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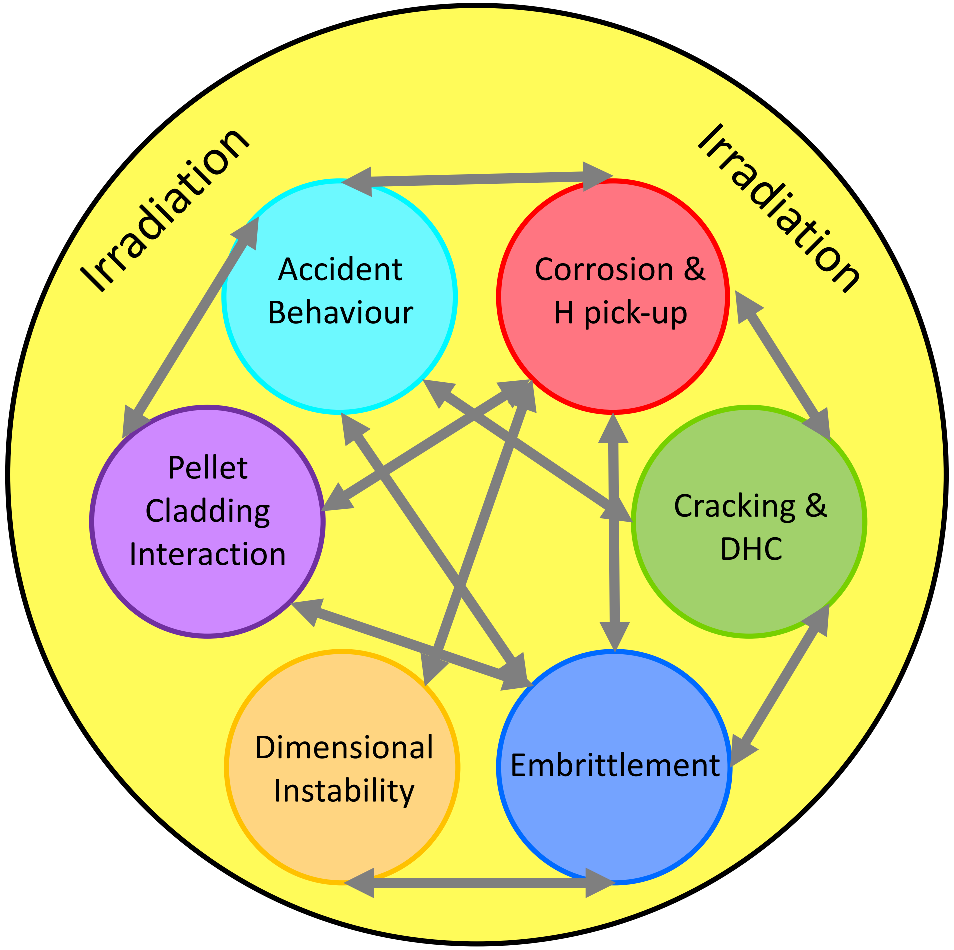
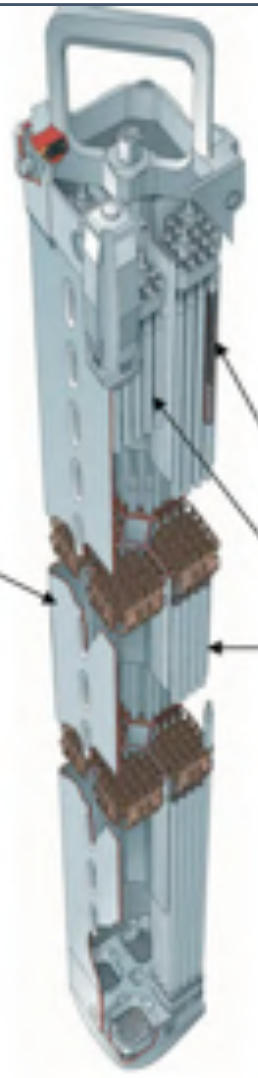


Schematic of the complex interactions between different degradation processes in Zr alloys in a nuclear reactor.

Reactor Environment

BWR
Boiling Water Reactor



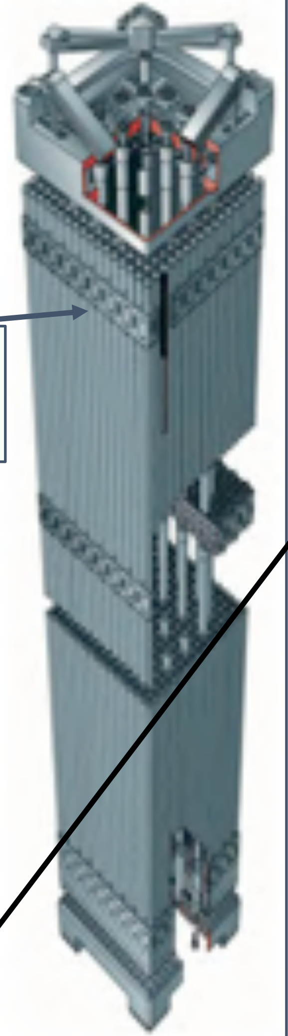
Channel material:
Zircaloy-2 in
β-quenched condition

Cladding tubes:
Zircaloy-2/Liner

Boiling water at
274 – 288°C
with
pH 5.6, 50ppb H_2

PWR
Pressurized Water Reactor

Cladding tubes:
Zircaloy-4/Zr-Nb alloys



Pressurised water
(~20MPa) at
290 – 338°C
with
pH 7.2, 3000ppb H_2

Radiolysis of water → oxidation. So, H_2 added to minimise radiolysis.

Primary water also usually has additions of 2 wt.ppm of LiOH (to control PH) and 1000 wt.ppm of H_3BO_4 (to control reactivity)

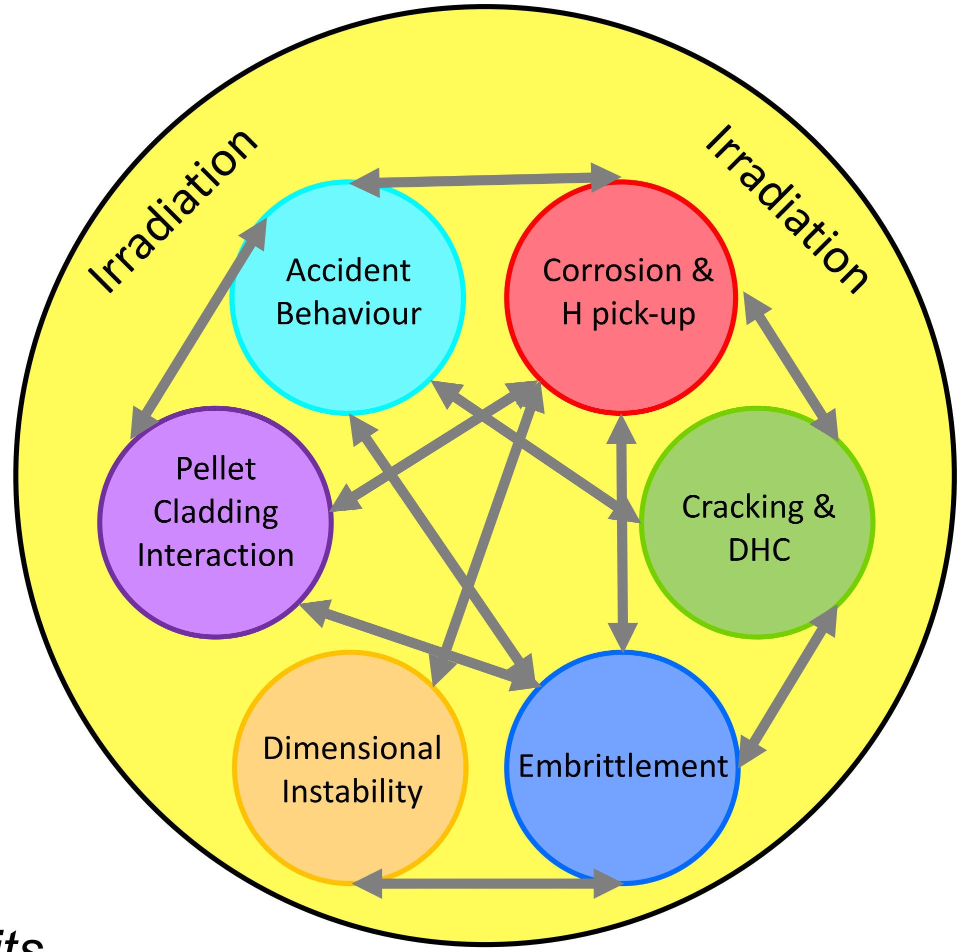
Zr Alloy Degradation

Reactor environment gives rise to multiple, complex, inter-linked processes;

- Corrosion and hydrogen pick-up

- Pressurised water at around 300°C is extremely aggressive.
- Hydrogen is by-product of corrosion process.

- Hydride precipitation and embrittlement.
- Irradiation damage and irradiation hardening.
- Irradiation growth and creep.
- Fretting fatigue.
- Pellet-Cladding interaction.



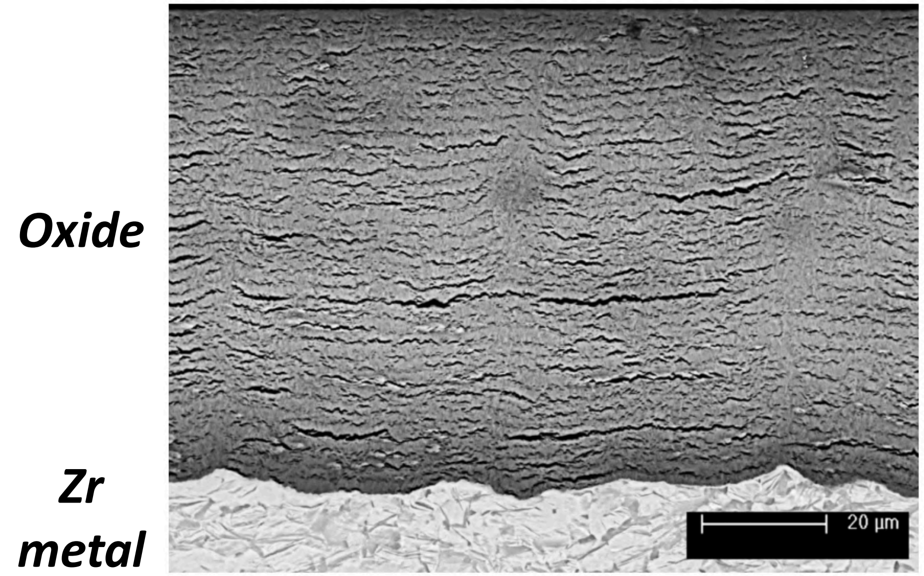
Material properties must be maintained within strict safety limits.

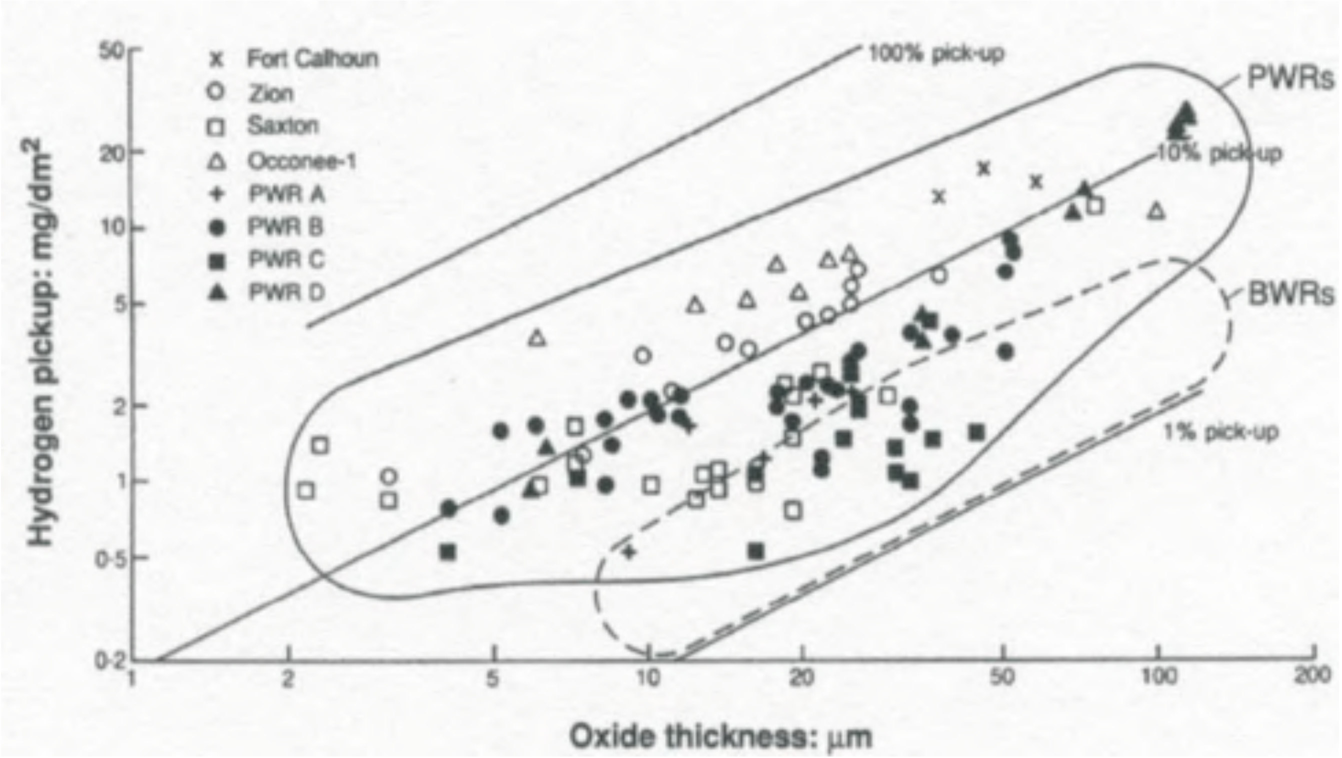
Zr Oxide

- Zr forms dense layer of stable oxides with high melting point and well bound to the metal.

- In most environments, this is more stable than Ti or Steel.

- Oxide layer protects from hydrogen ingress and hydriding.



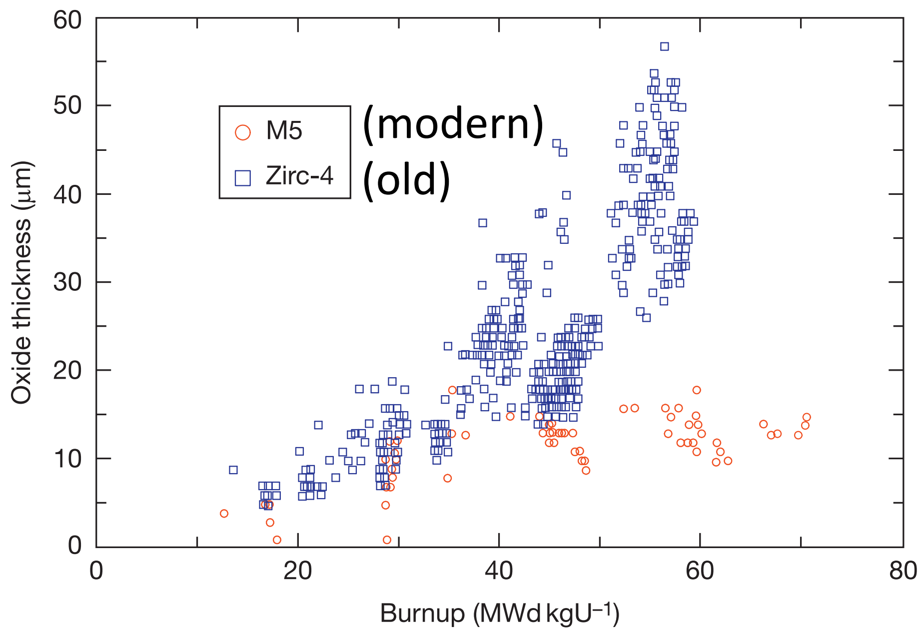


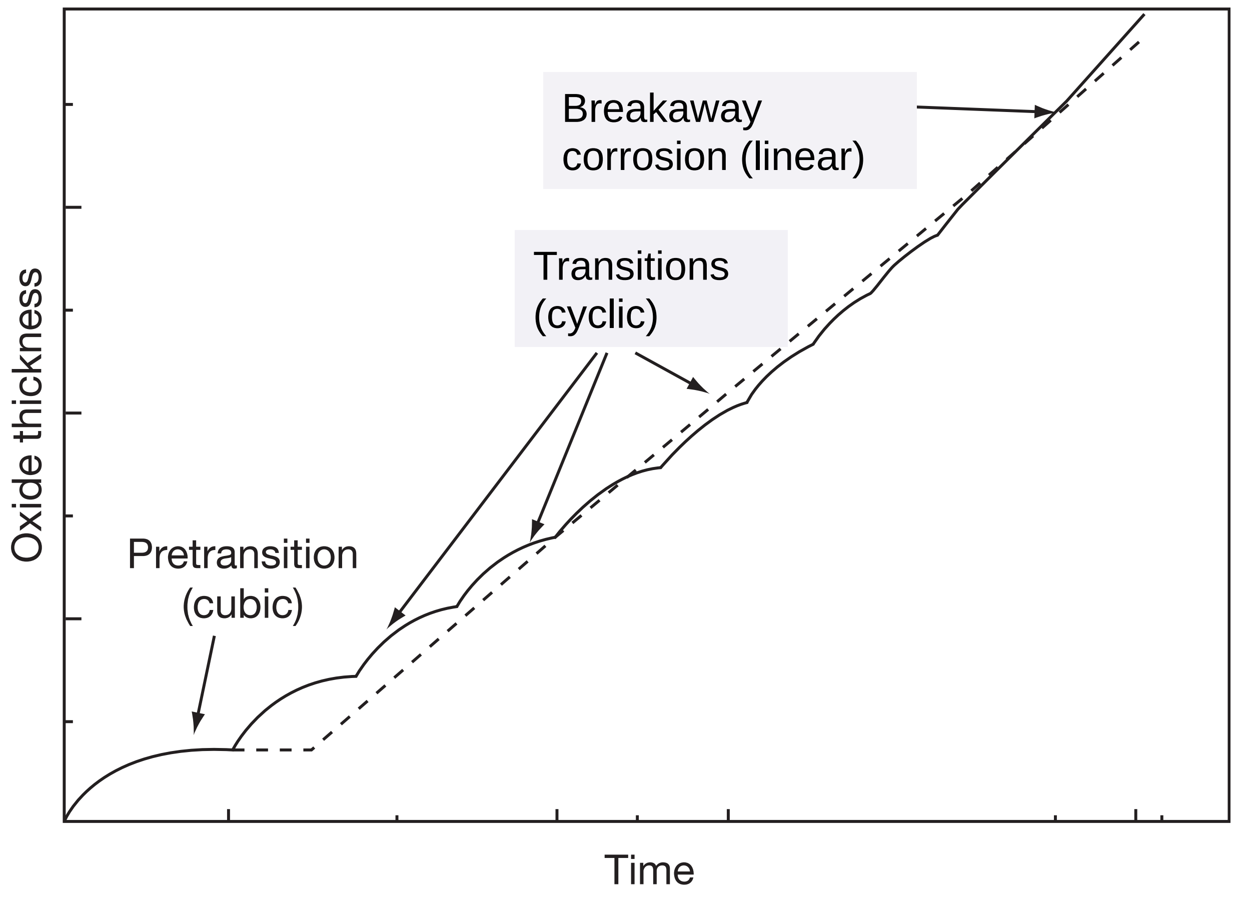
Why is hydrogen pickup less in BWRs than PWRs?

