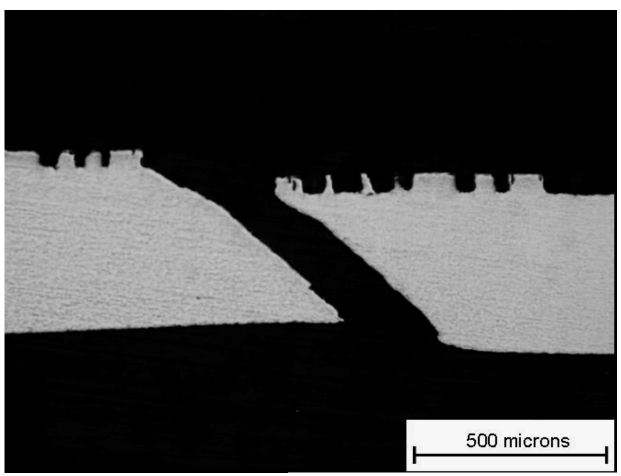
93 µm Blister
Broken at 25 °C
M020

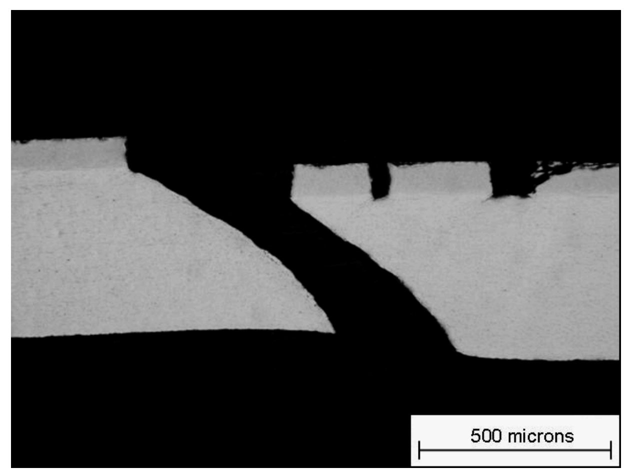




40 µm Blister
Broken at 25 °C
M014

53 µm Blister
Broken at 300 °C
M025





83 µm Blister
Broken at 300 °C
M023

At 300 C, 45 degree shear

And here are a few more examples

Square-bottom, blunted cracks,
Strain concentration at corners,

Initiates mixed mode I and II
cracks

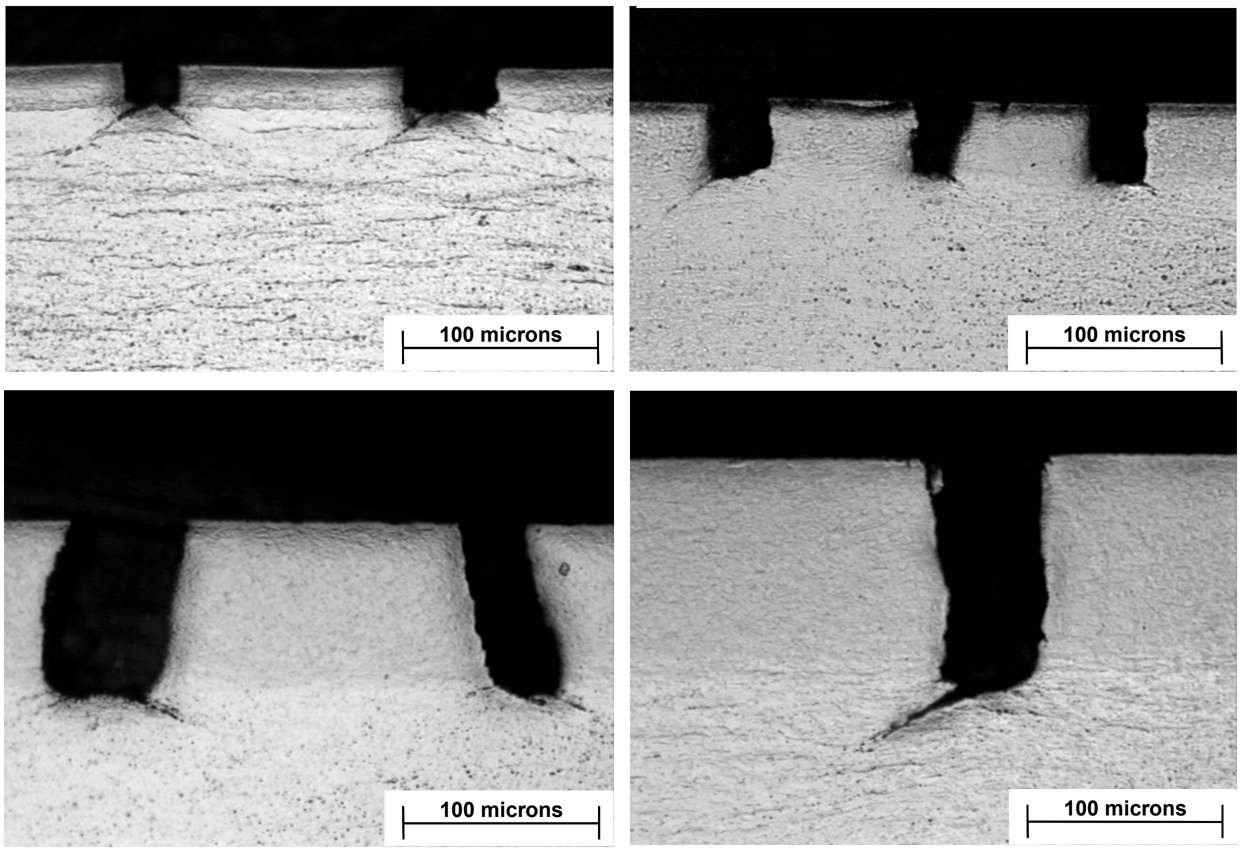
