

# Nuclear Fuel Performance

NE-533

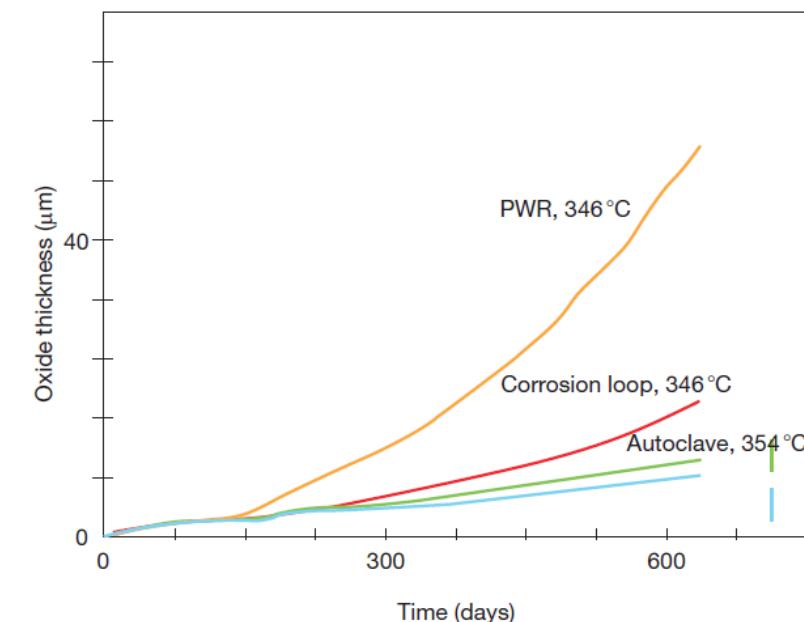
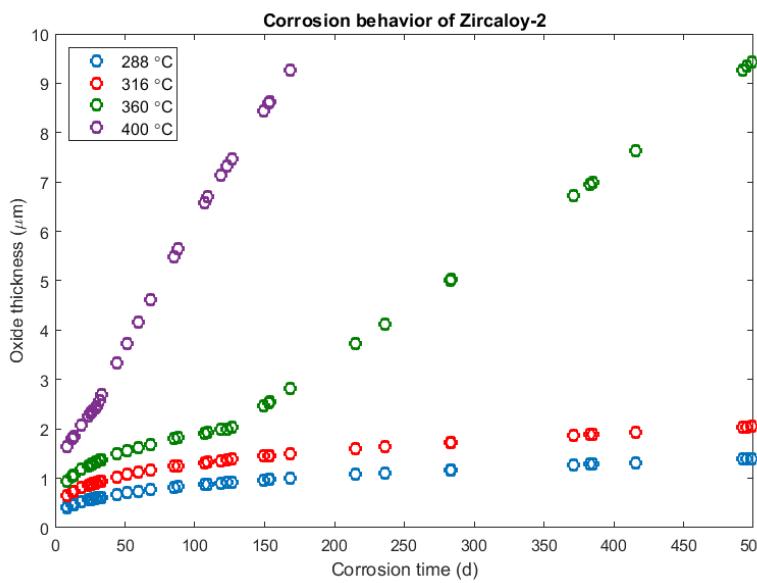
Spring 2023

## Last time

- Exams graded: 101 average, no curve
- Cladding oxidizes, forming  $\text{ZrO}_2$
- The limiting step for oxidation is the oxygen transport through the oxide layer
- Can determine oxide thickness from weight gain, or from time/temperature

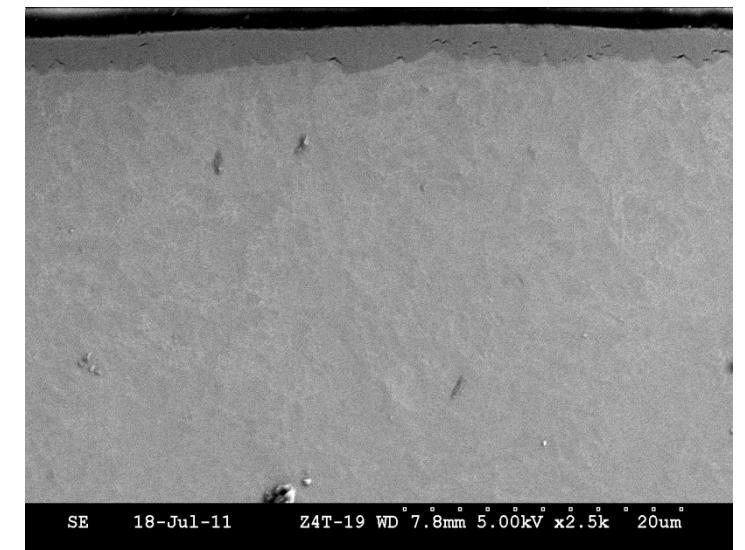
# Other factors affecting corrosion

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



# Impact of Corrosion

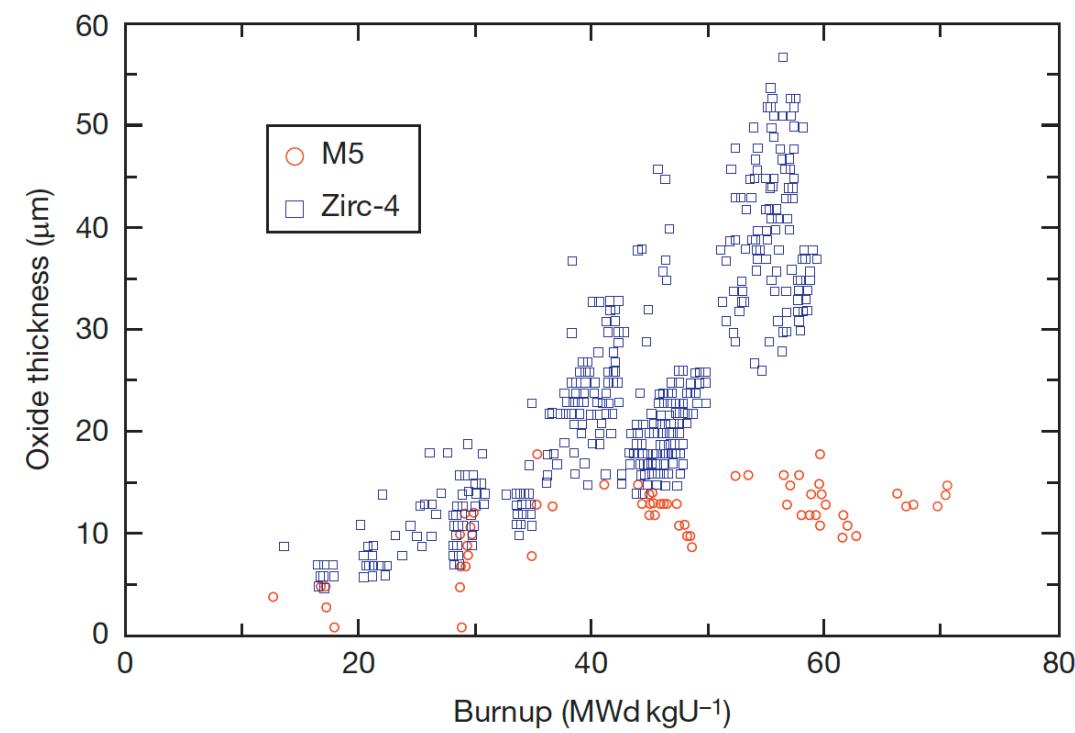
- The oxide layer has a low thermal conductivity, restricting heat transport
  - For Zircaloy,  $k = 22 \text{ W}/(\text{mK})$
  - For  $\text{ZrO}_2$ ,  $k = 1.7 - 2.7 \text{ W}/(\text{mK})$
- The oxide layer is much more brittle than the zircaloy
  - Zircaloy metal is removed as brittle oxide is added to the material
- Oxidation produces hydrogen that can enter the cladding and form brittle hydrides