Zr-alloy, steam tested for 600 days at 415°C

Zr Oxide

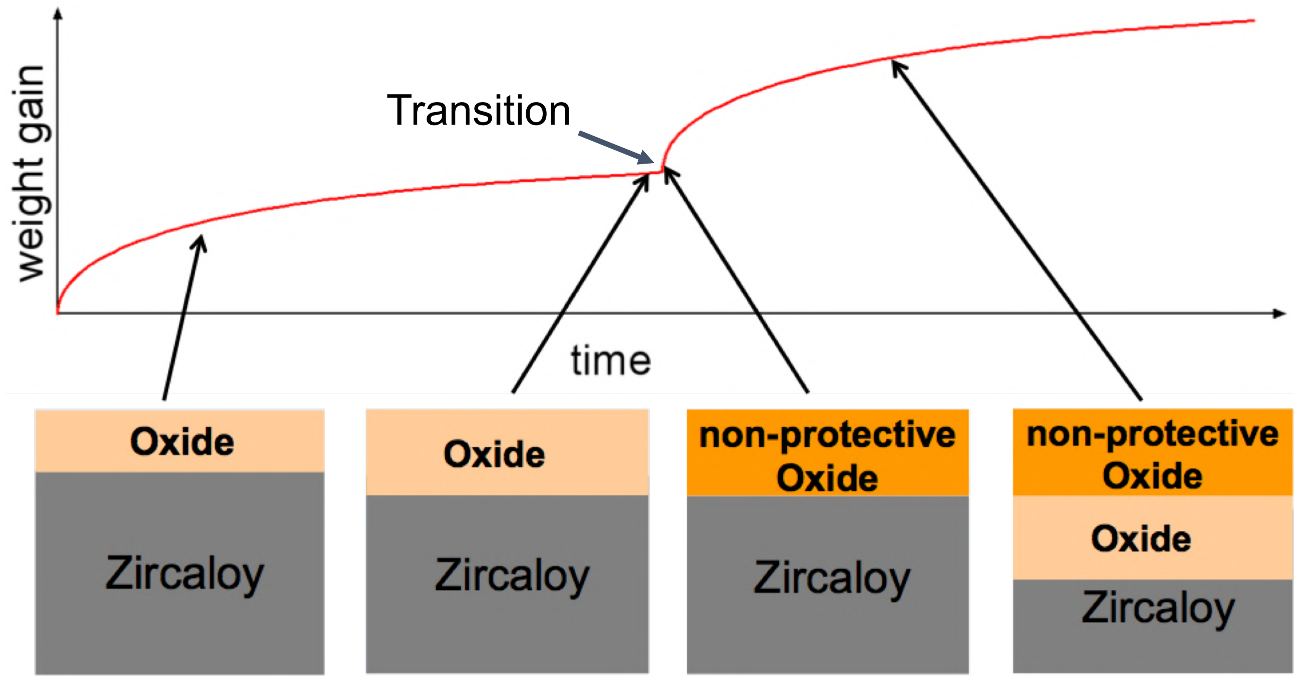
- If oxide gets too thick it can form thermal barrier between fuel and coolant.
- Mechanism poorly understood.
- Development largely empirical.



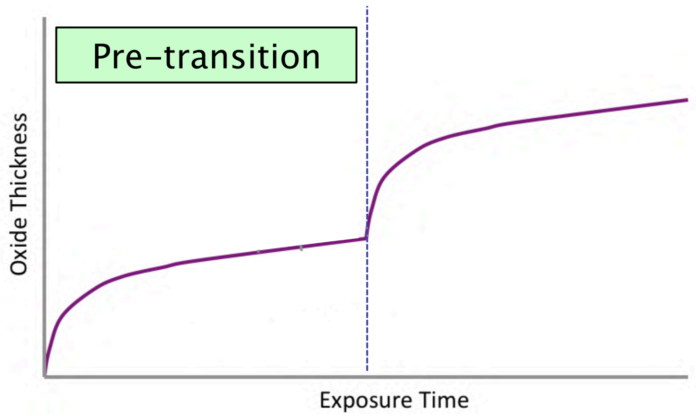


Cladding Corrosion

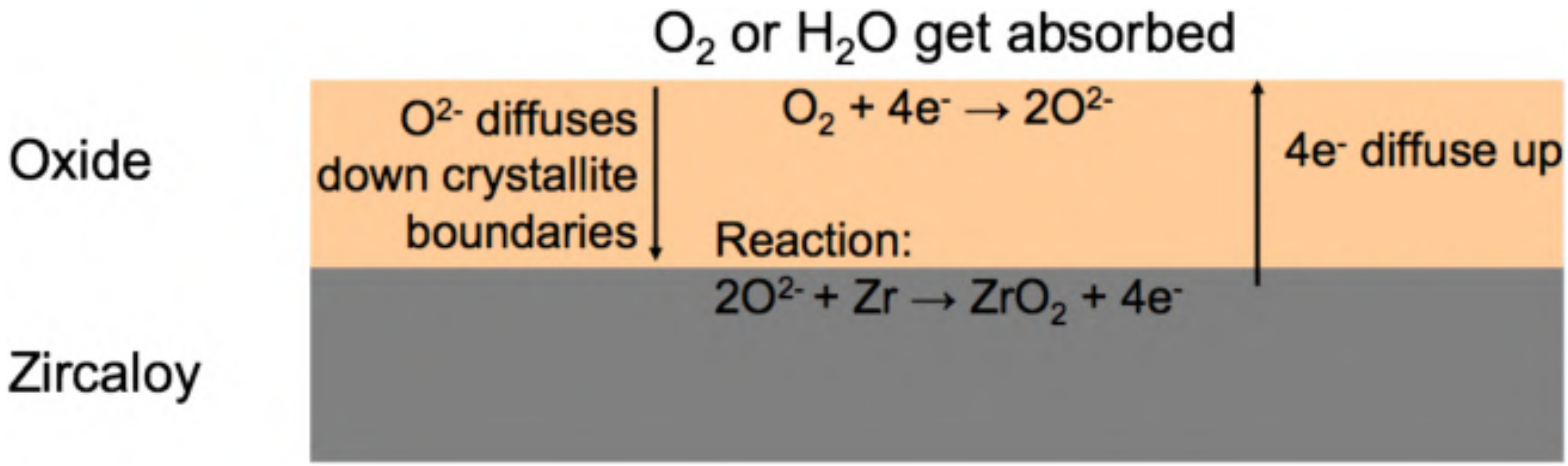
- $Zr + 2O^{2-} \rightarrow ZrO_2 + 4e^-$
- Oxygen ions diffuse faster through the oxide than Zr ions.



Cladding Corrosion



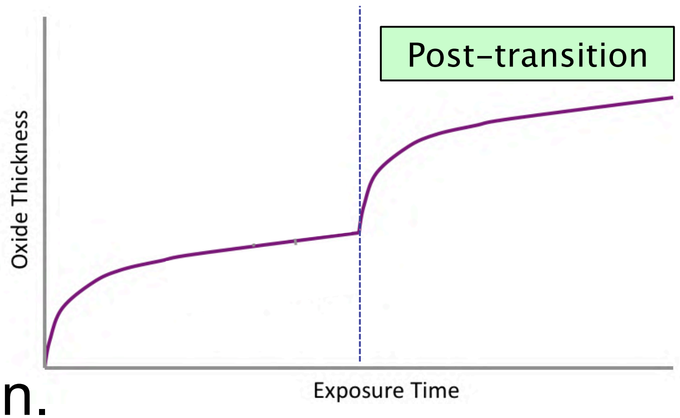
- ***Pre-transition;***
- Formation of the oxide takes place at metal/oxide interface.
- Corrosion rate slows as oxide thickens.

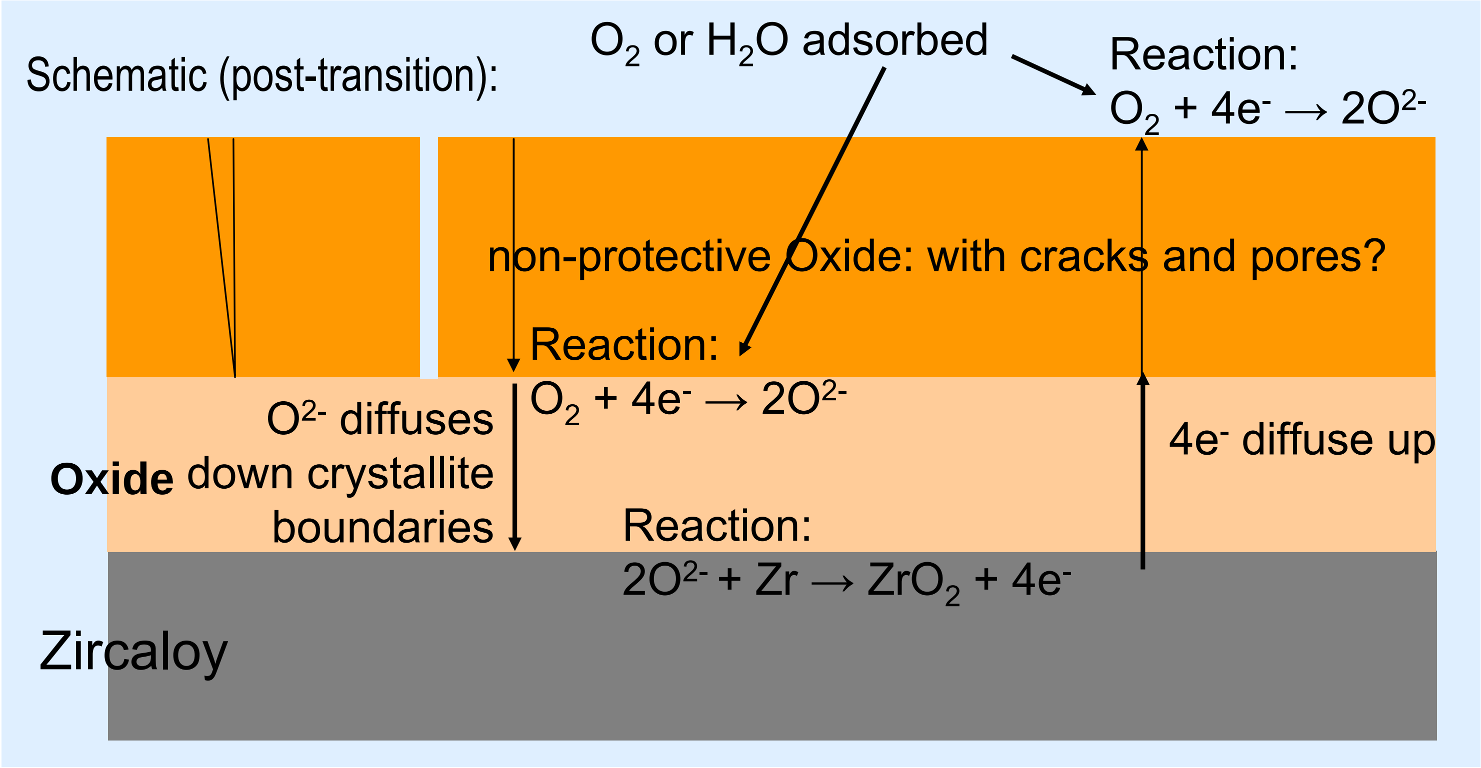


Cladding Corrosion

- ***Post-transition;***

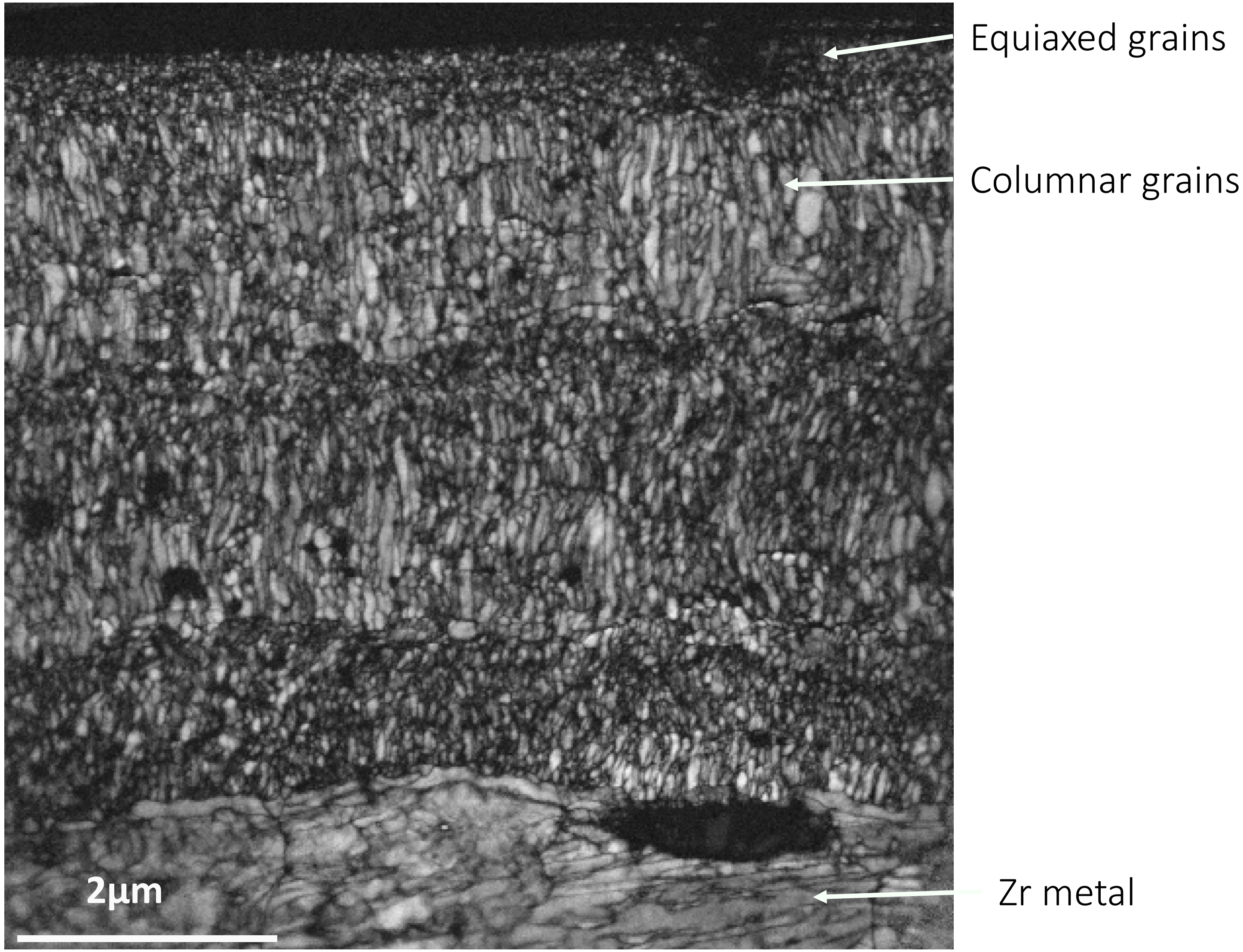
- Part of protective oxide breaks down.
- Oxidising species can penetrate the non-protective oxide.
- Shorter path for oxygen and hydrogen → accelerated corrosion.





Zr Oxide Microstructure

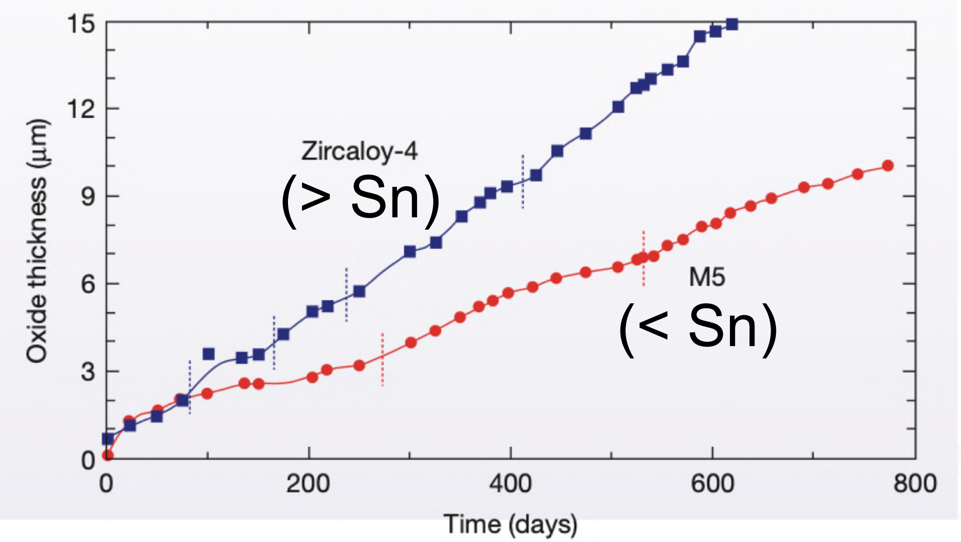
- Periodic layered structure of alternating columnar and equiaxed grains.