26 μm
M028

53 μm
M025

83 μm
M023

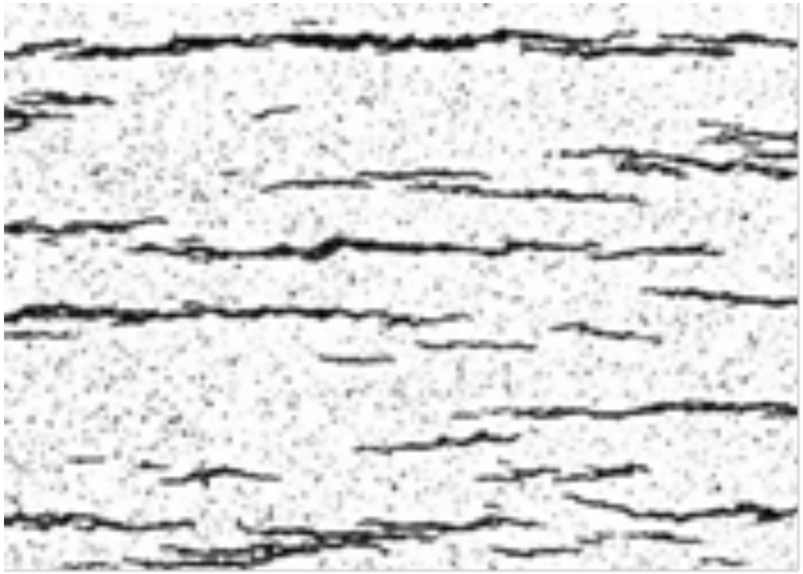
127 μm deep

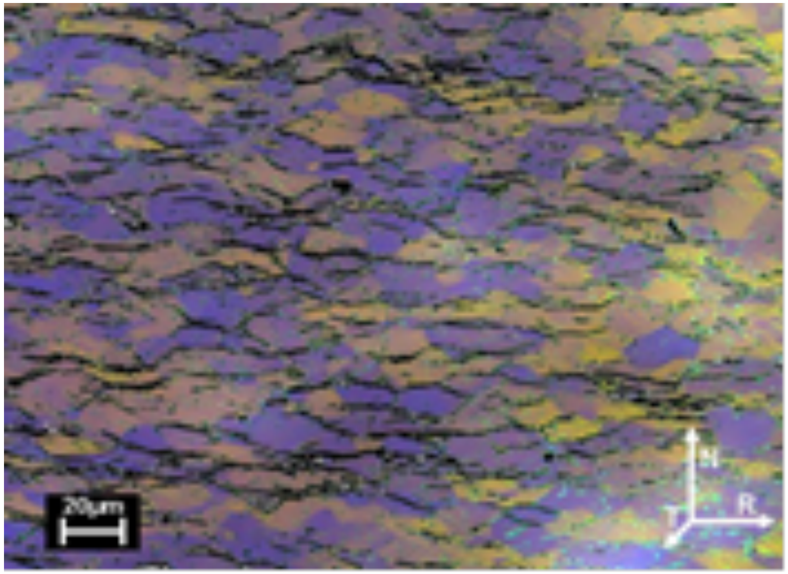
M024



- Failure occurs by crack propagation on 45º angle

Under reactor conditions, hydride platelets precipitate circumferentially





- Circumferential precipitation occurs because of
  - The coolant pressure
  - The crystallographic texture in the as fabricated cladding