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

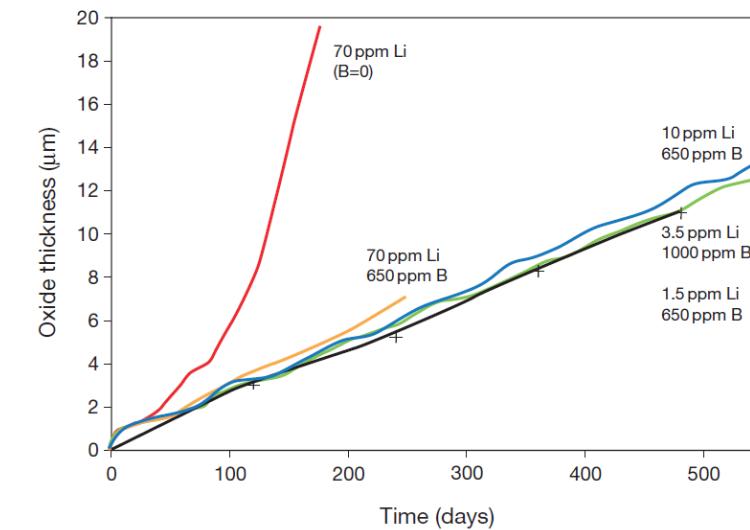
# Corrosion Control

- 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



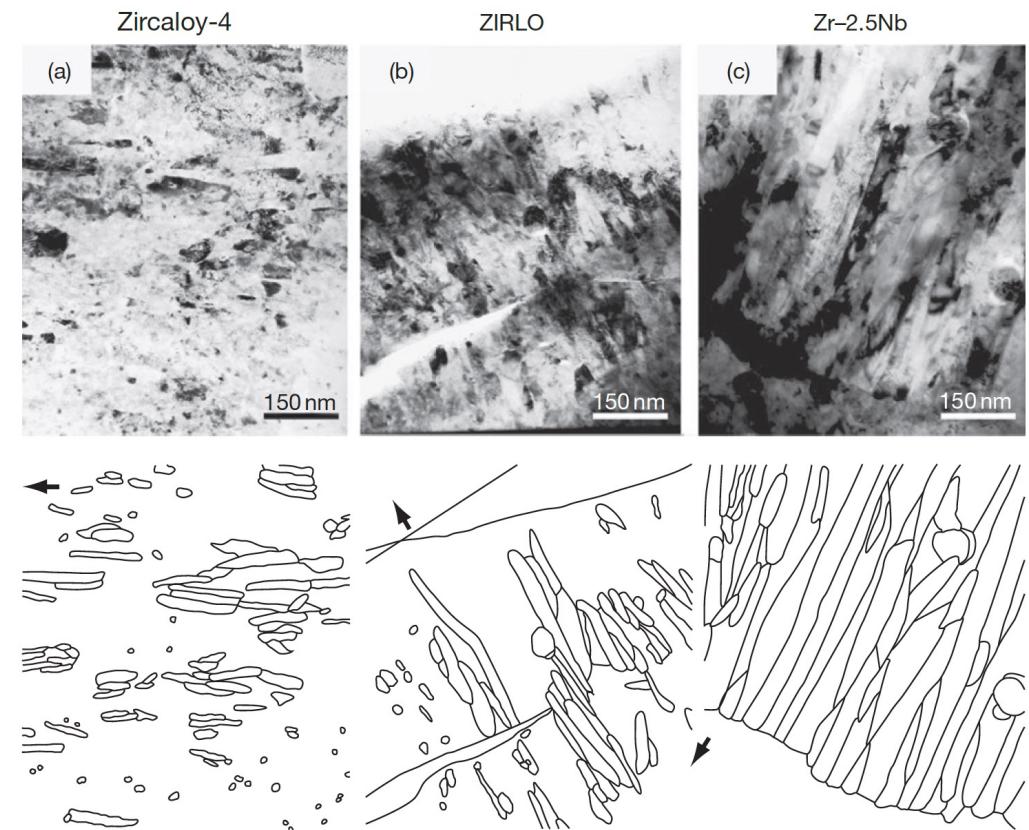
# Corrosion Control

- 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 H<sub>3</sub>BO<sub>3</sub> (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 O<sub>2</sub> 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



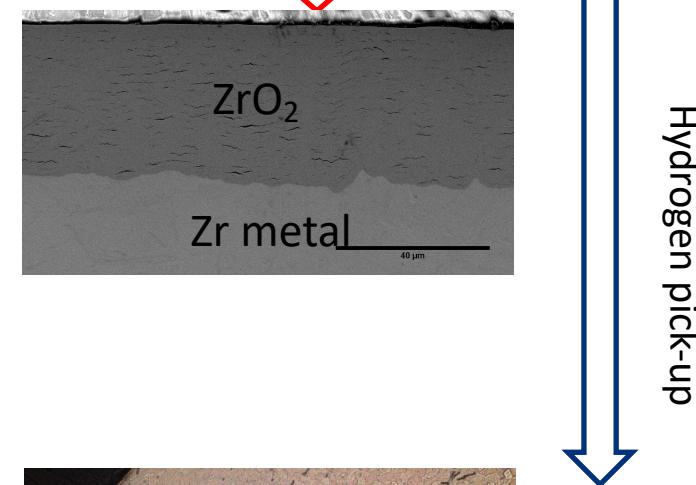
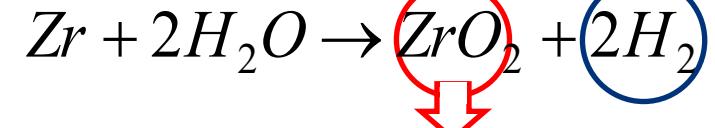
# Corrosion Summary

- Corrosion is the environmental degradation of materials
- Cladding oxidizes, forming  $\text{ZrO}_2$
- 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 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
- Hydrogen pickup causes hydrogen embrittlement, loss of fracture toughness, delayed hydride cracking, accelerated corrosion, and accelerated irradiation growth

Corrosion reaction:

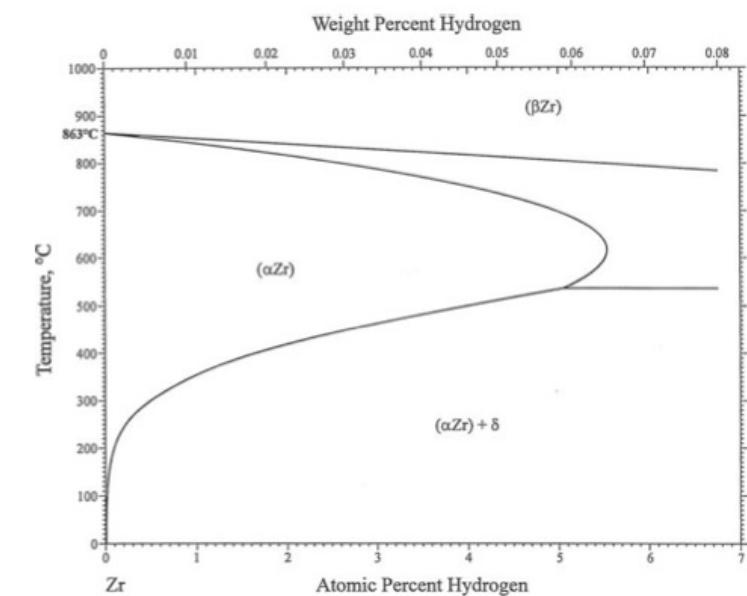
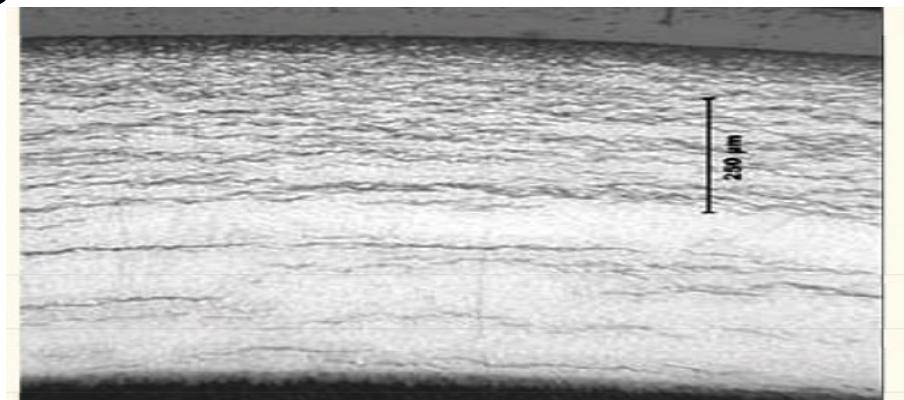


# Hydrogen Diffusion

- The diffusion coefficient of H in Zr is  $D_{Zr}^H = D_o^H \exp(-E_m^H / k_B T)$   
 $E_m^H = 0.47\text{eV}$      $D_o^H = 7 \times 10^{-3} \text{cm}^2/\text{s}$
- 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