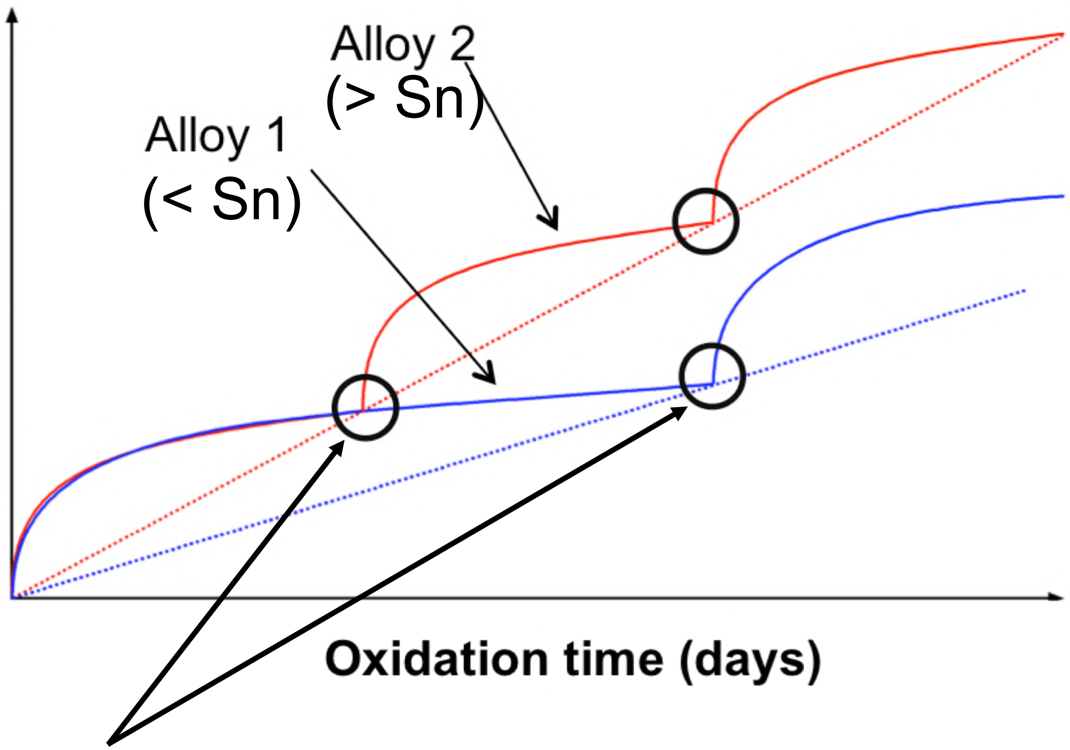


Zr-alloy (Nb, low Sn) after 585 days exposure to pure water at 360°C

Cladding Corrosion

- Time of transition may determine overall corrosion rate.
- Decreasing Sn content delays time of transition.

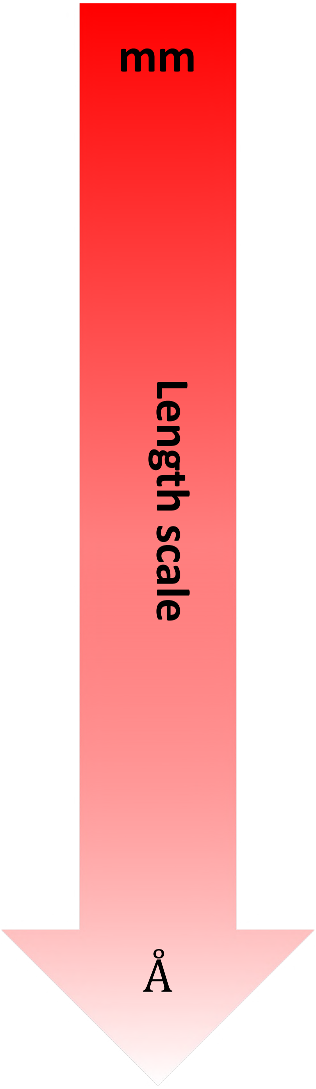




Why does oxide become unprotective?

How do we study corrosion mechanisms?

- ***In-situ electrochemical impedance spectroscopy;***
  - Oxide properties.
- ***Synchrotron X-ray diffraction (SXRD);***
  - Stress, oxide phase fractions, texture, in-situ studies.
- ***Raman spectroscopy;***
  - Stress, oxide phase fractions
- ***Scanning electron microscopy (SEM);***
  - Microtexture.
- ***Transmission electron microscopy (TEM);***
  - Oxide microstructure, nano porosity, metal/oxide interface.
- ***3D atom probe;***
  - Nano chemical analysis.



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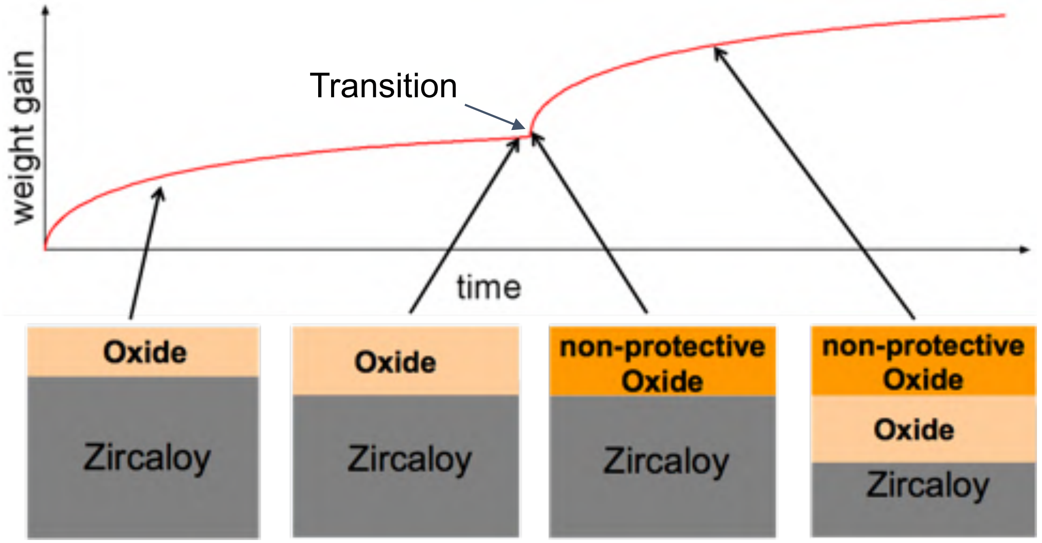
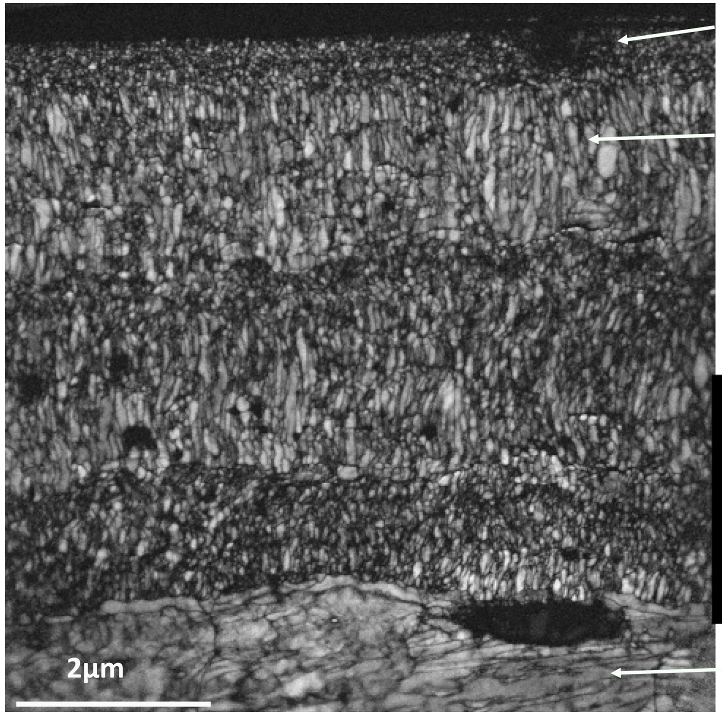
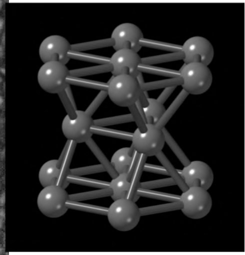


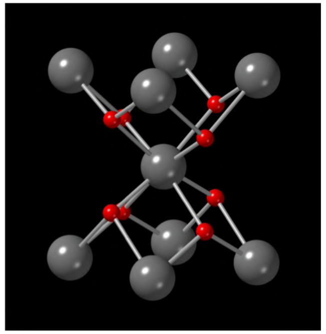
Schematic of the cyclic oxide weight gain and transition between protective and non-protective oxide.

Why does oxide become unstable / unprotective?

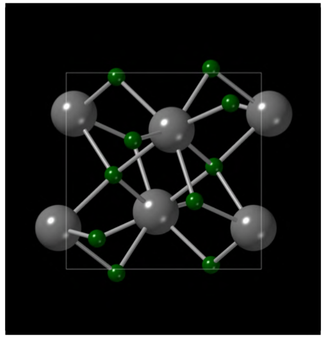
- ***What we know;***
- Oxide consists of nano-sized ***equiaxed*** and ***columnar*** grains
- Oxide made up of two phases
  - Tetragonal phase is stress stabilised
  - Tetragonal grains stabilised by *grain size, compressive stresses and alloying elements (Sn)*
  - Tetragonal → monoclinic = volume increase







Tetragonal, $a = b \neq c$, $\alpha, \beta, \gamma = 90°$



Monoclinic, $a = b \neq c$, $\alpha \neq 90°, \beta, \gamma = 90°$

Why does oxide become unstable / unprotective?

- ***What we know;***
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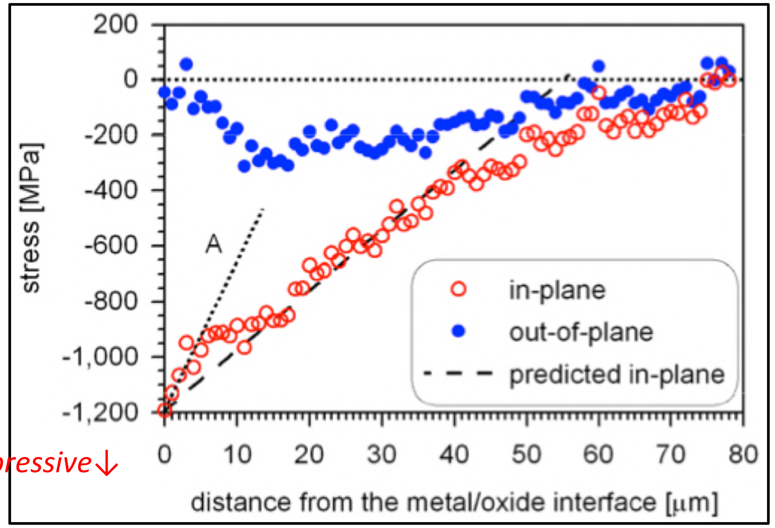
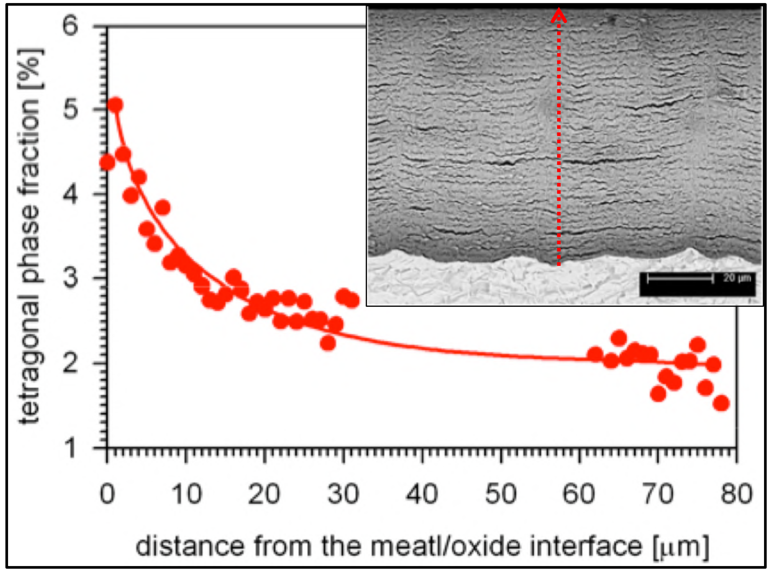
- Oxide made up of two phases
  - Tetragonal phase is stress stabilised
  - Tetragonal grains stabilised by *grain size, compressive stresses and alloying elements (Sn)*
  - Tetragonal → monoclinic = volume increase
- Large compressive stresses in the oxide
  - due to volume expansion of Zr → ZrO_2 (1.56)
  - stress becomes lower away from metal/oxide interface

compressive↓





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  - Tetragonal → monoclinic = volume increase
- Large compressive stresses in the oxide
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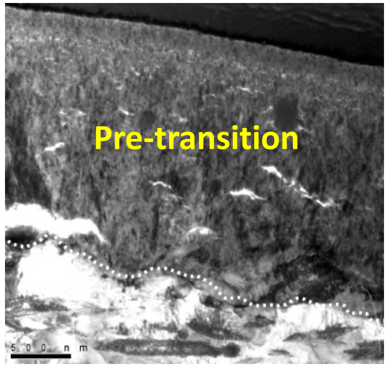
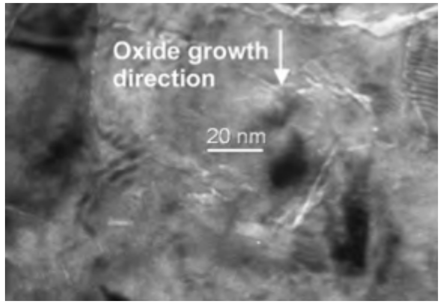
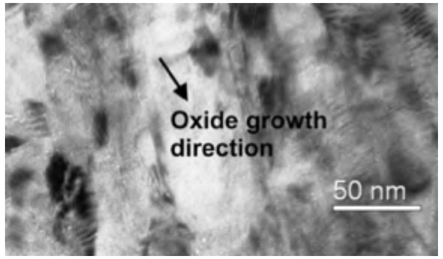
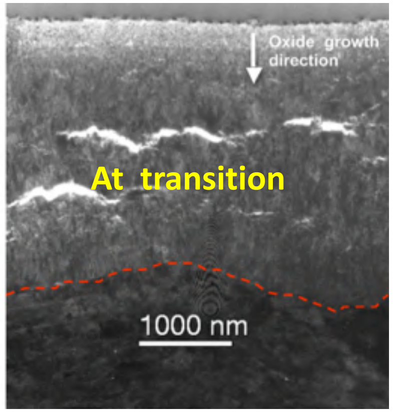
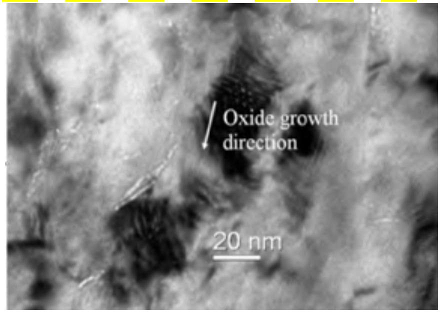
  - stress becomes lower away from metal/oxide interface
- TEM shows porosity at grain boundaries
  - At transition, nano-porosity links up and extends close to the metal/oxide interface.