In used fuel after drying, the hydrides can reprecipitate with a radial orientation

- Temperature increases during drying and the hydrides dissolve
- Fission gas release during drying pressurizes the tube
- When the temperature drops, the new stress state can cause the hydrides to reform with a different orientation

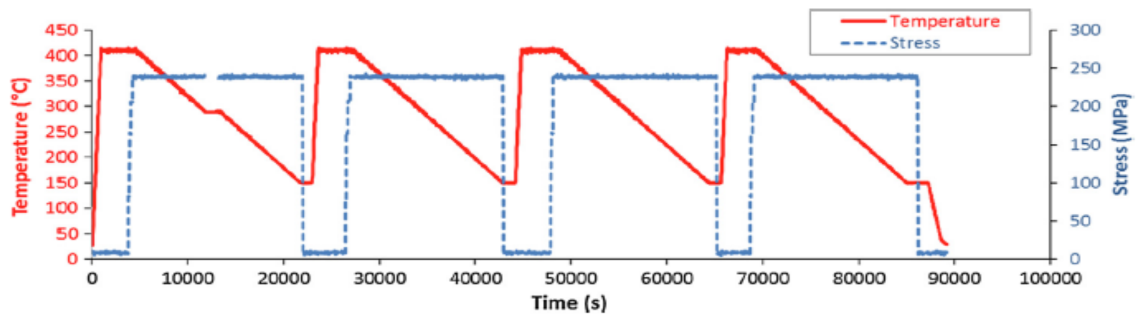
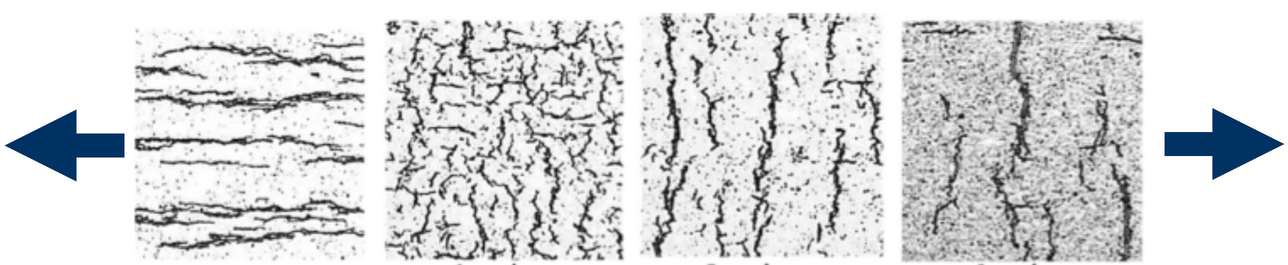


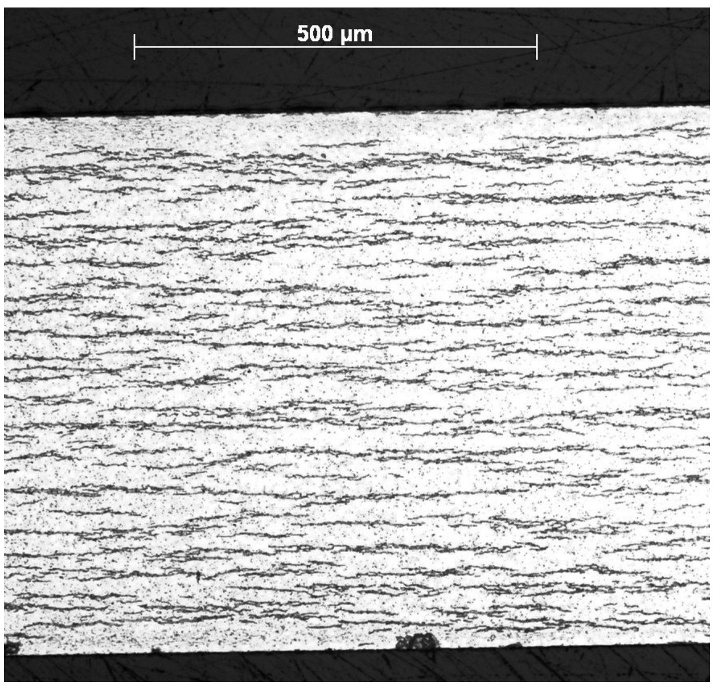
Fig. 1. Example of four thermo-mechanical cycles as applied to a sample with 192 wt.ppm of hydrogen.