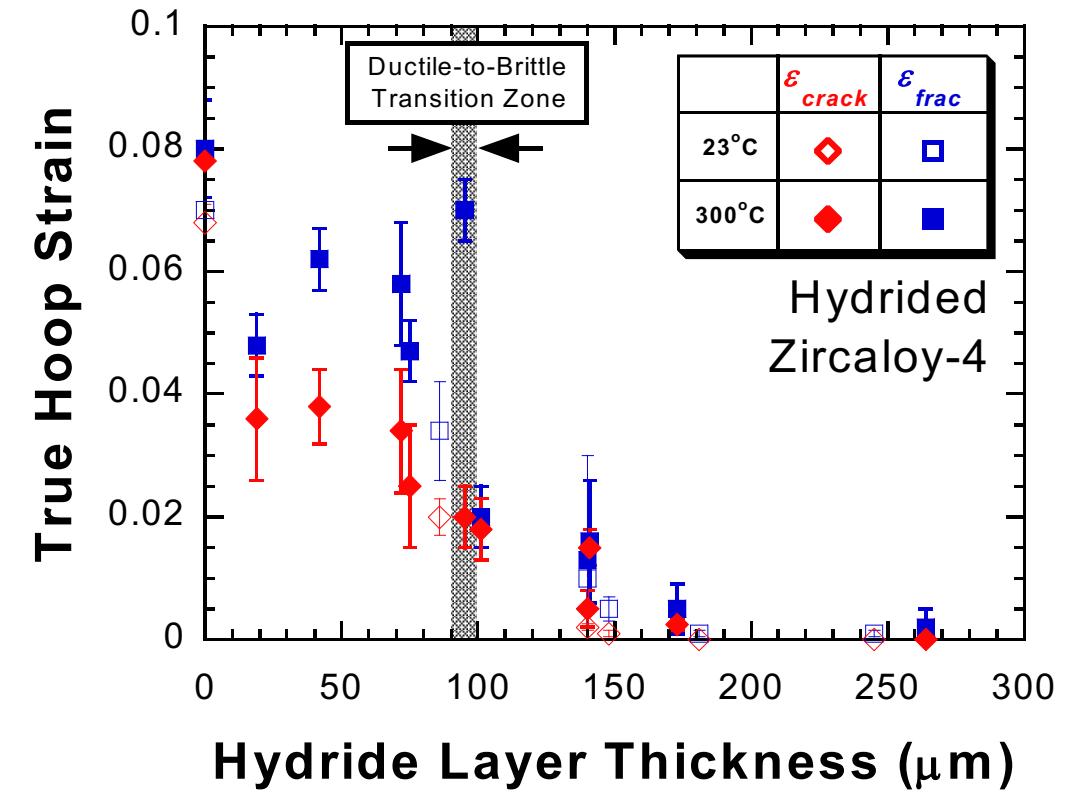
# Hydriding

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



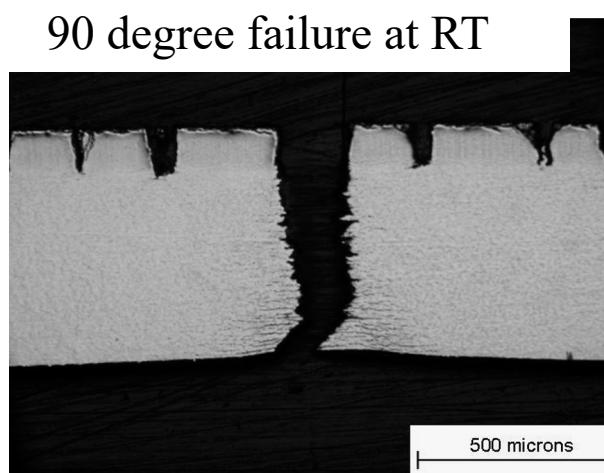
# Effect of Hydrides

- 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

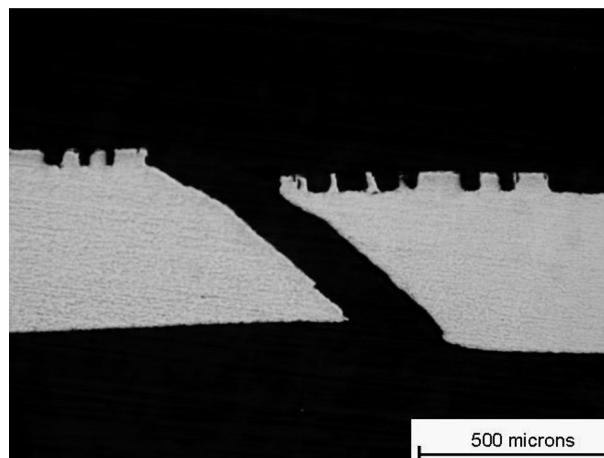


## Blister failure examples

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

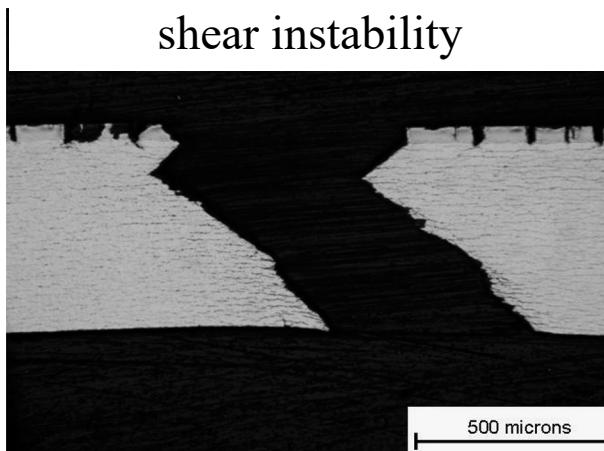


**53 µm Blister  
Broken at 300 °C  
M025**

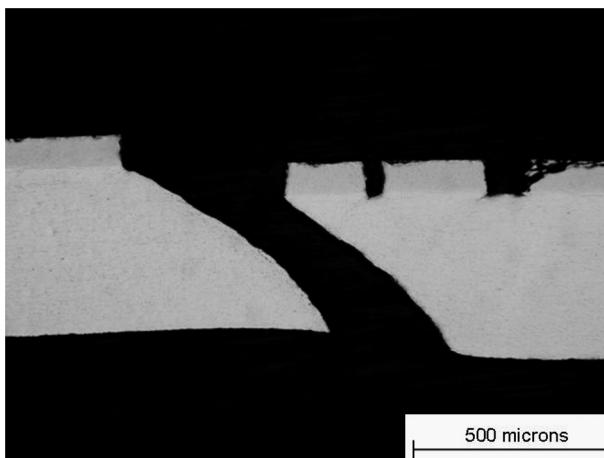


But in small blisters =>  
shear instability

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



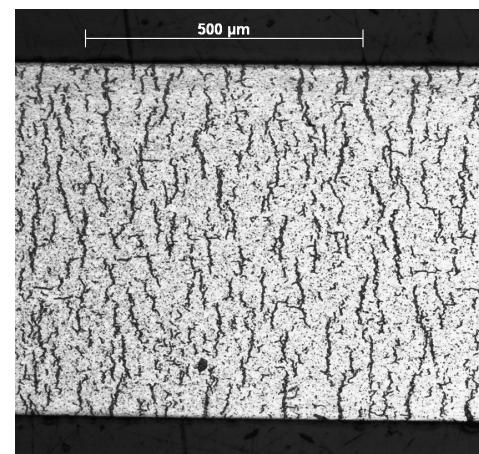
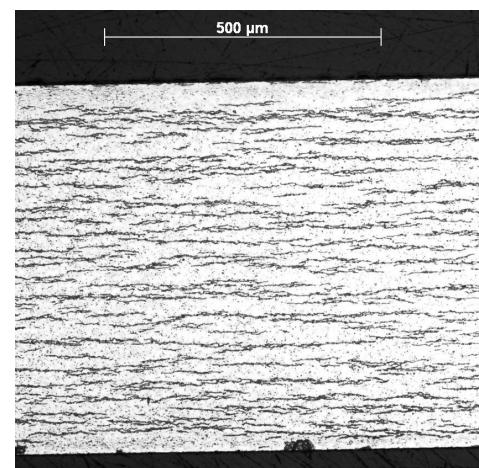
**83 µm Blister  
Broken at 300 °C  
M023**



At 300 C, 45 degree shear

# Circumferential vs Radial Hydrides

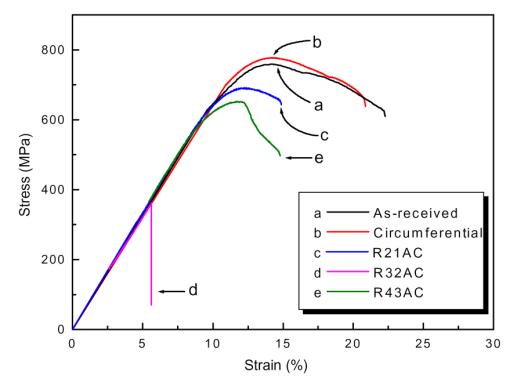
- Under reactor conditions, hydride platelets precipitate circumferentially
- In used fuel after drying, the hydrides can reprecipitate with a radial orientation
- The hydrides reform in a radial direction due to the tensile hoop stress
- Radial hydrides provide easy crack paths and significantly decrease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



25 °C

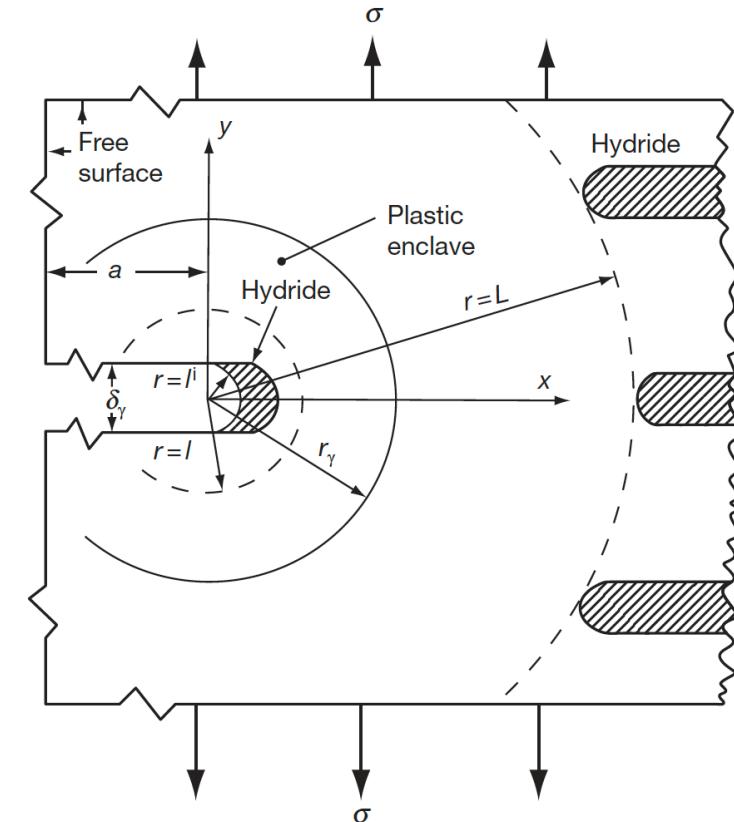


At Yield Load  
100 Microns



# 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



# Hydrogen Pickup

- 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
  - $J_H = 2 f J_O$
- 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%?

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

- First, we must determine the weight of H that has entered the cladding
  - $\rho_{\text{ZrO}_2}$  is 5.68 g/cm<sup>3</sup>, of which  $32/(91+32) = 0.26 = 26\%$  is O, thus 1.47 g/cm<sup>3</sup> of O
  - A 1 micron oxide layer corresponds to a weight gain of 14.7 mg/dm<sup>2</sup> 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  $0.15 \times 2 \times 4.42 \times 10^{22} = 1.33 \times 10^{22}$  atoms of hydrogen/dm<sup>2</sup>, 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  $600 - 80/\text{PBR} = 600 - 80/1.56 = 549$  microns
  - The volume of zirconium is  $549 \times 10^{-4} (\text{cm}) \times 10 \times 10 = 5.49 \text{ cm}^3$
  - $\rho_{\text{Zr}} = 6.5 \text{ g/cm}^3$ , 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  $\delta$  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)