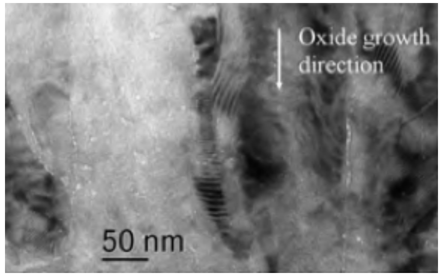








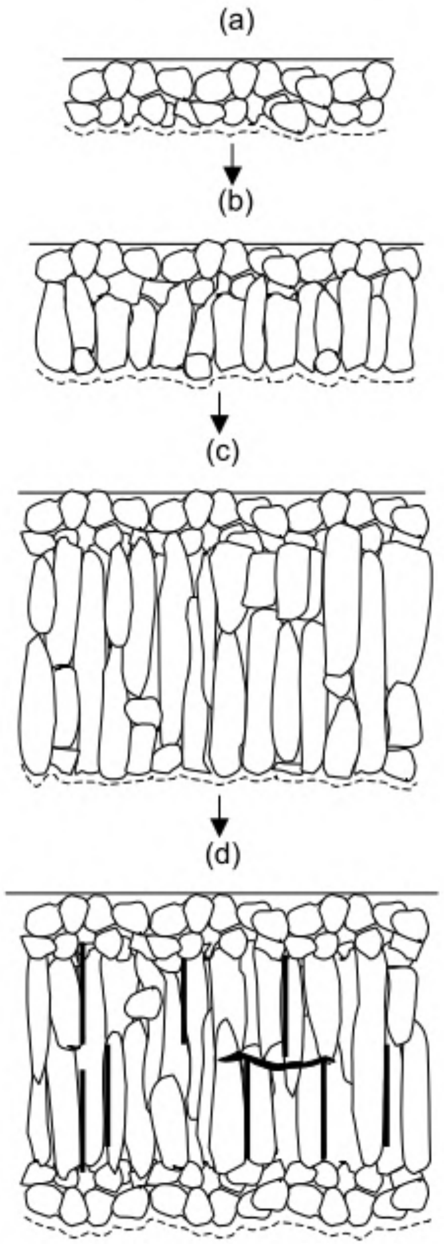
Linked pores at 350 nm from the m/o interface



Network of pores at 700 nm from the m/o interface

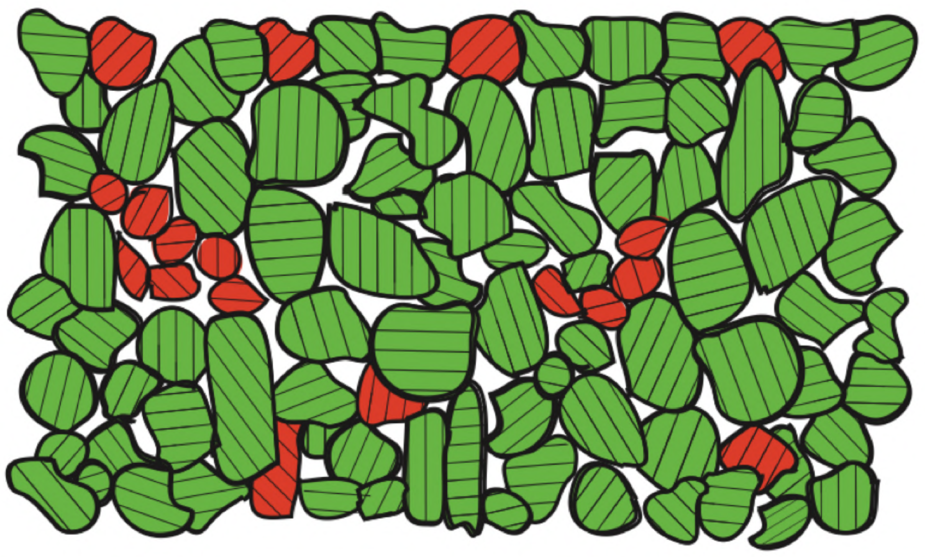
Transition Scenario

1. Monoclinic and tetragonal grains form.
2. Volume expansion from metal → monoclinic + tetragonal → higher stresses at metal/oxide interface.
3. Columnar oxide grains with favoured crystallographic orientation grow → slower corrosion rate.
4. Tetragonal grains remain stabilised by small size, compressive stress and alloying addition (Sn).
5. As oxide front grows, stress drops, which destabilises any tetragonal grains. (Note, *Sn → larger tetragonal grains, which become destabilised earlier.)*
6. Tetragonal to monoclinic transformation → volume expansion → cracking and interlinking of porosity.
7. Oxide becomes non-protective.
8. Nucleation rate increases and process repeats…

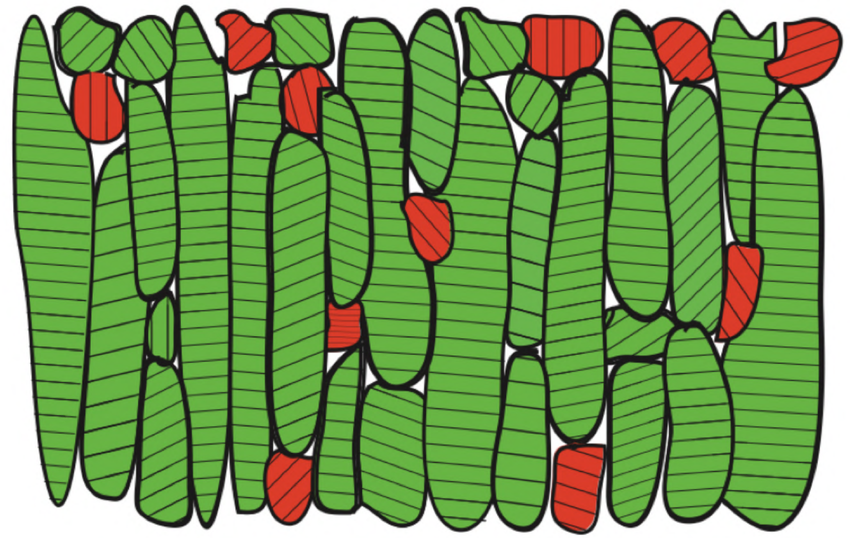


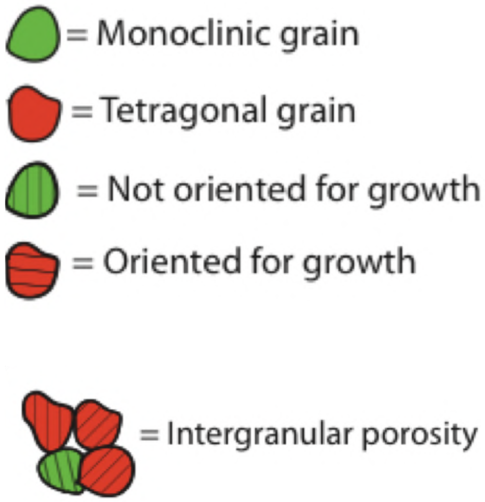
Equiaxed and Columnar Grains

Microstructure schematic - equiaxed



Microstructure schematic – columnar





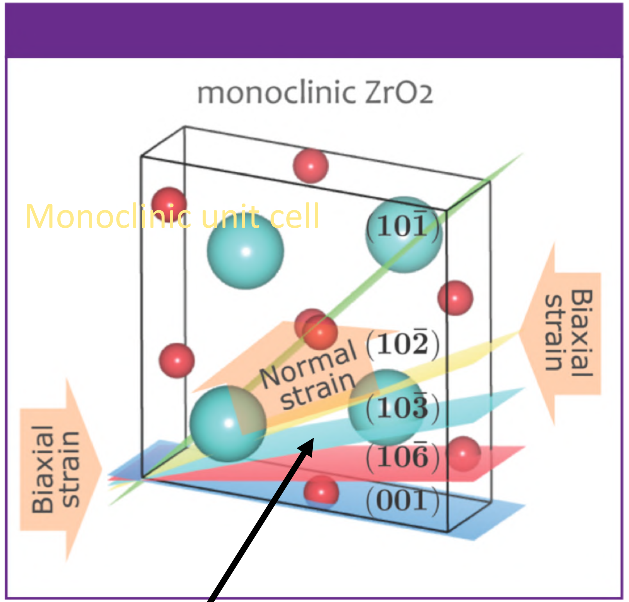
- Small equiaxed grains.
- High intergranular porosity.
- High-energy grain boundaries.
- ***Poor corrosion performance***.

- Large columnar grains.
- Low grain boundary density.
- Low-energy grain boundaries.
- ***Good corrosion performance.***

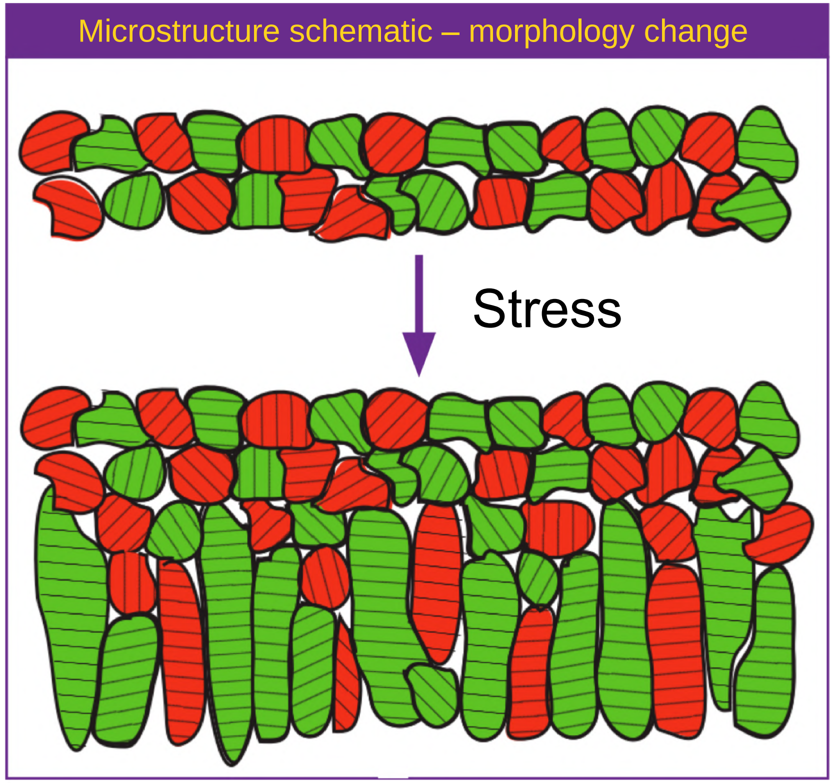
Equiaxed and Columnar Grains

Nucleation vs. growth depends on stress;

- ***Low stress*** → equiaxed grain growth with weak texture and poor corrosion performance.
- ***High stress*** → columnar growth of only [10-3] grains, with good corrosion performance.



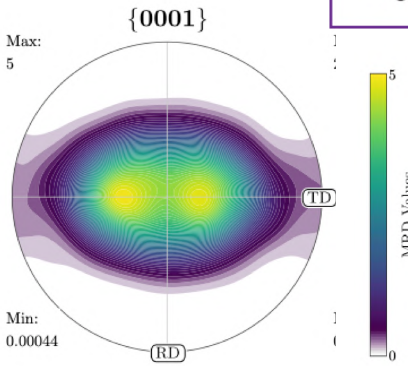
Low plane surface area and stiffness for (10-l), l=3,4,5,6



Texture dependence of Zr metal;

- ***Basal pole 30° from ND***

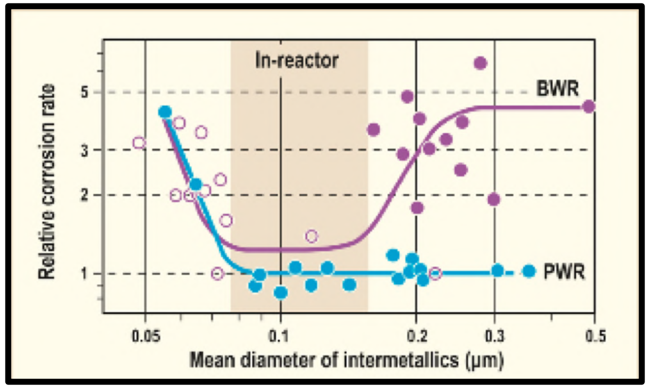
→ Higher stresses during metal-oxide transformation

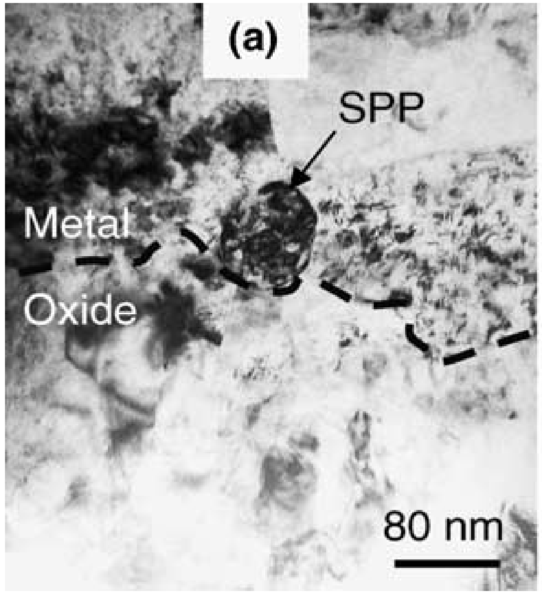


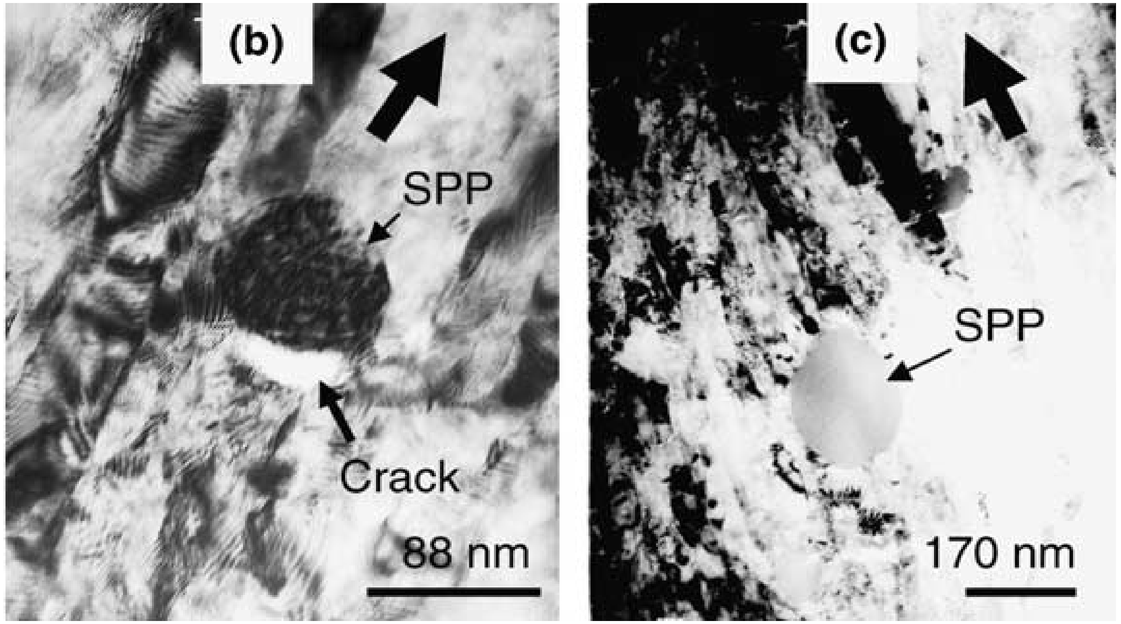
Role of SPPs in Cladding Corrosion

(Second Phase Particles)

- ***Types:*** $Zr(Cr, Fe)_2$, $Zr_2(Ni, Fe)$ and $Zr(Fe, Nb)$
- Seem to improve corrosion resistance.
- SPPs need a certain particle size distribution for optimum corrosion properties *(depends on alloying elements)*
- SPPs are more resistant to corrosion, they stay mainly uncorroded while the oxidation front passes, then corrode slowly in the oxide layer.
- *However, SPPs are also observed to nucleate cracks at metal oxide interface*



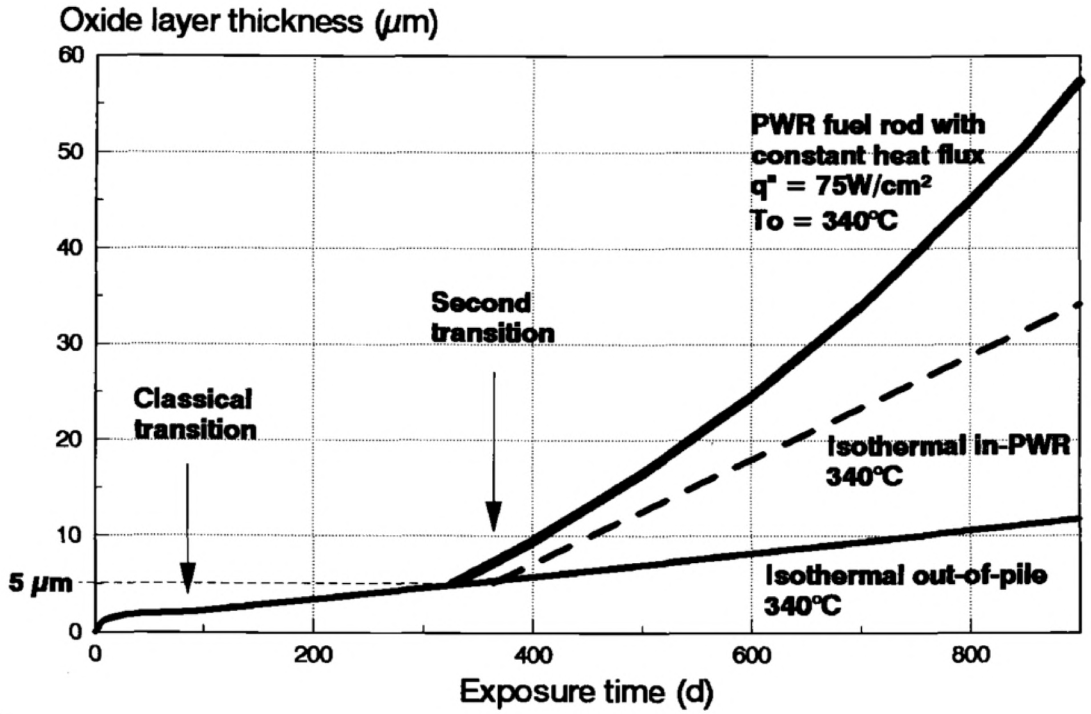




Effect of Irradiation on Corrosion

→ ***Accelerated corrosion***

- Irradiation damage in the metal *(SPP dissolution, damage)*
- Irradiation damage in the oxide (*increase tetragonal fraction*)
- Conductivity changes *(charged species mobility)*
- Water radiolysis *(increased oxidation)*



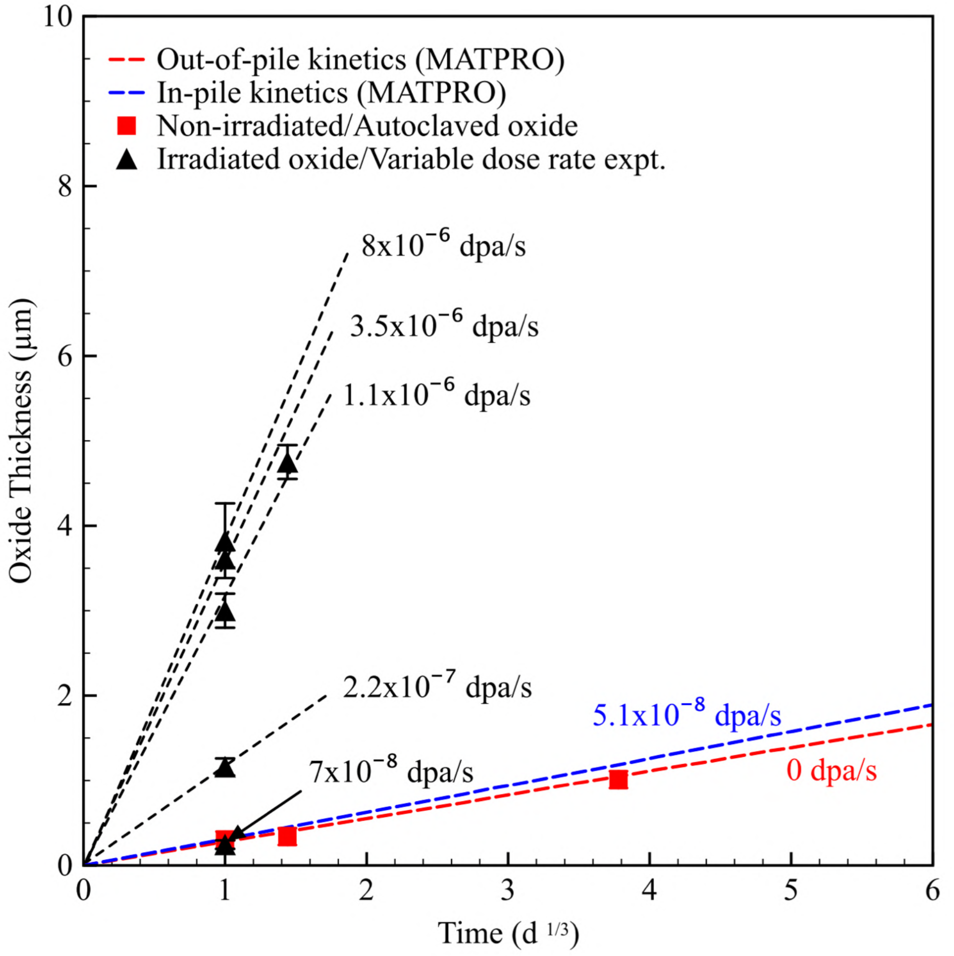


Fig. 5. Experimental measurements of the dependence of oxide layer thickness on damage rate.