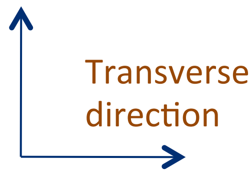


Colas et al, *Journal of Nuclear Materials*, vol. 440, no. 1–3.

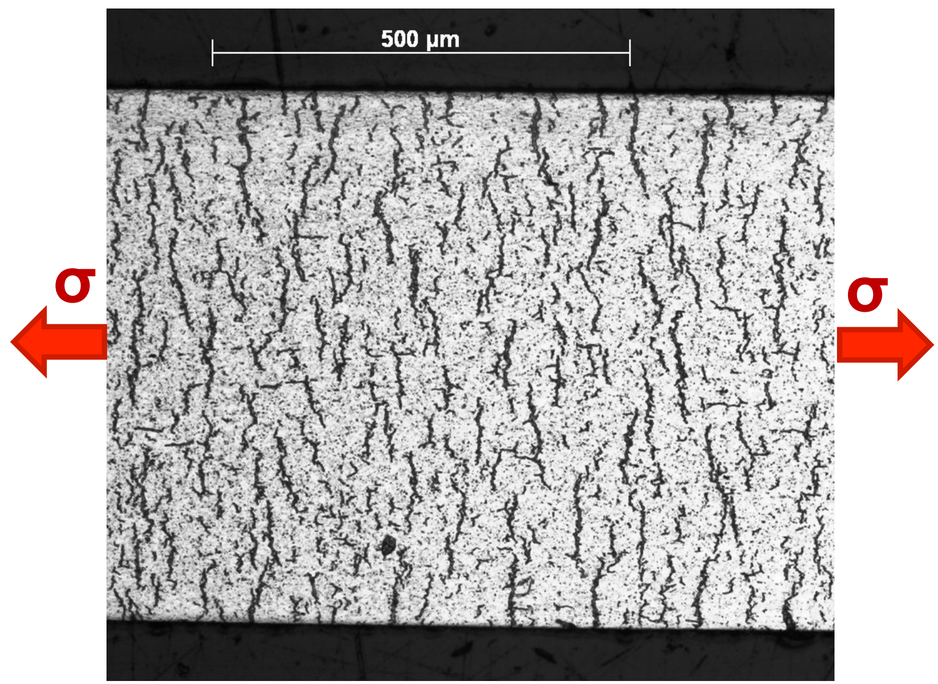
The hydrides reform in a radial direction due to the tensile hoop stress