$\rho_{oxide}$  oxide density

$\rho_{Zr}$  Zr metal density

$f_{ZrO_2}^O$  Fraction of oxygen in ZrO<sub>2</sub> mass

$PBR$  Pilling-Bedworth Ratio

$M_H$  moelcular mass of H

$M_O$  molecular mass of O

$t$  cladding thickness

# 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

# ACCIDENT SCENARIOS

# Kinds of Accidents

- Design basis accident: DBA
  - are postulated, credible accidents with low probability that are used to establish the design basis for the reactor and to define safety limits for its operation
- Beyond design basis accident: BDBA
  - accidents that fall outside of what is designed for, because they are deemed too unlikely to be included in design

# Reactivity Initiated Accident (RIA)

- Reactivity is the fractional departure from criticality:  $\delta k = (k - 1)/k$   
where  $k$  is your effective multiplication factor
  - $k = (\text{Neutrons produced in one generation})/(\text{Neutrons produced in the previous generation})$
  - $k = \varepsilon L_f p L_{th} f \eta$  – this is your six-factor formula
  - $\varepsilon$  = fast fission factor
  - $L_f$  = fast non-leakage factor
  - $p$  = resonance escape probability
  - $L_{th}$  = thermal non-leakage factor
  - $f$  = thermal fuel utilization factor
  - $\eta$  = reproduction factor

# Reactivity

- Reactivity =  $\rho = r = \delta k = (k - 1)/k$
- At steady state,  $k=1$ ,  $\rho=0$
- Reactivity is affected by the temperature and density of coolant, moderator, and fuel
- Ideally, nuclear reactors are designed so that a power increase will generate negative reactivity feedback
  - an increase in the reactivity (higher  $k$ ) leads to material changes, which in turn force a negative reactivity (lower  $k$ )

# RIA-PWR

- Design Basis Accident: Large and rapid insertion of reactivity caused by inadvertent ejection (PWR) or drop (BWR) of a control rod
- A control rod ejection or drop can occur by mechanical failure of the control rod drive mechanism or its housing, and the reactivity of the core can rapidly increase due to decreasing neutron absorption
- PWR
  - Control rod ejection accident (CREA)
  - Caused by mechanical failure of a control rod mechanism housing, such that the coolant pressure ejects a control rod assembly completely out of the core
  - Reactivity increase to the core occurs within about 0.1 s in the worst possible scenario
  - The most severe CREA would occur at normal coolant temperature and pressure, but with nearly zero reactor power

# RIA-BWR

- BWR
  - Control rod drop accident (CRDA)
  - Initiated by the separation of a control rod blade from its drive mechanism
  - Detached blade remains stuck in position until it suddenly becomes loose and drops out of the core in a free fall
  - Most severe CRDA would occur at with the coolant close to room temperature and atmospheric pressure, and the reactor at nearly zero power
- Other RIAs
  - inadvertent changes in coolant/moderator temperature and/or void fraction may add reactivity to the core

# RIA

- RIA leads to a fast rise in fuel power and temperature
- This power ramp can lead to failure of fuel rods and release of radioactive material (or potentially fuel) into coolant
- Release of hot fuel into water can cause rapid steam generation and pressure pulses, damaging other core internals
- Coolant pressure pulse could break the reactor coolant pressure boundary or damage the fuel and other core internals so that long-term cooling of the core would be impaired
- To prevent such consequences, safety criteria are set up to limit energy injection into the fuel

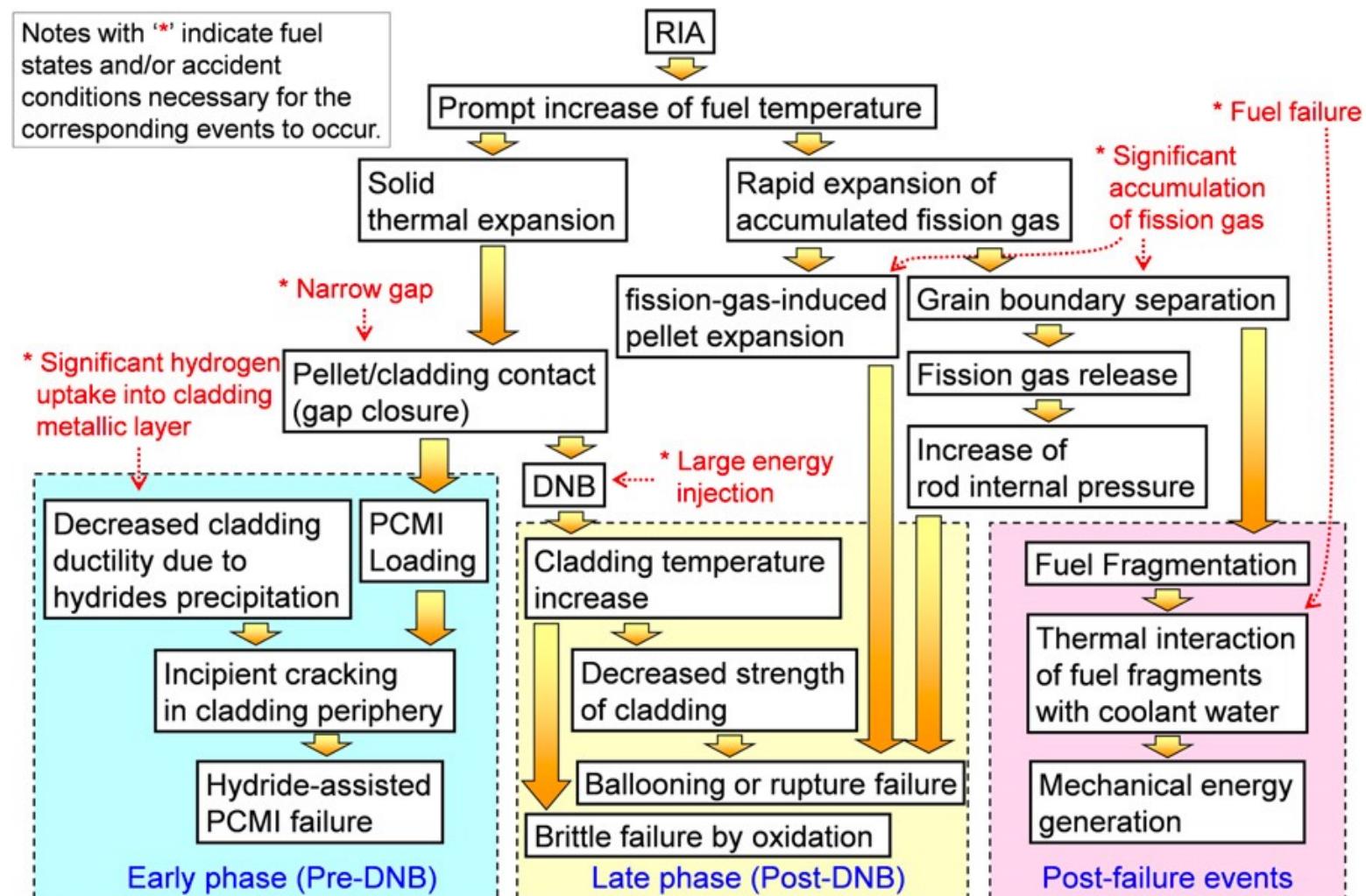
# History of RIA

- No RIA with severe consequences has occurred in PWRs or BWRs
- The first reactivity-initiated accidents occurred in the 1950s and 1960s and concerned the first generation of research reactors
  - 1952 accident in the NRX reactor at Chalk River
  - 1961 SL-1 accident in Idaho Falls
- Both resulted in severe damage and disruption of the reactor, and led to design improvements for later generations of RRs and commercial reactors
- Did not eliminate RIAs
  - K-431 Russian Echo-II nuclear powered submarine in 1985
  - Chernobyl nuclear power plant, Ukraine, in 1986