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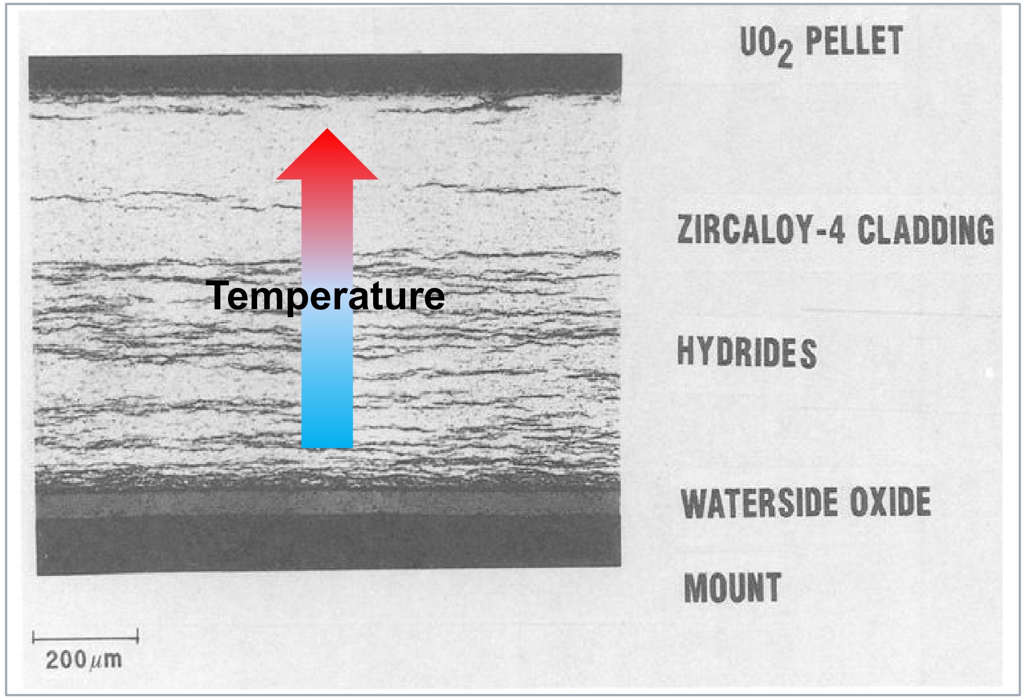
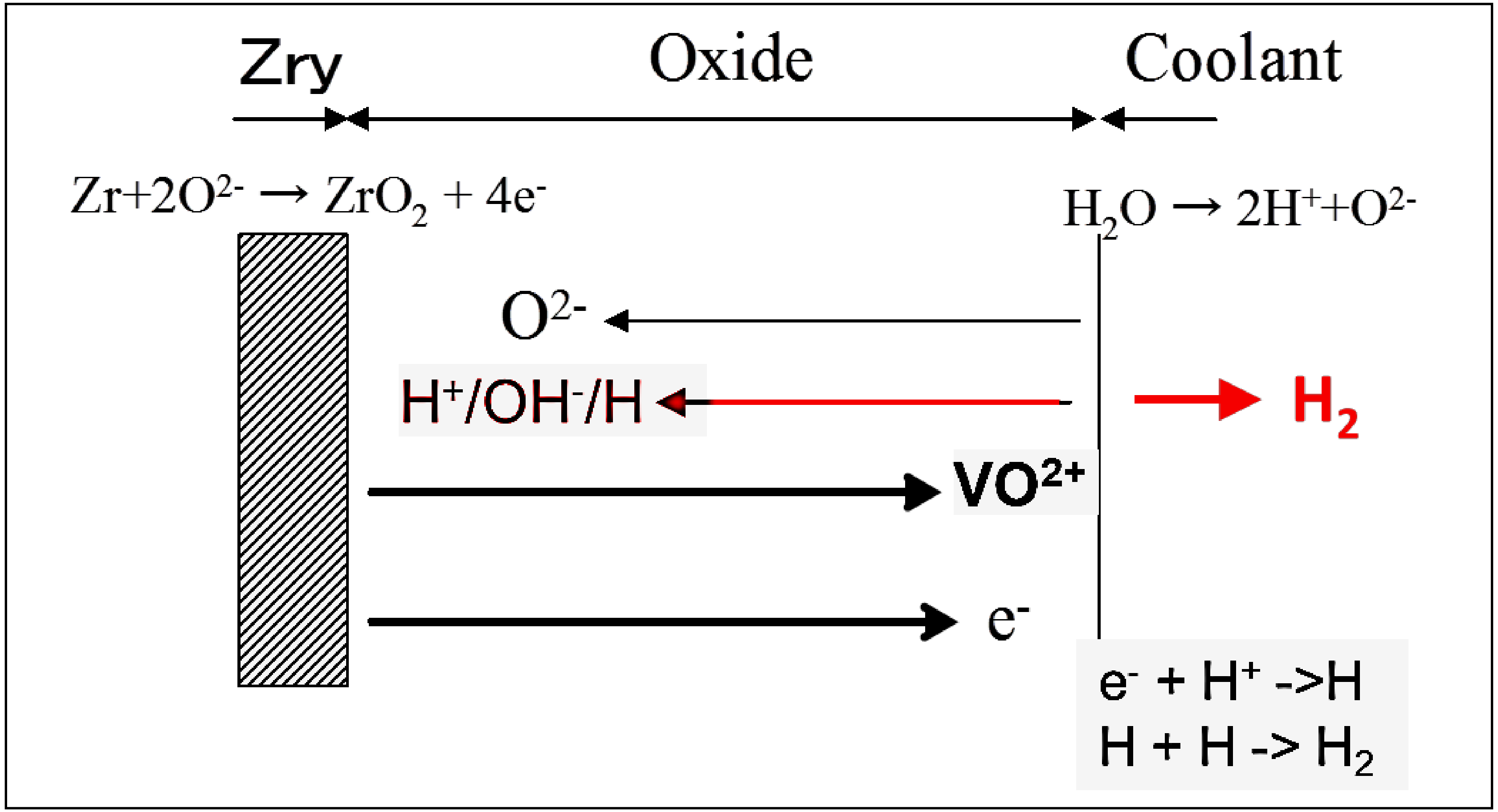


Hydride distribution within a Zr cladding tube, showing the effect of temperature gradient.

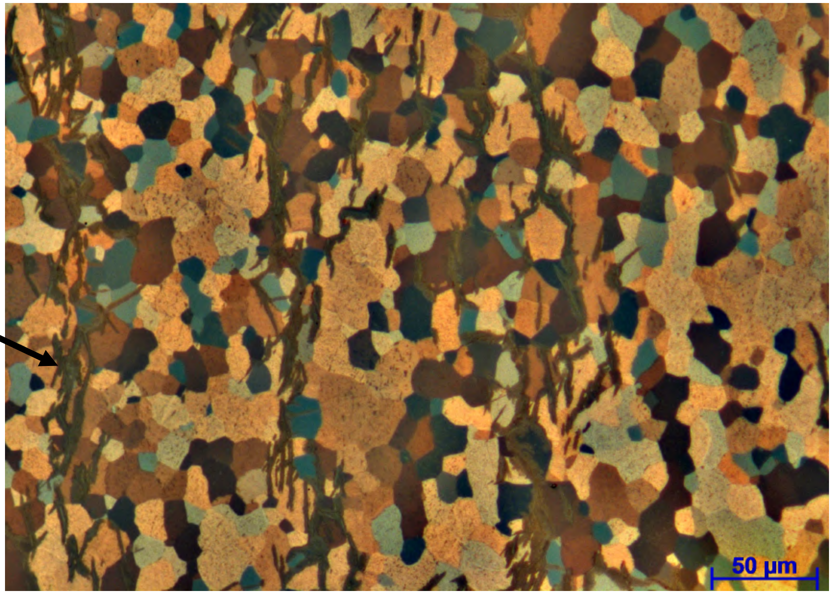
Hydrogen Pick-Up

- Hydrogen is taken up during corrosion of the cladding.
- Most dissociated H recombines into coolant water.
- Small fraction transported into Zr → ***hydrogen pick-up fraction***
- *Electrical conductivity plays an important role.*



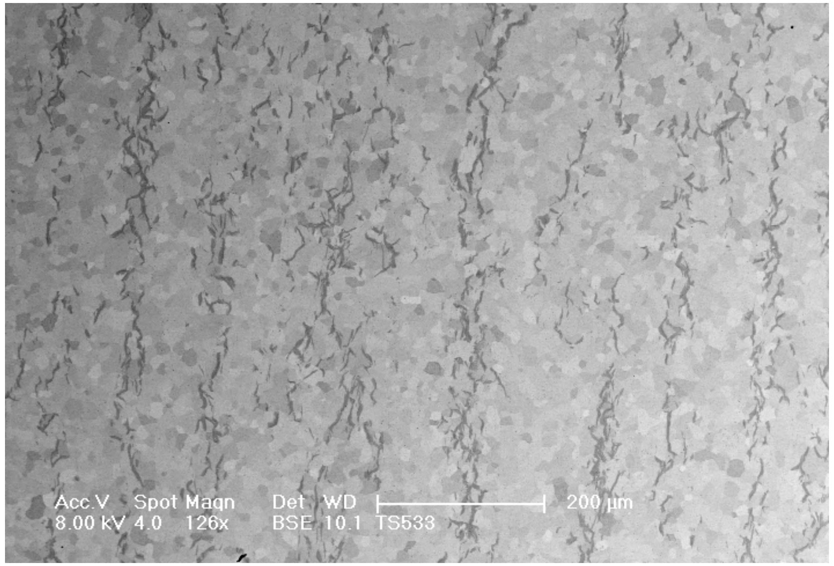
Why is hydrogen a problem?

- When the solubility limit is exceeded, H precipitates as ***zirconium hydrides***



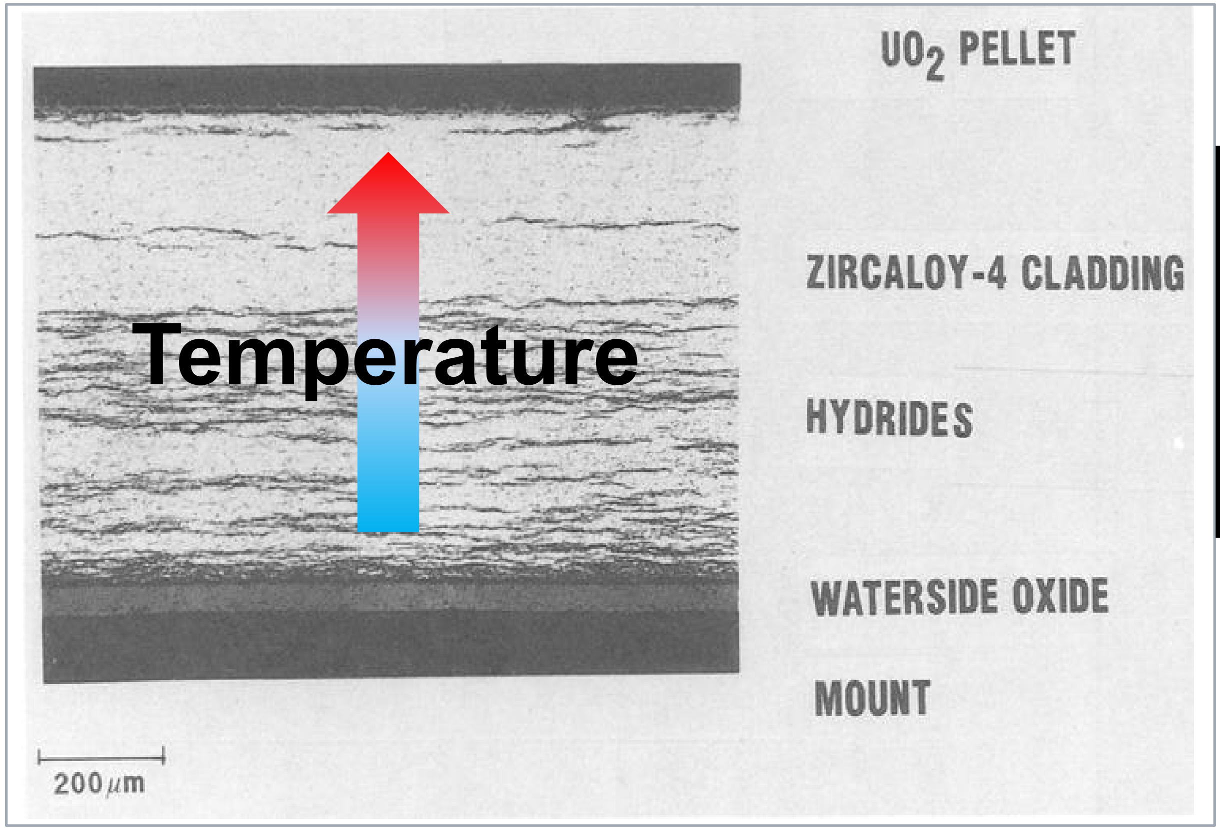
- Hydride precipitation affects corrosion performance and mechanical properties *(ductility, fracture toughness, creep and growth)*

- Number of different hydride phases
- *δ hydride (fcc) – stable - most common*
- *γ hydride (tetragonal) – metastable – rarely seen*
- *ε hydride (tetragonal) – stable – uncommon*

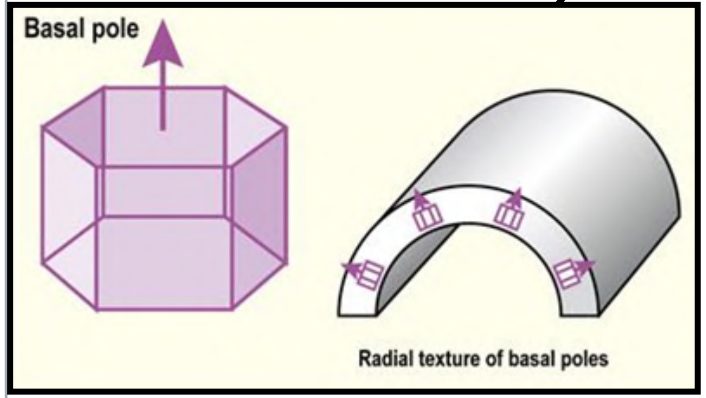


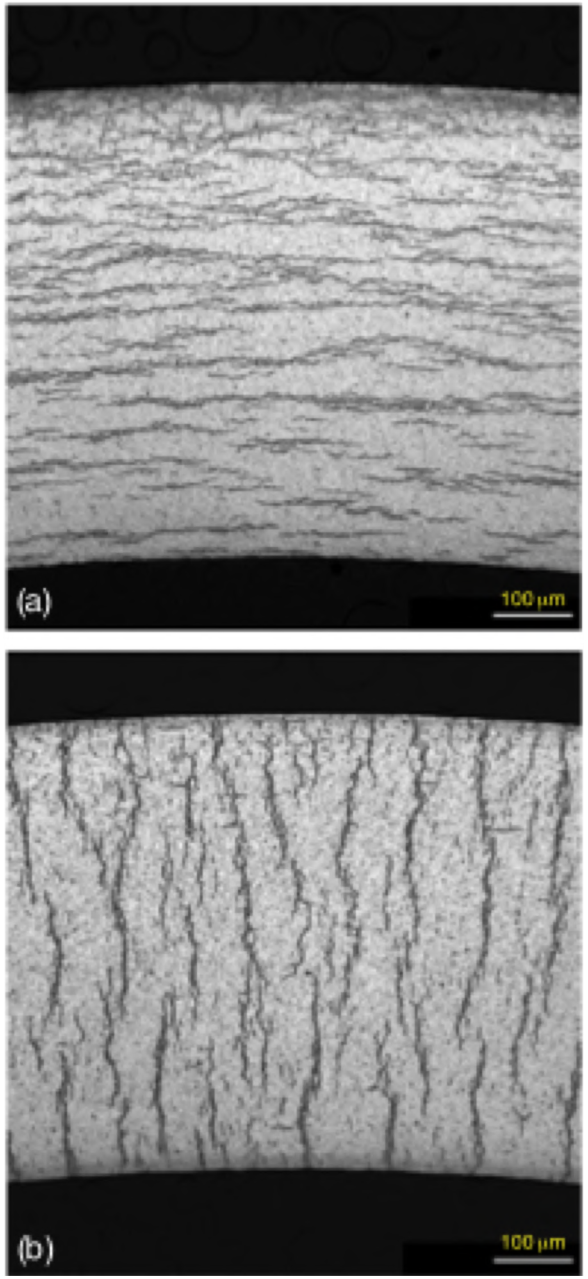
Hydride formation

- What produces these hydride distributions?