Hydrides formed under **no** applied load





Hydrides formed under **tensile** applied load



Kearns JNM 1967
Louthan JNM 1963

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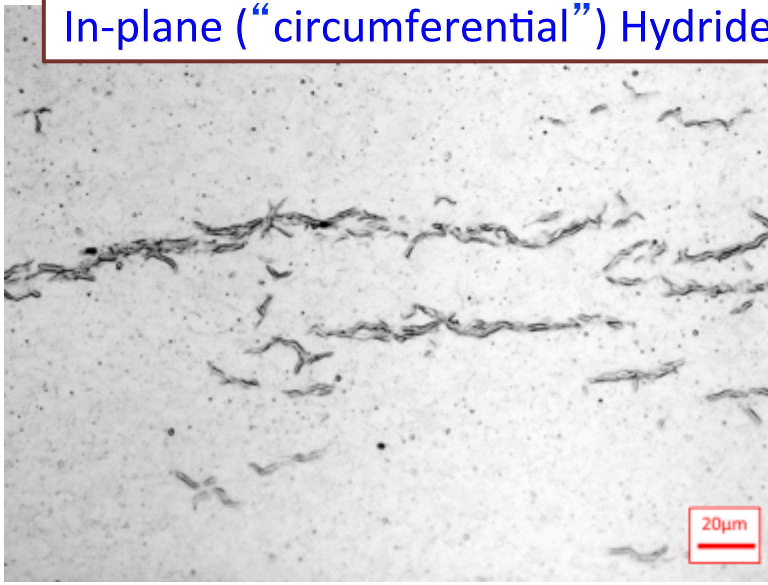
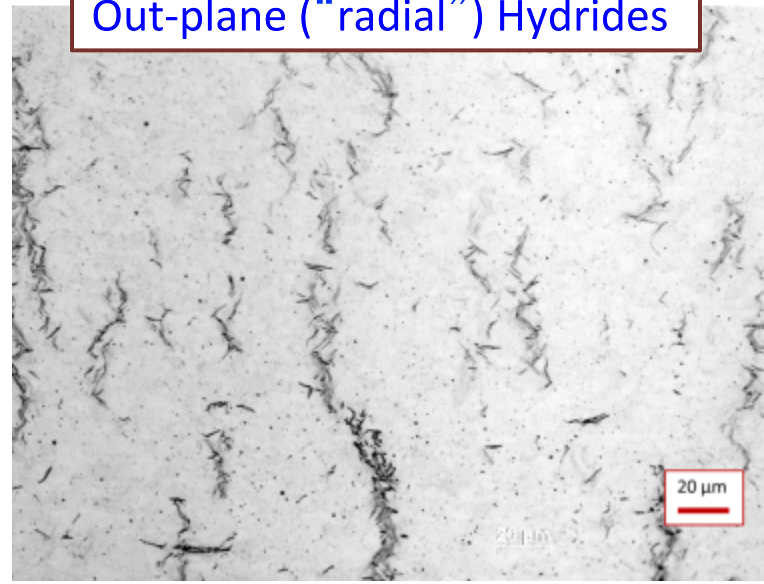
Hydride Microstructures