# Chernobyl RIA

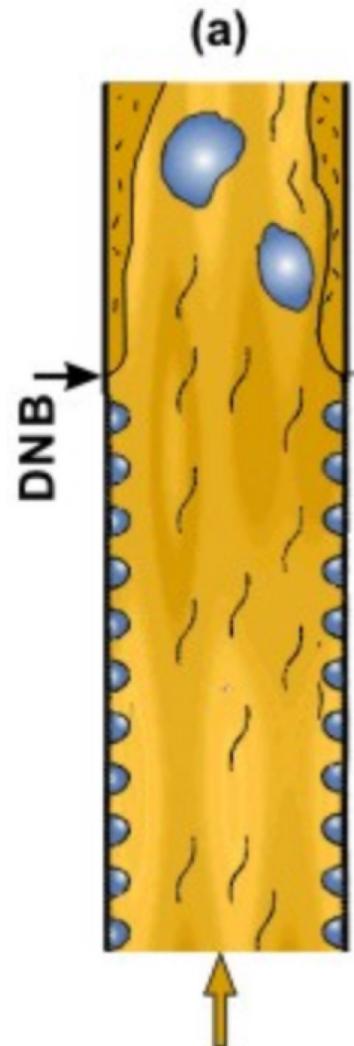
- Light water graphite moderated pressure tube design (RBMK)
- Severe consequences of the Chernobyl accident were due to the fact that RBMKs lack not only a reactor containment, but also some of the inherent feedback mechanisms
- Accident occurred under a reactor test, where normal operating guidelines were ignored and safety systems were shut off
- Chernobyl accident prompted new research into reactivity initiated accidents
  - focused on high burnup fuel, where previous safety standards had largely been on fresh fuel or low BU

# Sequence of RIA



# Departure from Nucleate Boiling

- If the heat flux of a boiling system is higher than the critical heat flux (CHF) of the system, the bulk fluid may boil, or in some cases, regions of the bulk fluid may boil where the fluid travels in small channels
- Large bubbles form, sometimes blocking the passage of the fluid
- This results in a departure from nucleate boiling (DNB) in which steam bubbles no longer break away from the solid surface of the channel, bubbles dominate the channel or surface, and the heat flux dramatically decreases
- Vapor essentially insulates the bulk liquid from the hot surface, increasing surface temperatures



# Microstructural Effects

- Rapid increase in temperature increases pressure of bubbles
- $PV = nRT$
- Rapid pressure increase leads to cracking in fuel

BWR fuel (61 GWd/t) test at 377 J/g (90 cal/g)

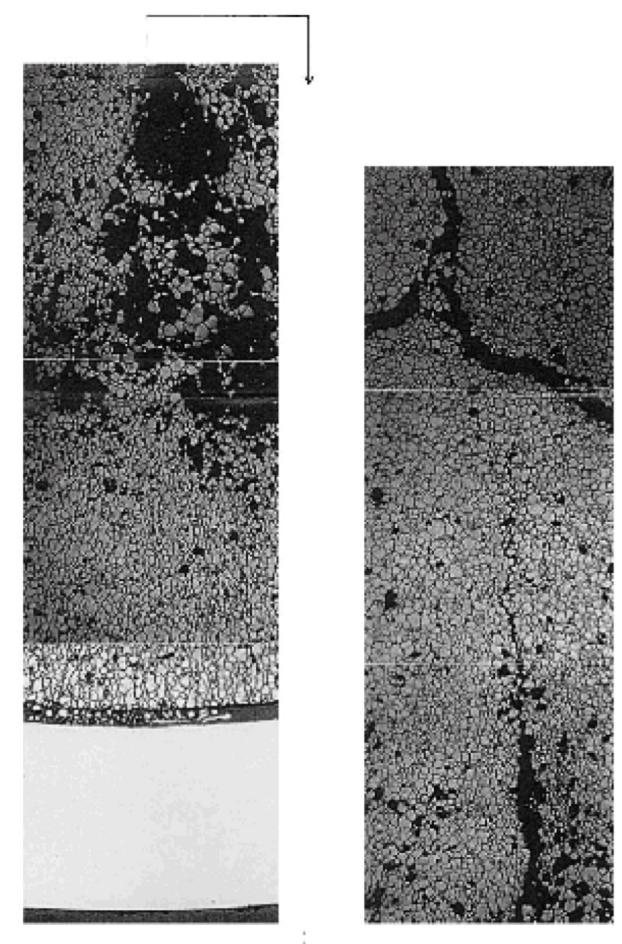
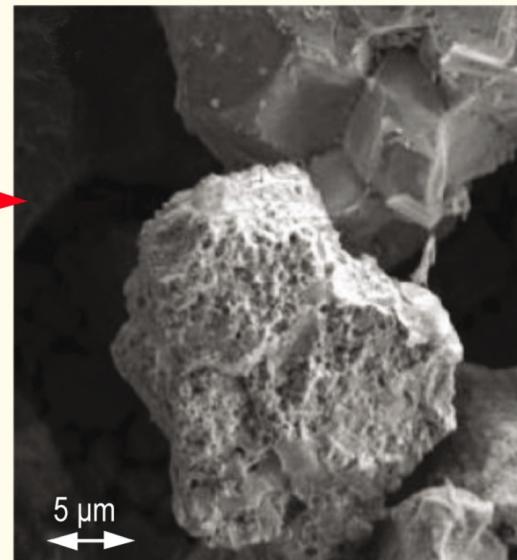
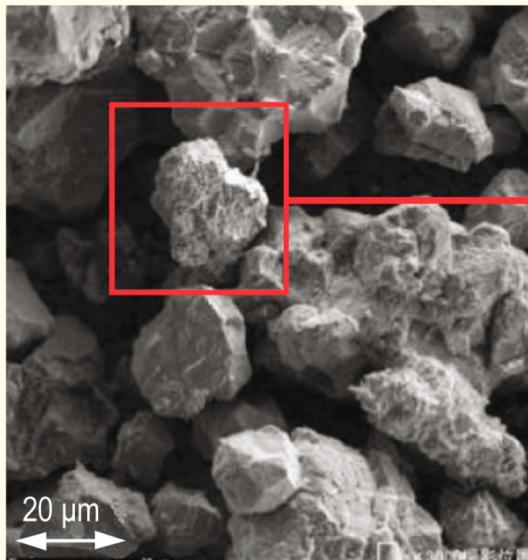
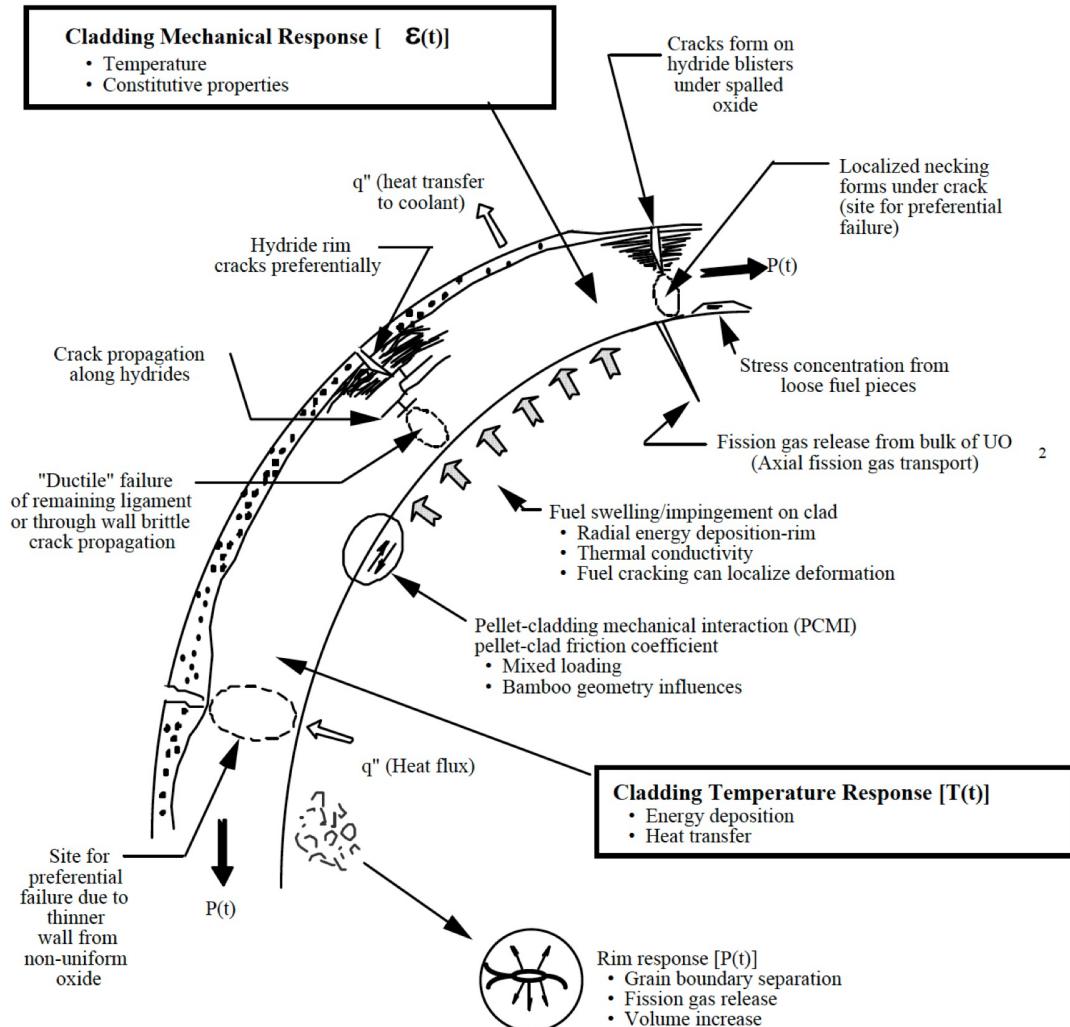