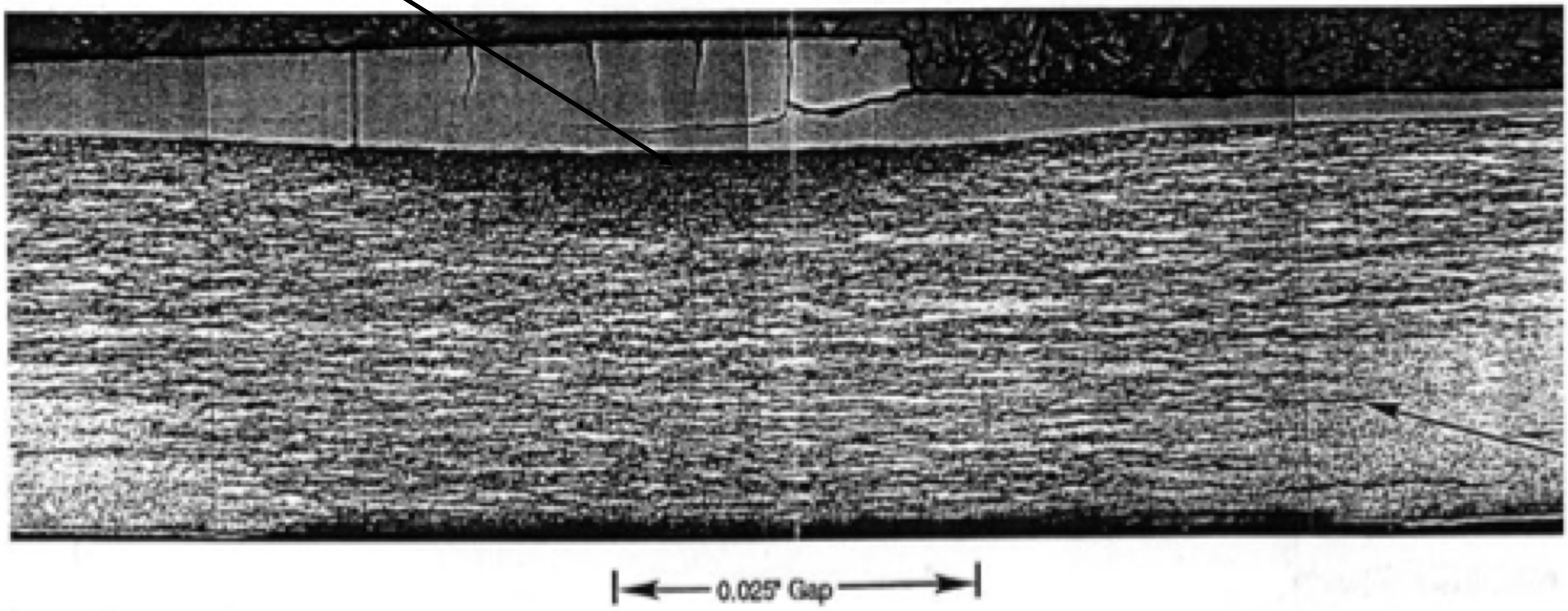
Texture



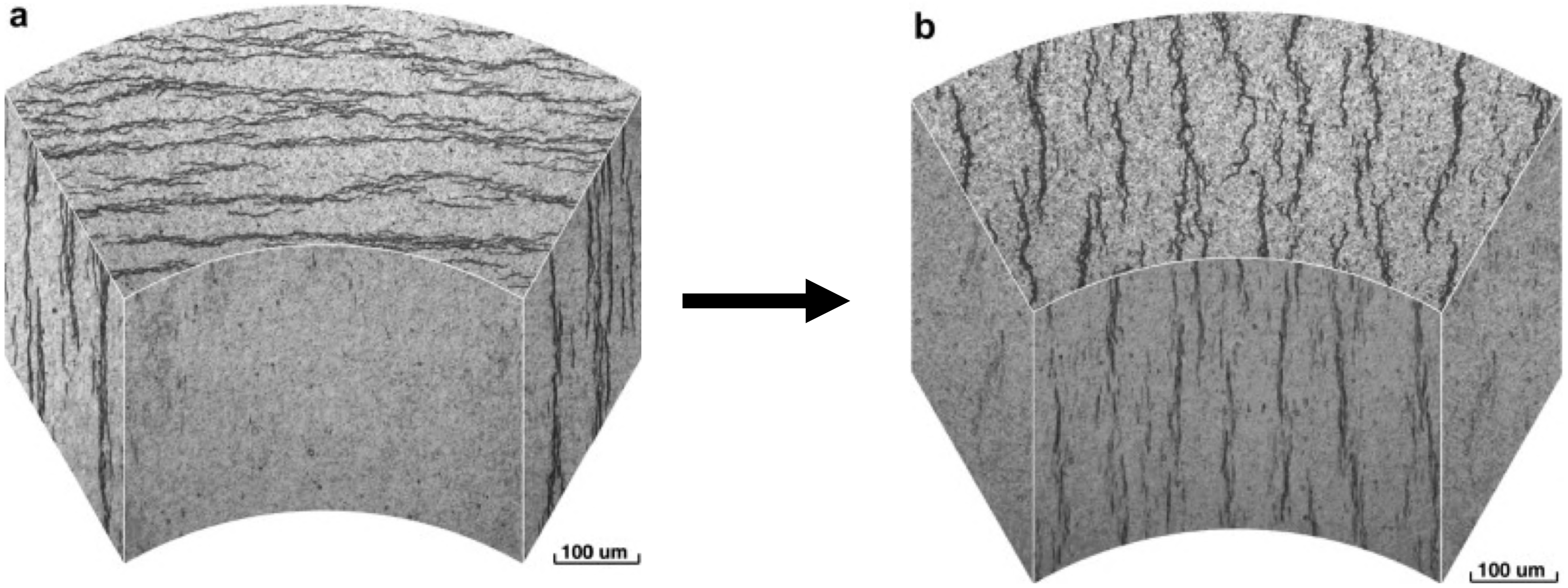


Hydride formation during operation

- Hydrogen can diffuse to cold spots (sites of oxide spalling) and form ***hydride lenses***



Hydride reorientation

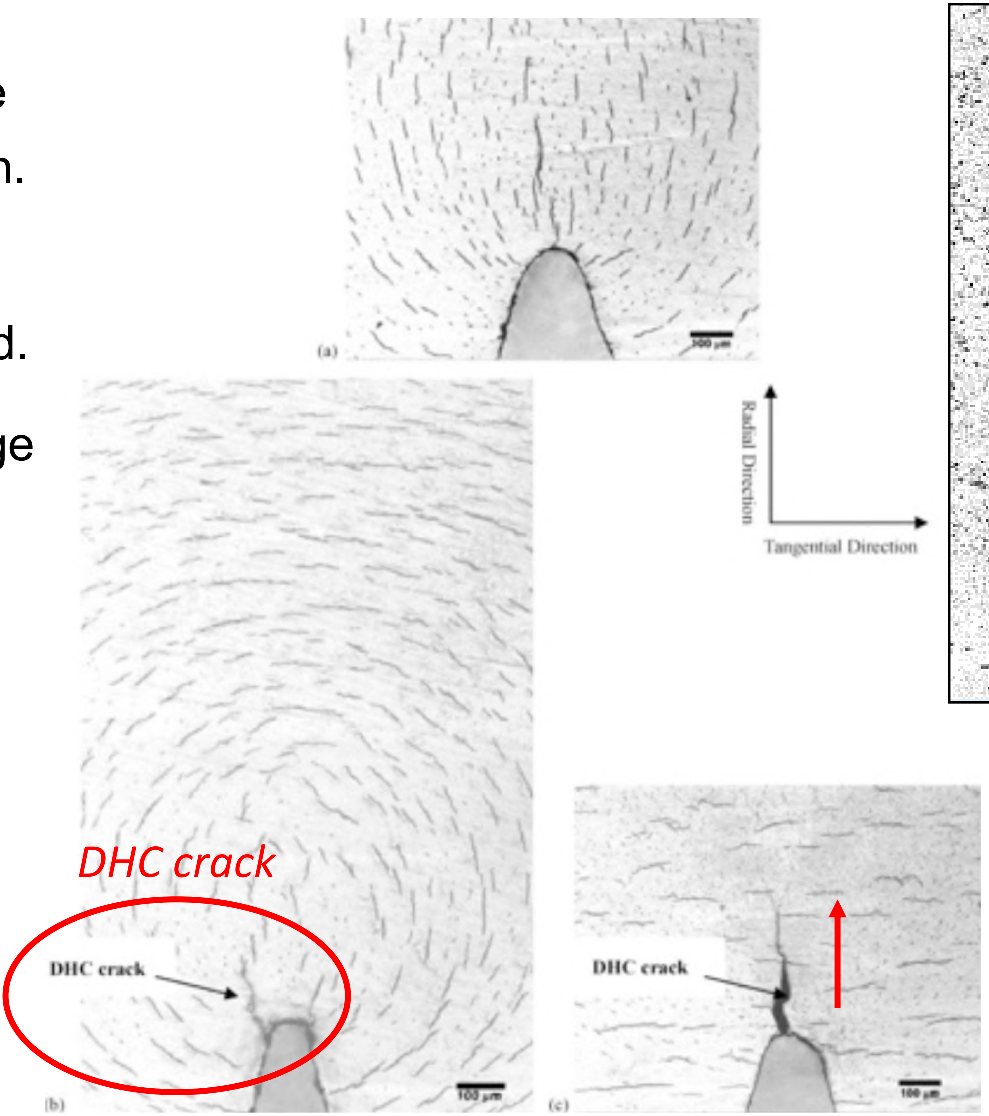


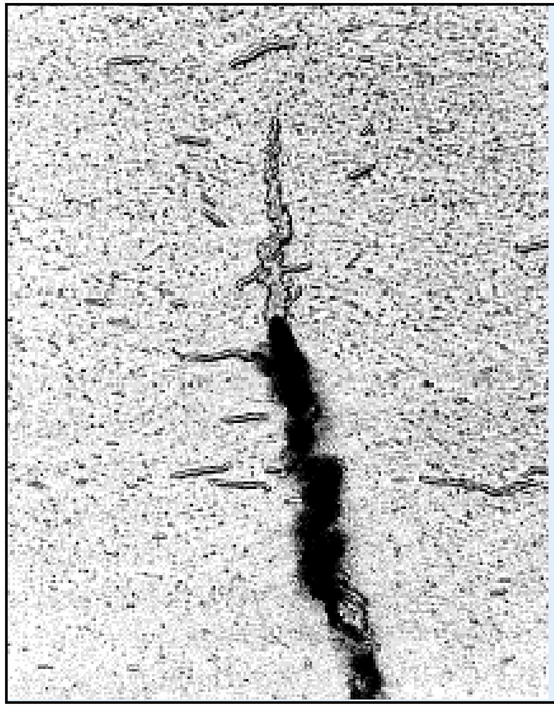
- Dissolution of circumferential hydrides and formation of radial hydrides.
- At high burnups, large internal pressure (hoop stress), higher H content.
- Stress reorientation can occur if there is a significant temperature variation.

Delayed Hydride Cracking (DHC)

1. Hydrogen diffuses to region of high tensile stresses, i.e. in front of a crack tip or notch.
2. At the crack tip, hydride platelets will precipitate once solubility limit is exceeded.
3. Brittle hydrides grow and crack due to large stresses.
4. Process repeats.

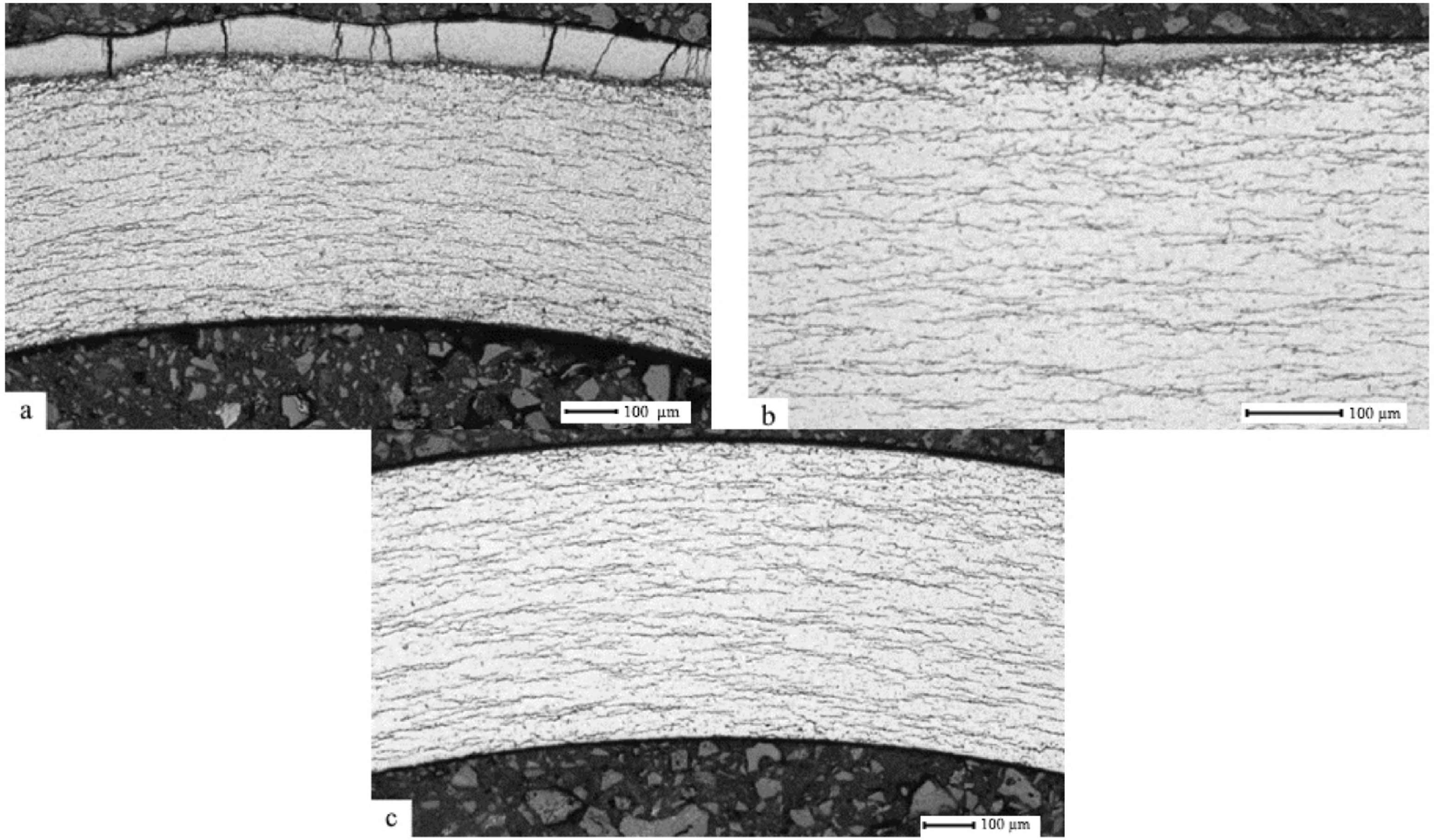
- ***Crack propagation rate determined by diffusion rate of hydrogen.***
- ***DHC also important for dry storage!***





How to minimise risk of DHC

- Keep hydrogen concentration below critical value.
  - Low initial hydrogen.
  - Low hydrogen ingress.
- Minimise hydrogen pick up.
  - Operational restrictions.
- Improve material properties.
  - Crystallographic texture.
- Minimise fabrication defects.