In-plane (“circumferential”) Hydrides

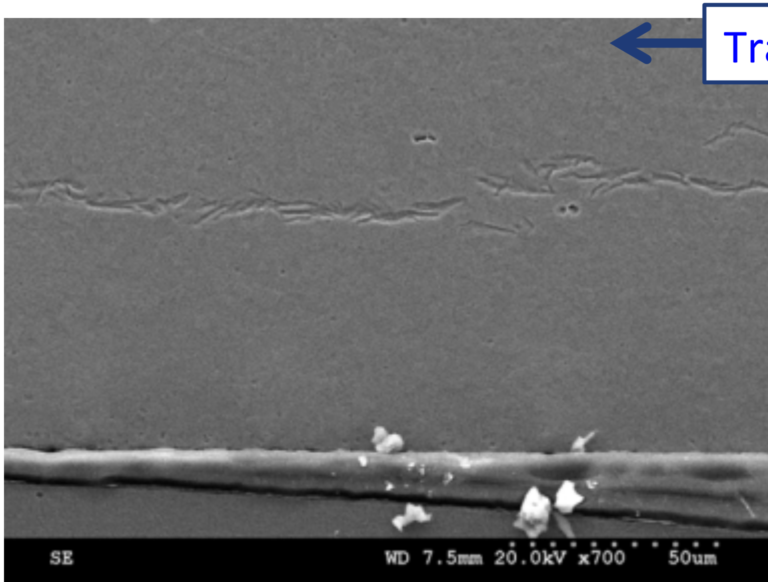


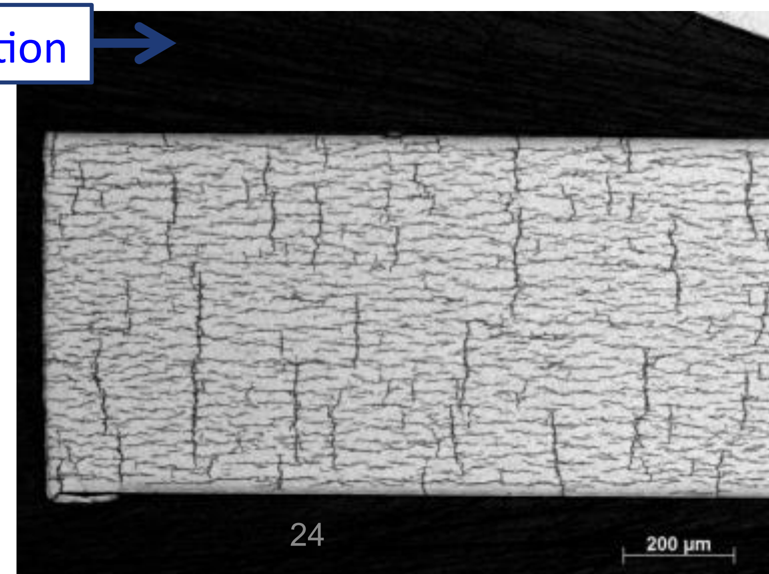
Out-plane (“radial”) Hydrides



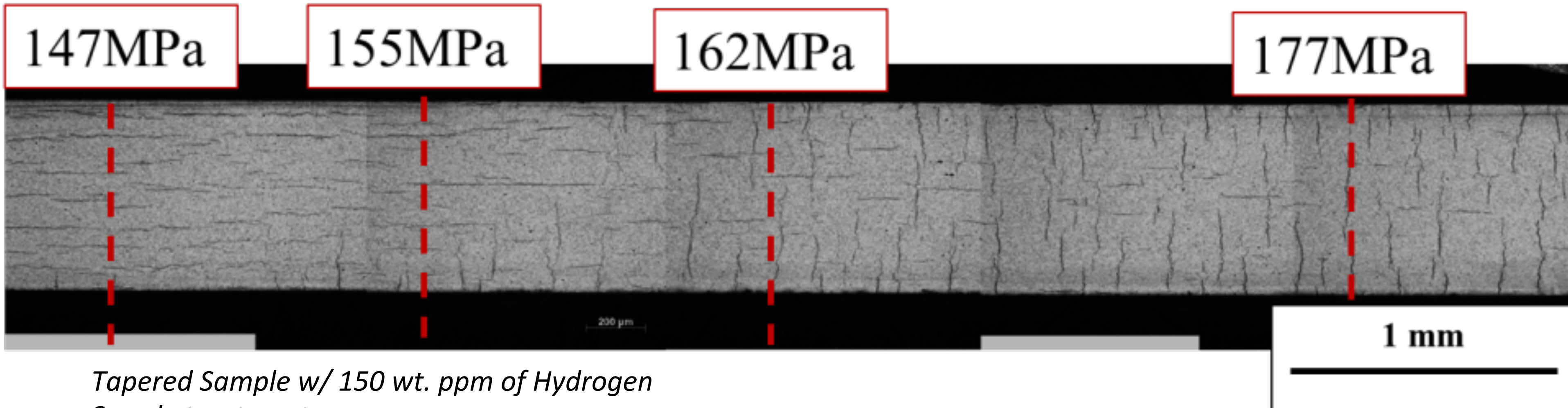
Normal Direction

Transverse Direction





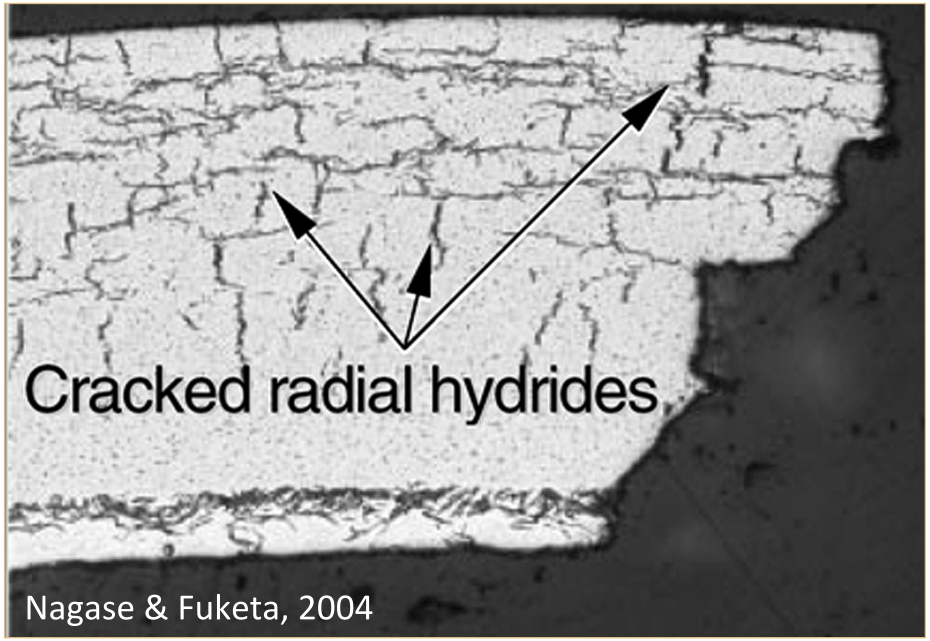
There is a critical tensile stress at which the hydrides reorient