Figure – Redrawn and modified from original by A.N.T. INTERNATIONAL 2010

# Cladding Response

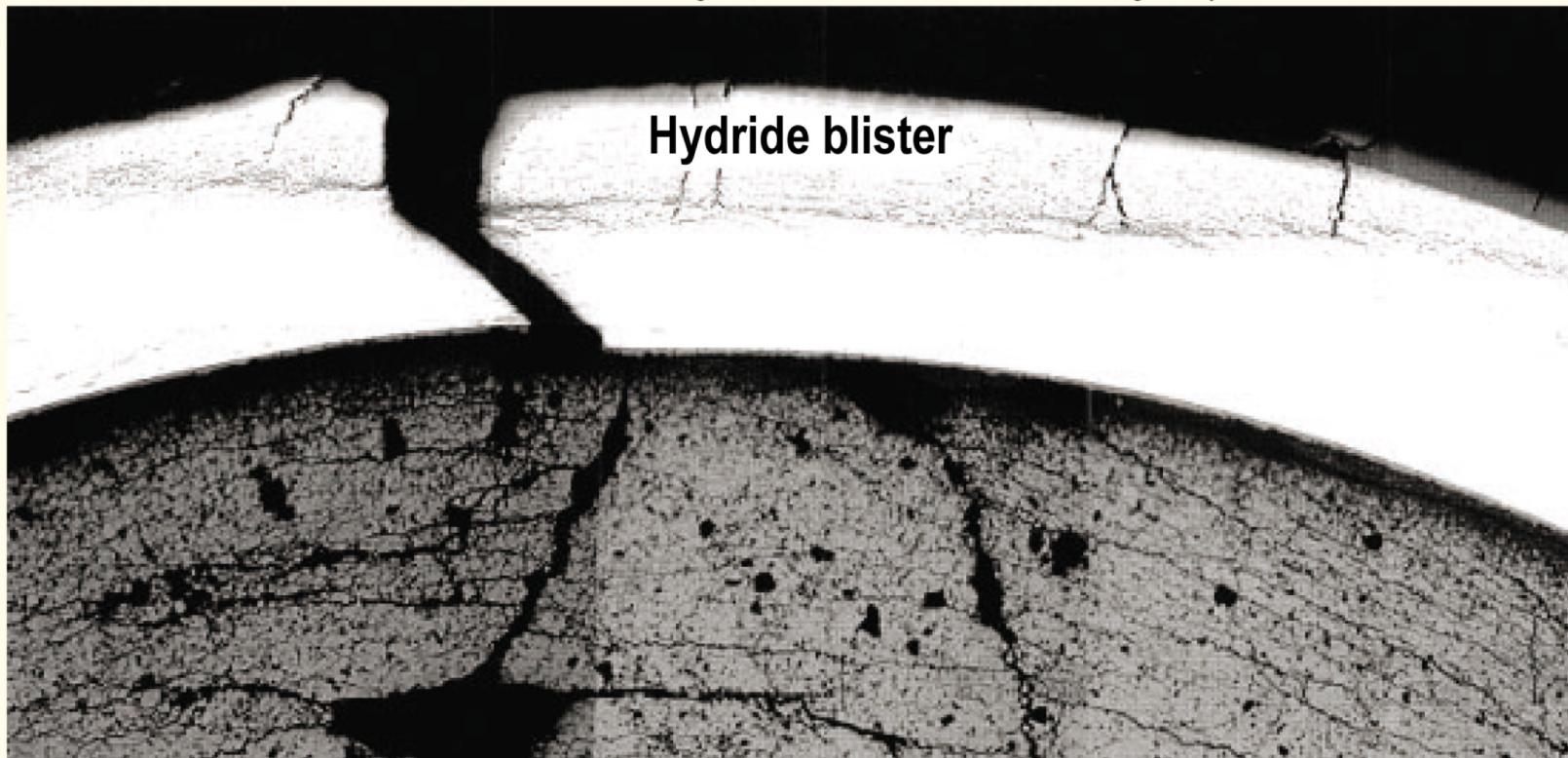
- Take into account burnup, corrosion (oxide layer and hydrides), damage accumulation, FCMI, internal pressure, etc. to properly evaluate strain in cladding
- Temperature spike leads to a stress spike, and higher likelihood of cladding failure
- Cladding fails either due to PCMI, ballooning/burst, or severe oxidation and partial melting