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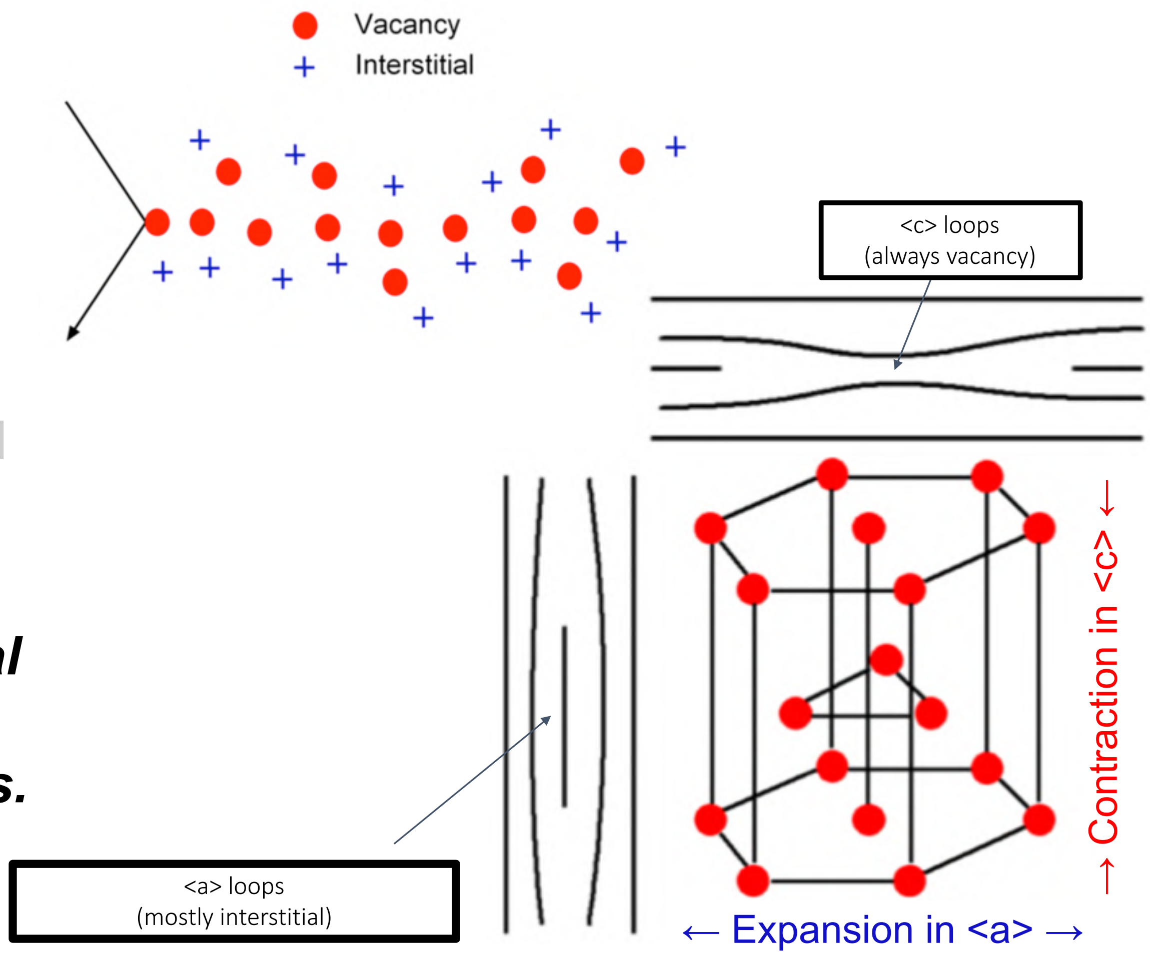
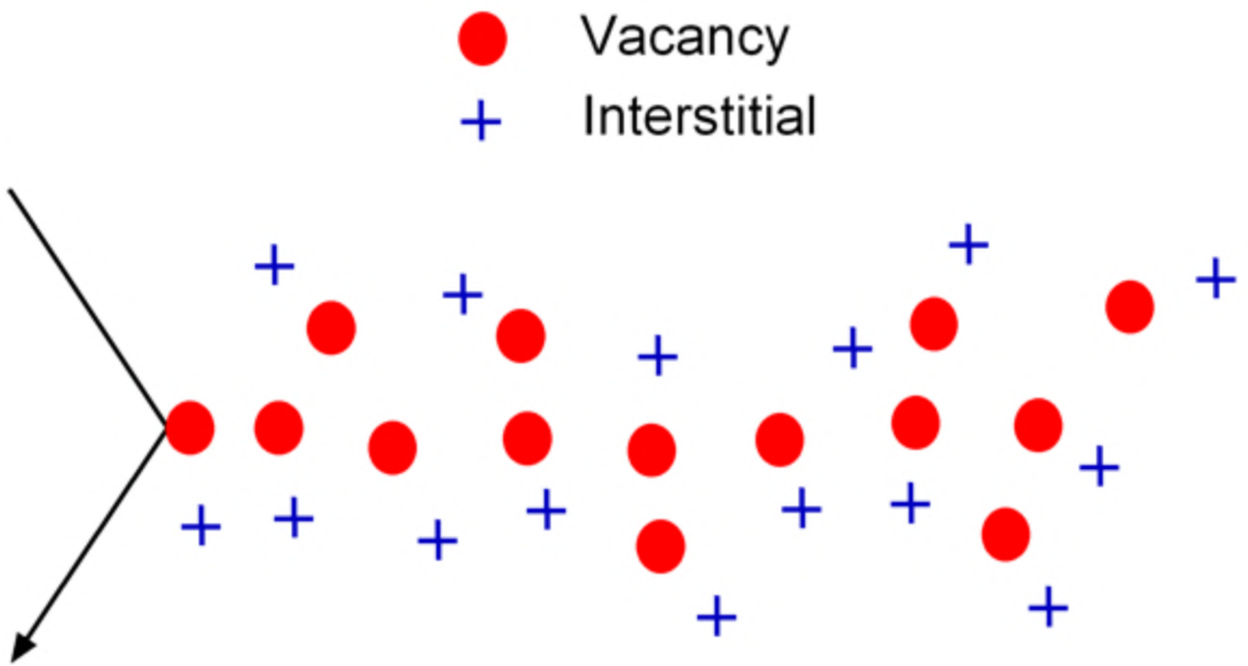


Schematic of neutron irradiation and subsequent irradiation growth of the Zr hcp lattice due to a diffusion anisotropy difference.

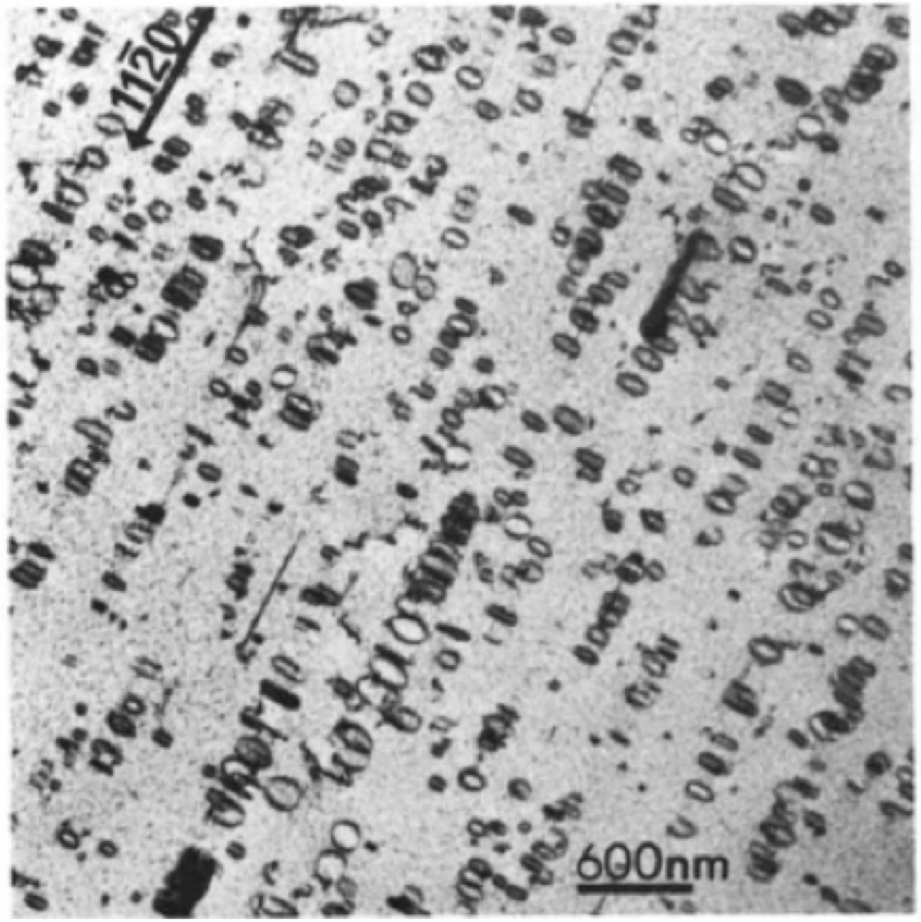
Basics of Neutron Irradiation

- Fast neutrons collide with lattice atoms *(snooker ball analogy)*
  - Collision between Primary Knock-on Atom (PKA) and lattice atom results in collision damage cascades.
  - Zr → 440 displaced atoms per cascade
  - Each displaced atom *(interstitial)* leaves behind a *vacancy*
  - *Displacement per atom (DPA) ~ 20 DPA over fuel assembly lifetime*



Basics of Neutron Irradiation

- 2/3 of interstitials and vacancies recombine immediately
- Some vacancies cluster at damage site
- Remaining interstitials and vacancies diffuse through lattice to sinks, forming…
  - Edge and screw dislocations
  - ***Interstitial and vacancy dislocation loops***



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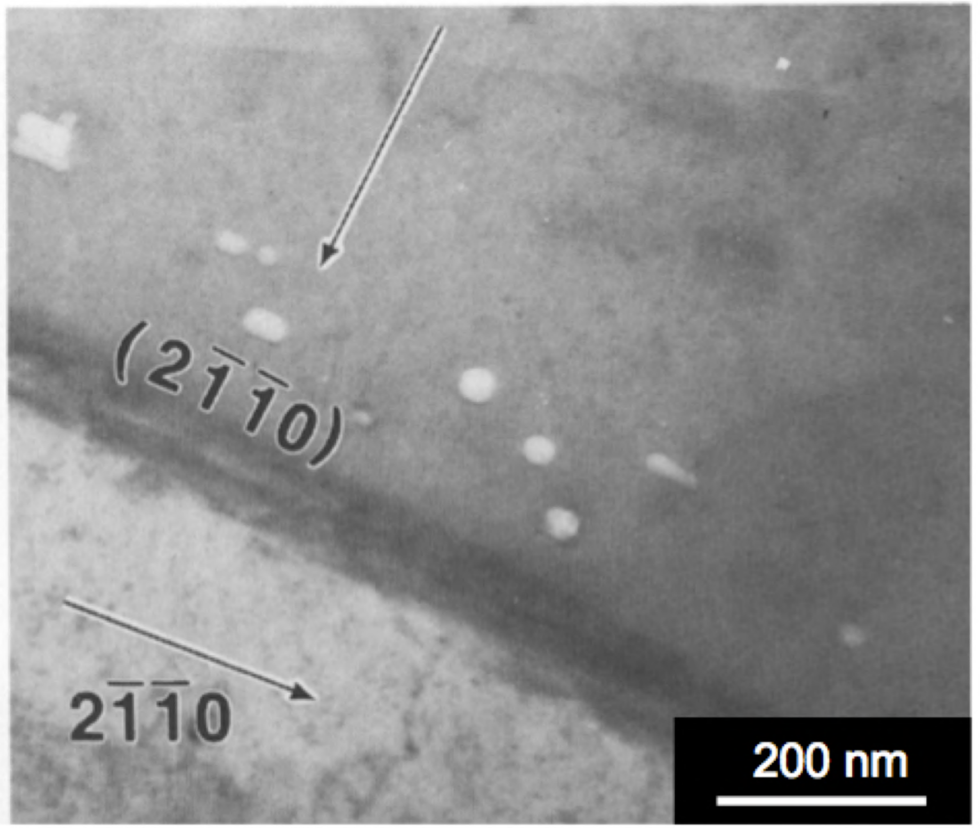
which diffuse to…

  - ***Grain boundaries***



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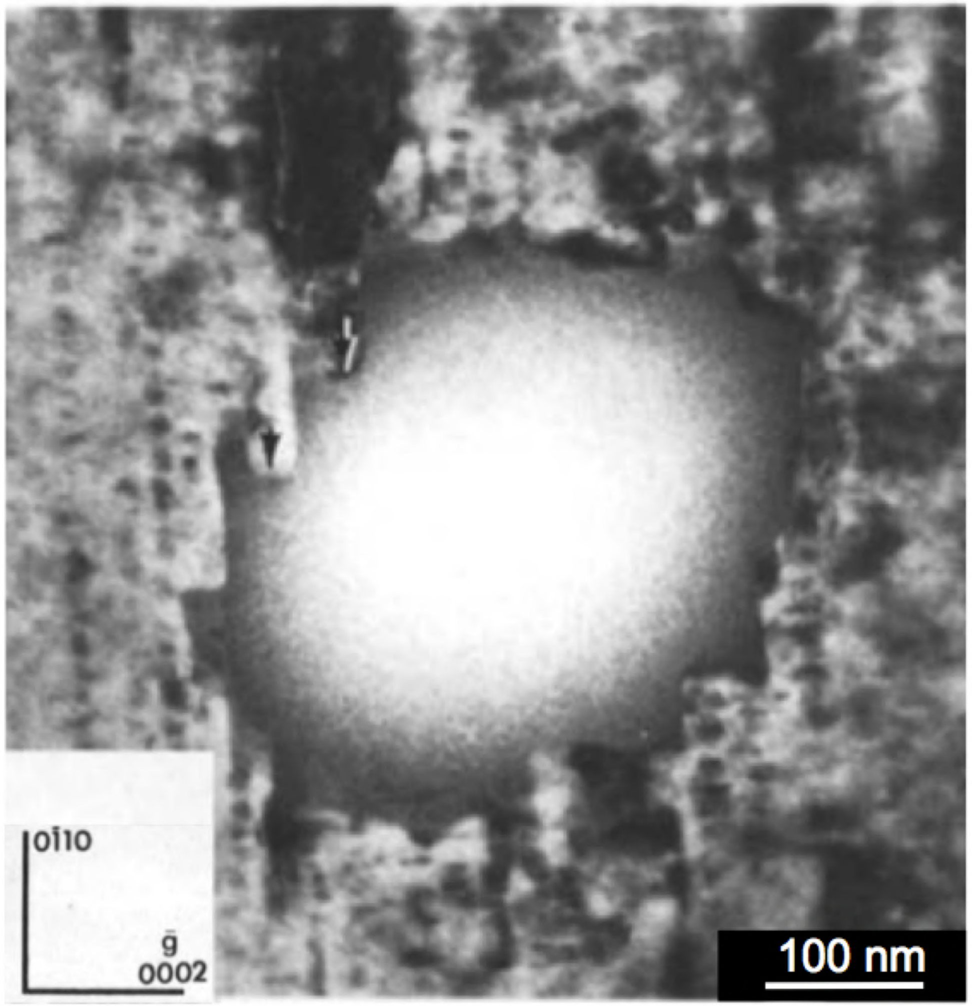
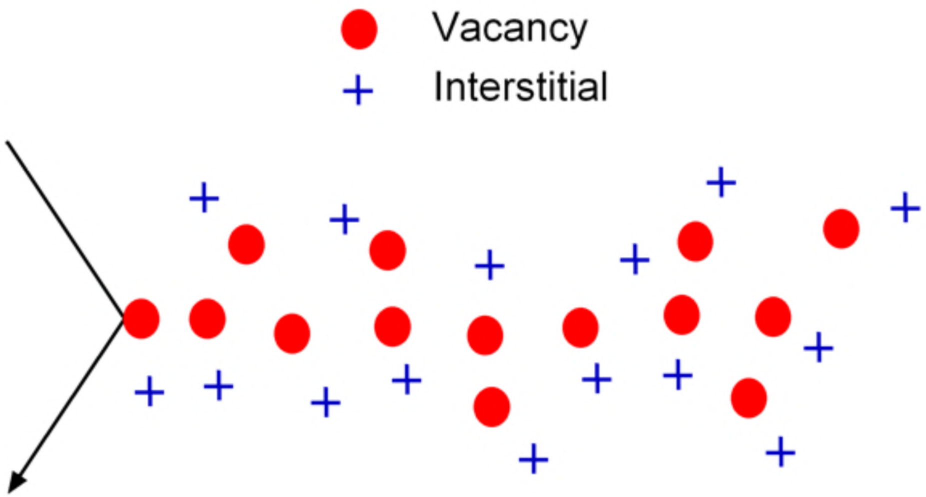
which diffuse to…

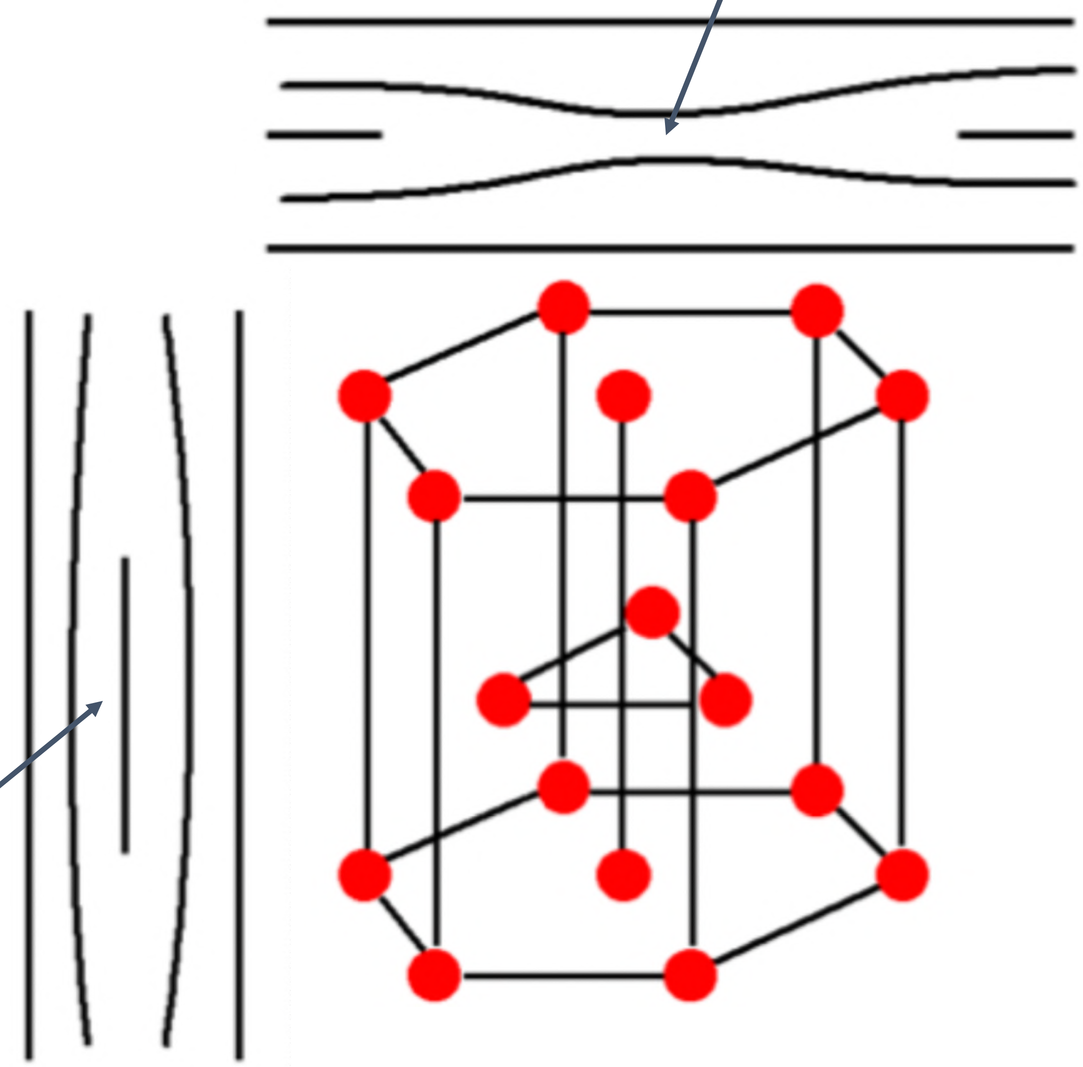
  - Grain boundaries
  - ***Second phase particles (SPPs) and solute atoms***