Tapered Sample w/ 150 wt. ppm of Hydrogen
2-cycle treatment,

- Hydride orientation changes as a function of stress level
- The critical stress to reorient hydrides during re-precipitation when in uniaxial tension is approximately **150 MPa**

Radial hydrides provide easy crack paths

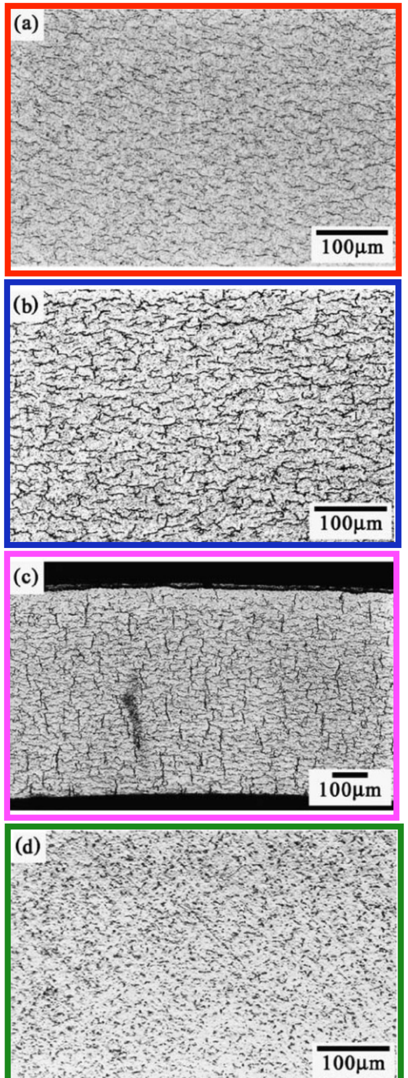


25 °C

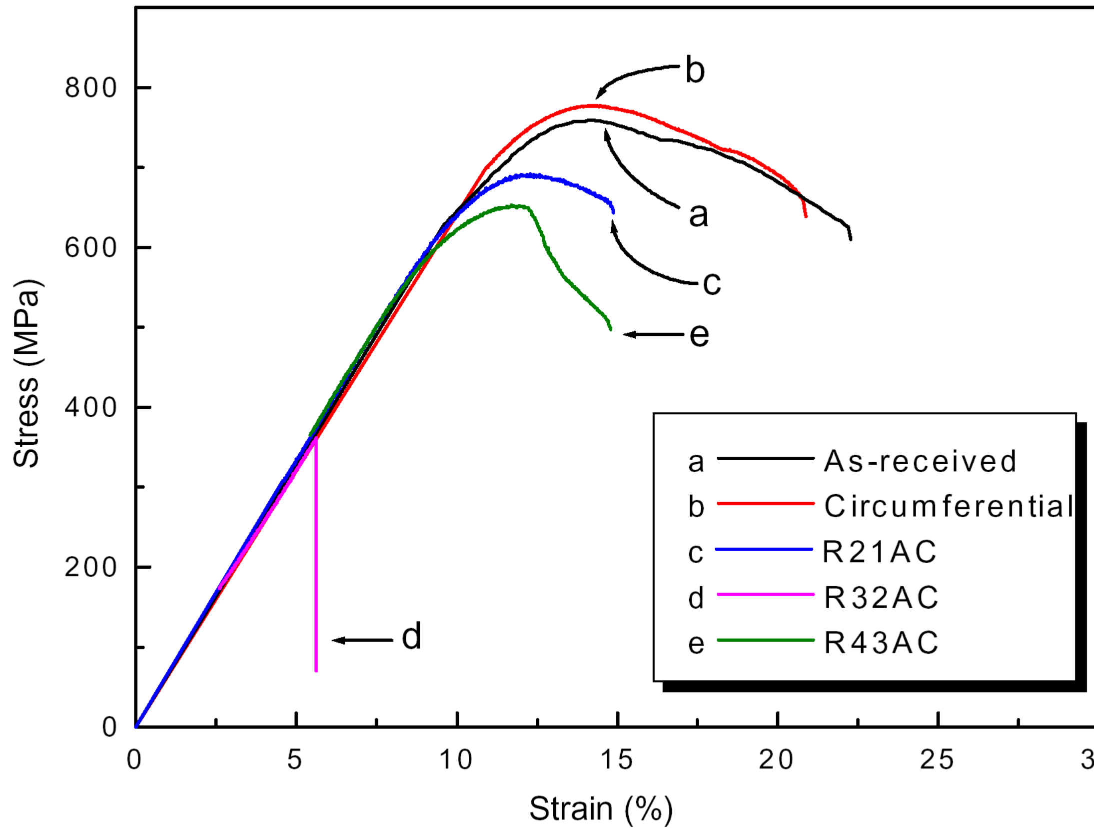
At Yield Load

100 Microns