# Cladding Response

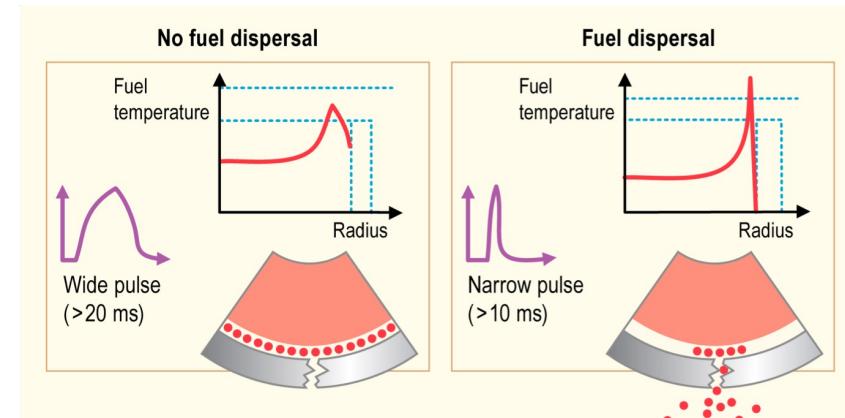
- PCMI failures results from the fuel pushing out on the cladding, causing it to break

Figure – Redrawn and modified from original by A.N.T. INTERNATIONAL 2010



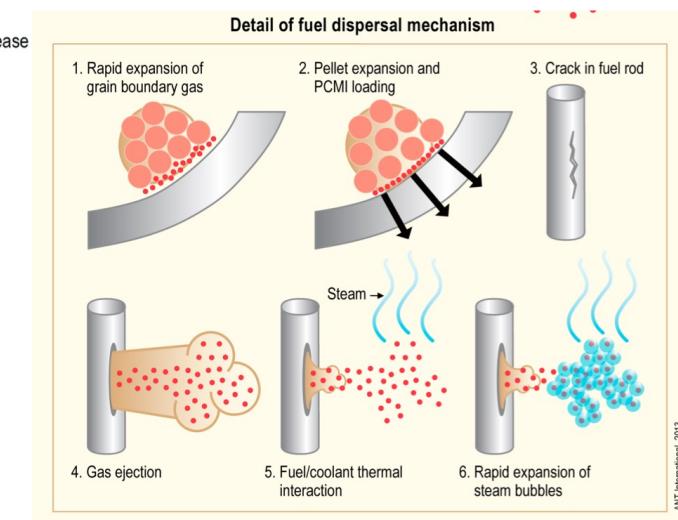
- The amplitude and width of the power pulse can have dramatic impacts on the effects of the RIA
- Pulse is typically defined by FWHM, and by total energy deposition (integration of pulse)
- More rapid temperature spike is more damaging
- Reactor state and type during typical accident scenarios determine pulse width

# Pulse Width



Estimated pulse widths and core-wide maxima of fuel pellet radial average enthalpy and enthalpy increase for various scenarios of CREA and CRDA. The data are compiled from realistic and moderately conservative computer analyses of cores with UO<sub>2</sub> fuel.

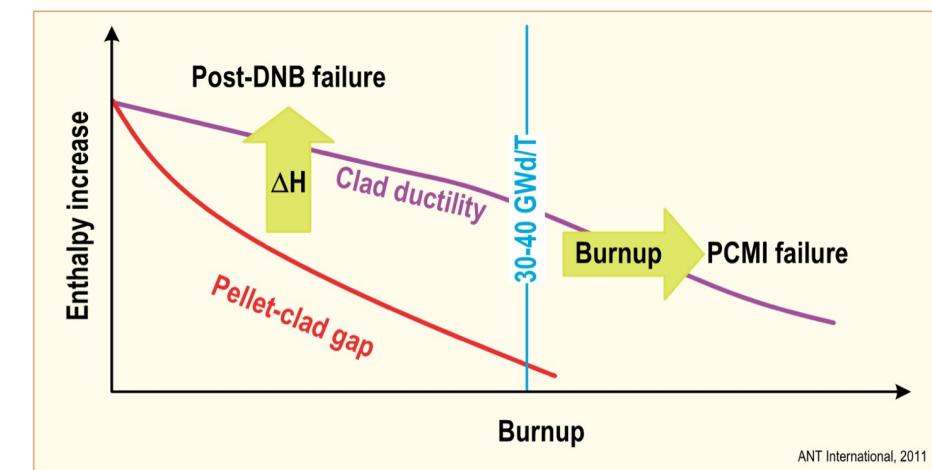
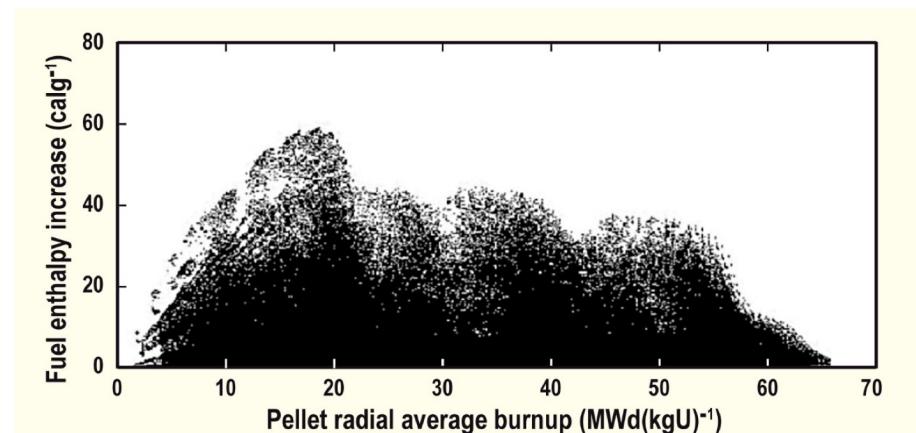
Reactor, accident scenario	Pulse width [ ms ]	Max fuel enthalpy [ J(gUO <sub>2</sub> ) <sup>-1</sup> ]	Max ent. increase [ J(gUO <sub>2</sub> ) <sup>-1</sup> ]	Rod worth [ 10 <sup>-5</sup> ]	Literature sources [ references ]
<b>PWR:</b>					
CREA HZP	25–65	110–320	40–250	600–940	[9, 10, 14–18]
CREA HFP	400–4500	230–350	1–130	40–200	[10, 14, 17, 19–21]
<b>BWR:</b>					
CRDA CZP	45–75	140–460	130–450	700–1300	[10, 11, 14, 22]
CRDA HZP	45–140	160–00	90–320	600–1300	[10, 22, 23]
<b>HZP:</b> Hot zero power, <b>HFP:</b> Hot full power, <b>CZP:</b> Cold zero power					
ANT International, 2016					



# Effect of Burnup

- Fuel rod damage correlates with the peak value of fuel pellet specific enthalpy; the higher the enthalpy increase, the more extensive is the damage
- Fuel enthalpy increases are higher in fresh fuel
- Cladding failure occurs at lower fuel enthalpy increases for irradiated than for fresh fuel rods, and that the susceptibility to failure increases with increasing fuel burnup
- The degree of cladding waterside corrosion, is very important for survivability of preirradiated fuel rods
- Safety criteria are defined in terms of limits on the radially averaged fuel pellet specific enthalpy, or the increase of this property during the accident

$$h_f(T_f) = \int_{T_0}^{T_f} c_f(T) dT$$



# RIA Summary

- Reactivity insertion accident
  - often in PWR/BWR dependent upon control rod ejection/drop
  - can be caused by changes in coolant
- Shorter pulses have greater impact than longer pulses (given same energy deposition)
- Effects of RIA depend on burnup
  - fission gas, FCMI, oxide layer, hydrides, cladding pressure, etc.