Radial hydrides significantly decrease the ductility of the cladding

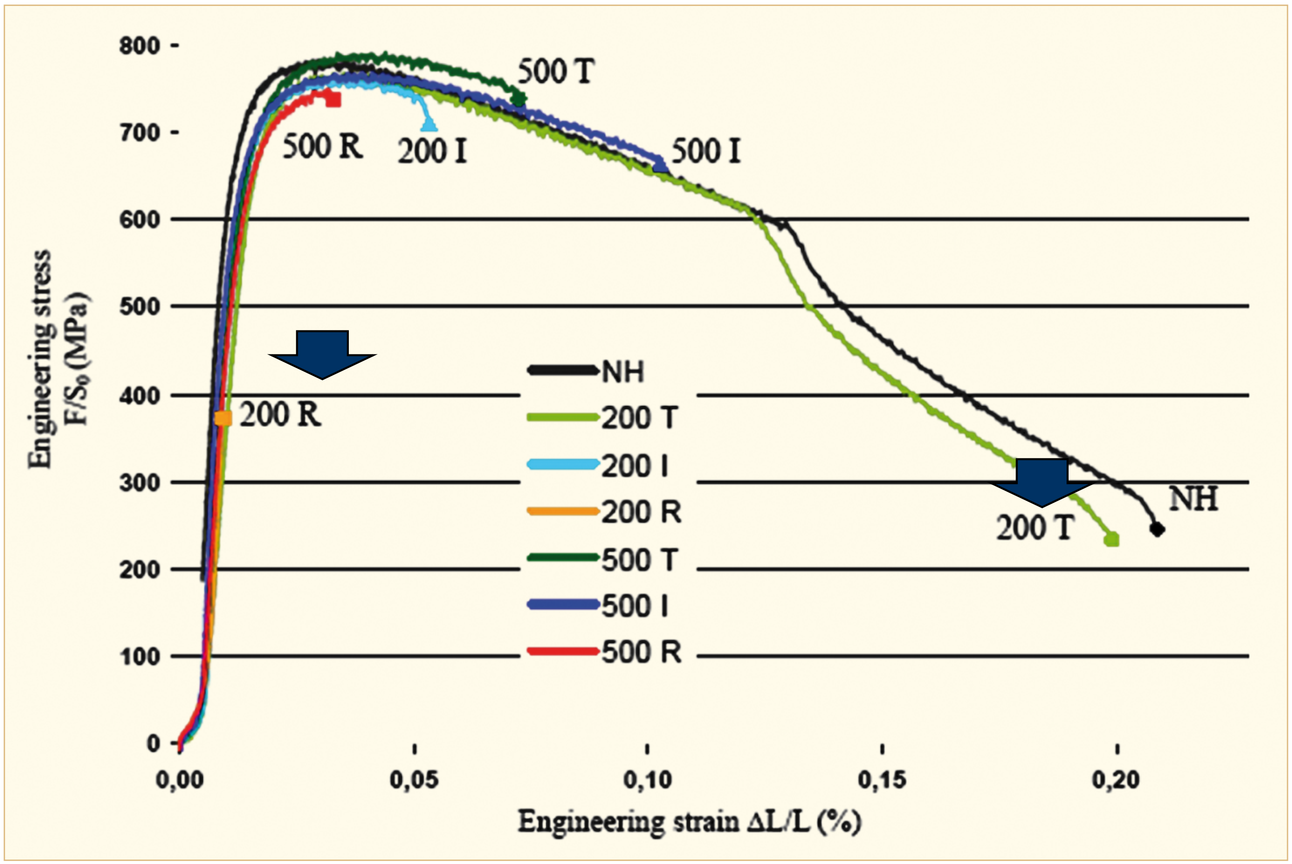


Ring tests at 20˚C : specimen with radial hydrides had lowest ductility, Hong &Lee, 2005



Radial hydrides significantly decrease the ductility of the cladding

Specimen	200T	200I	200R	500T	500I	500R
Radial hydrides Length proportion (%)	3	18	64	1	10	12



Racine et al., 2005

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