Irradiation Induced Growth

- Diffusion anisotropy difference
  - Basal planes are preferred vacancy sinks
  - Prismatic planes are preferred interstitial sinks

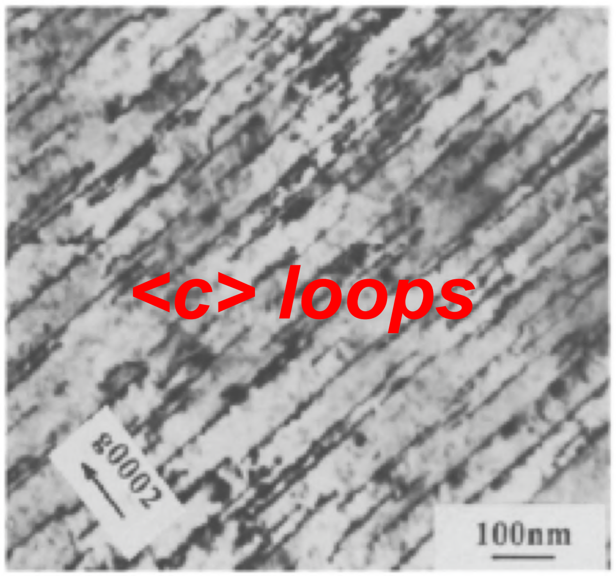


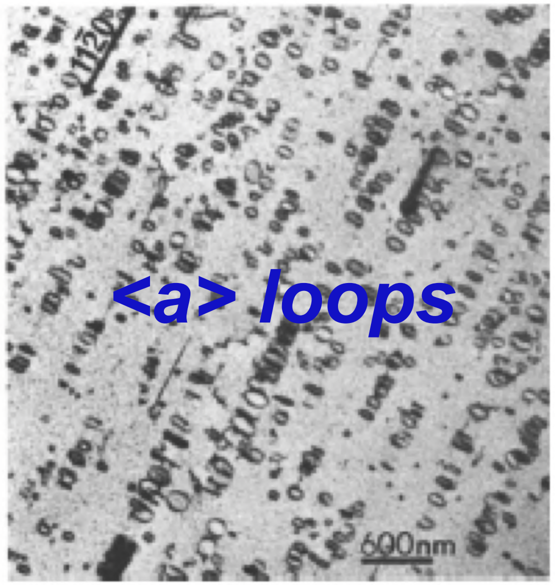


Irradiation Induced Growth

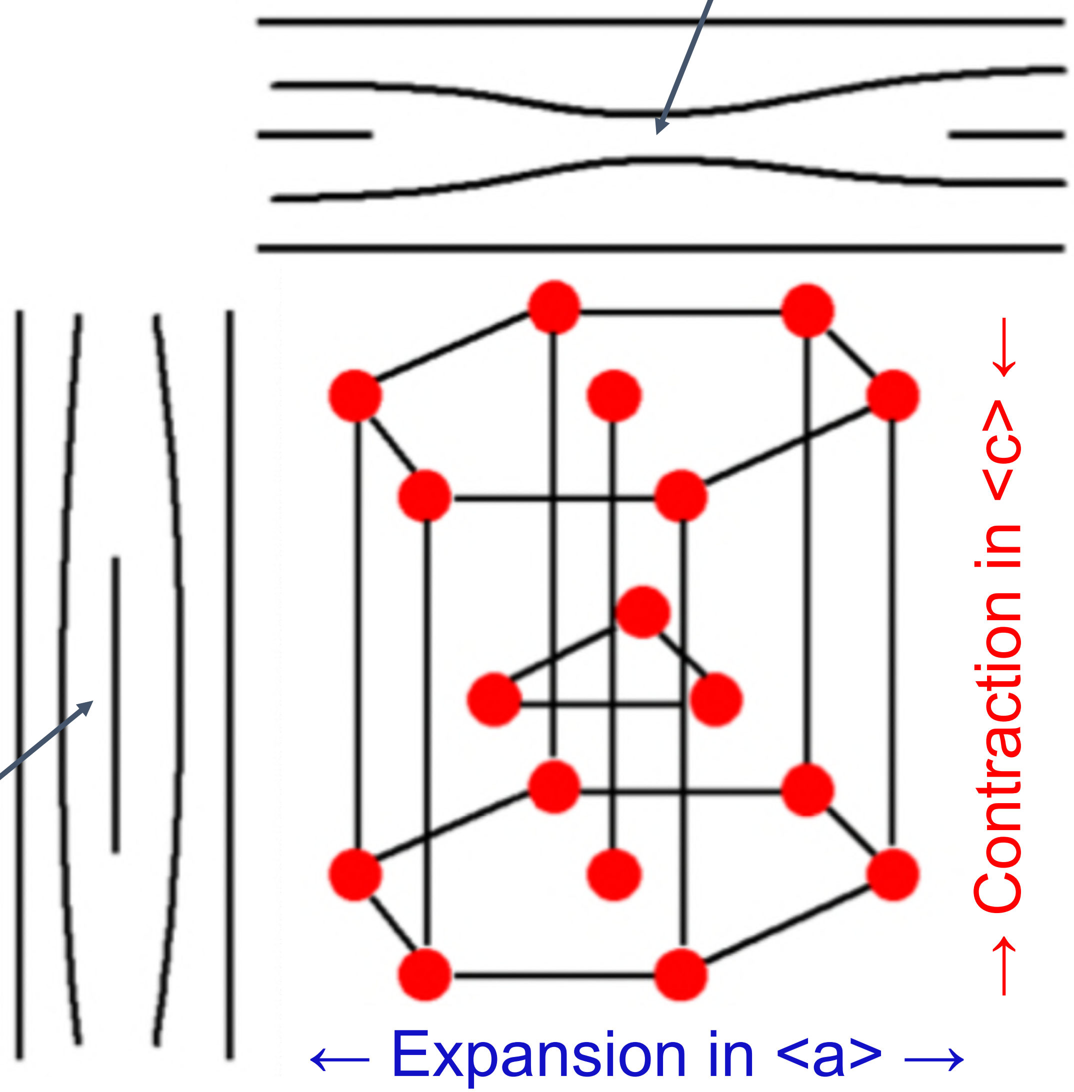
<c> loops
(always vacancy)

- Diffusion anisotropy difference
  - Basal planes are preferred vacancy sinks
  - Prismatic planes are preferred interstitial sinks
- Volume conserved shape change.





<a> loops
(mostly interstitial)



Texture Effect

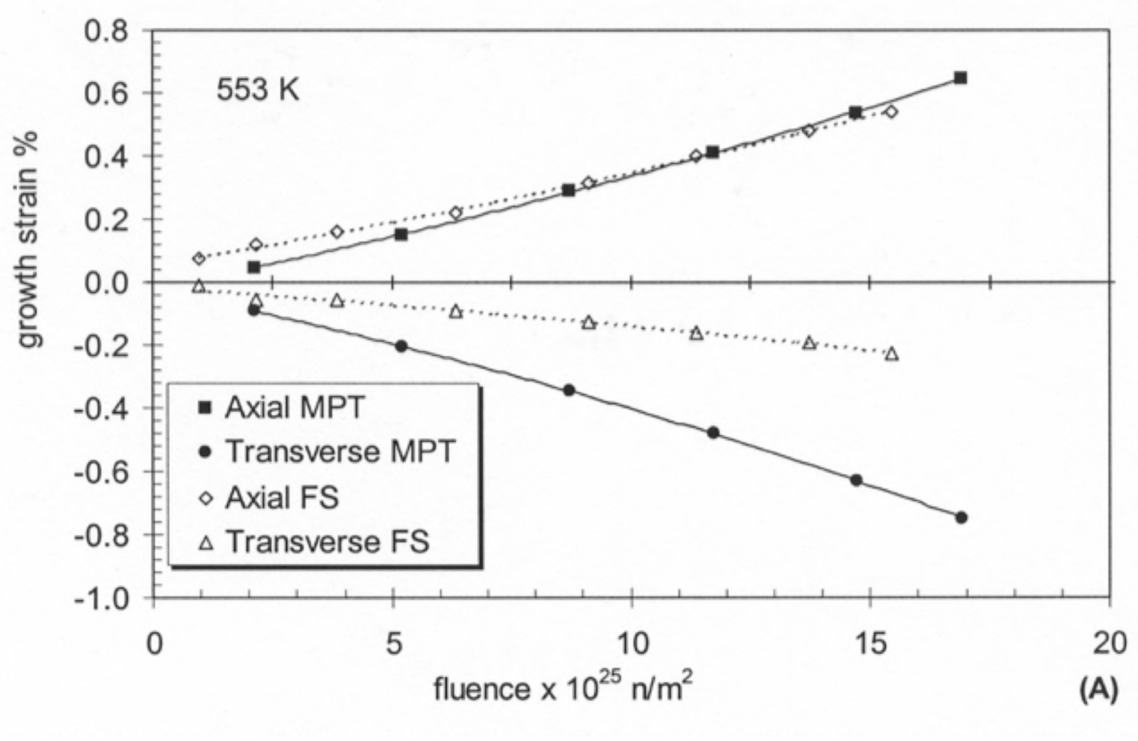
- Growth strain;

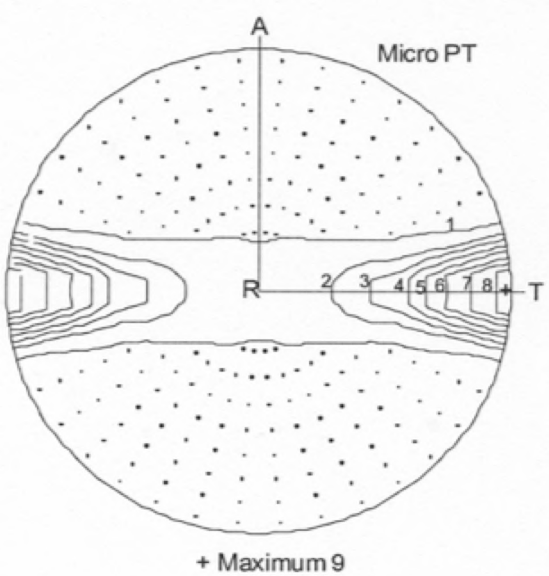
+ve (tensile) in axial direction

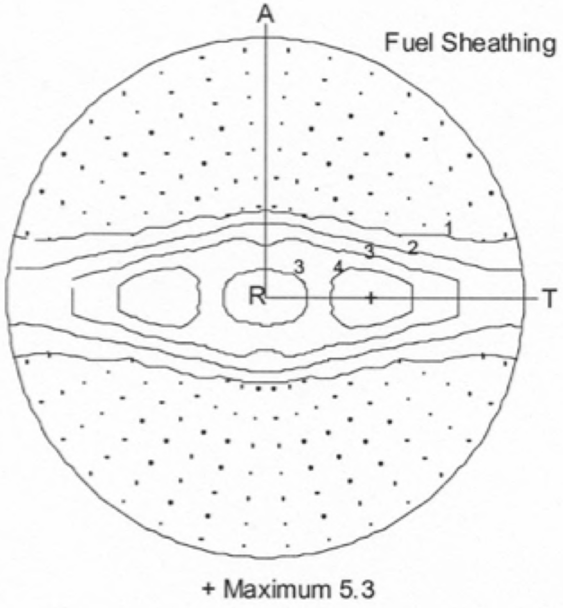
–ve (compressive) in transverse (hoop) direction.

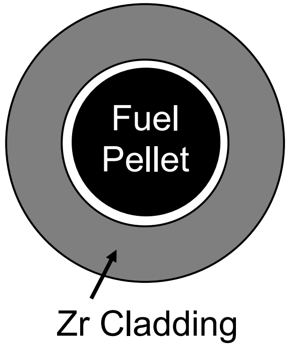
- Radial texture gives lower growth strain.

particularly in transverse (hoop) direction.

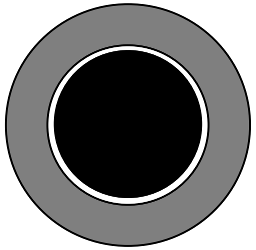




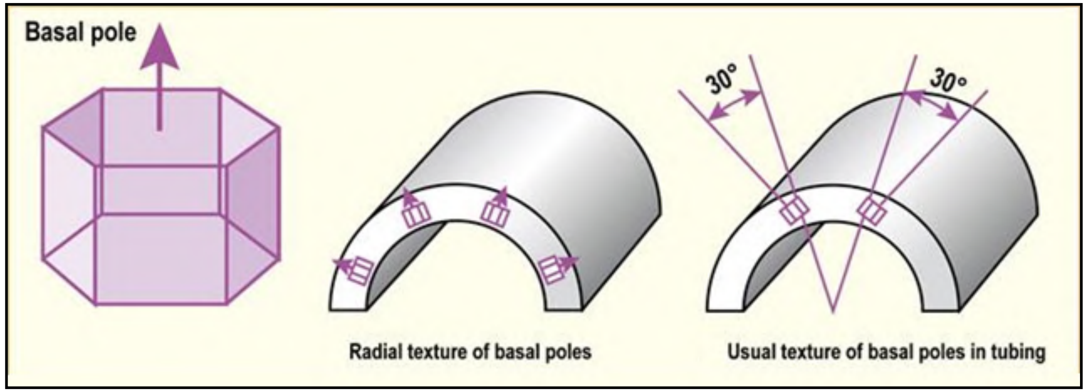




Radial texture

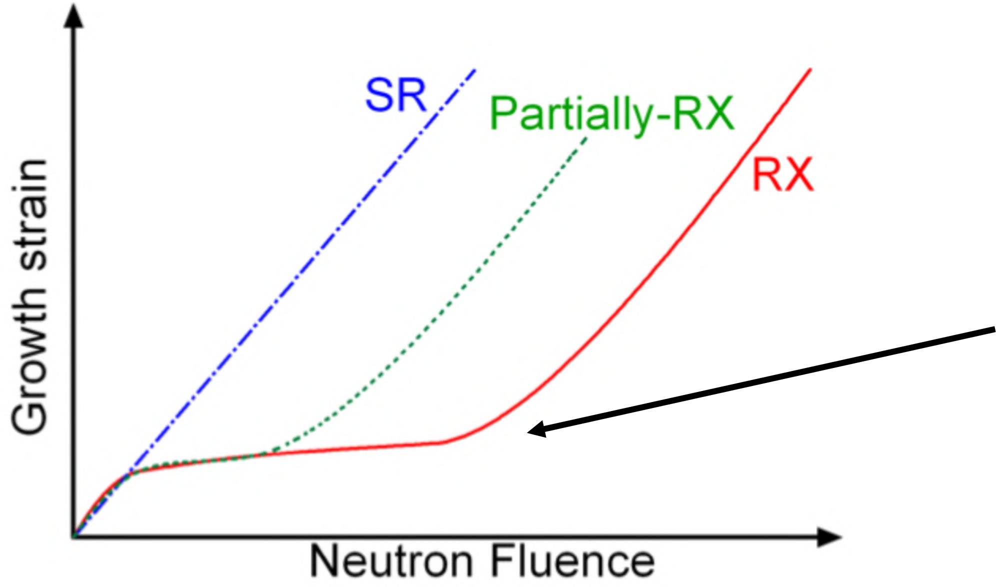


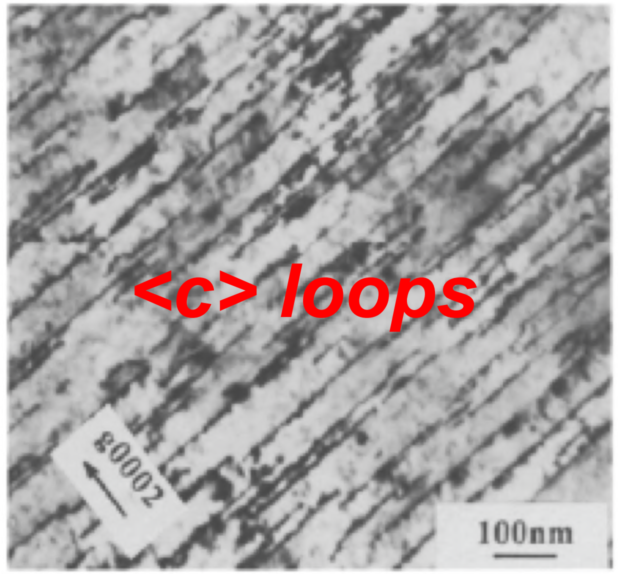
Growth along <a>
Contract along <c>



Breakaway Growth

- First <a> loops form and no <c> loops.
- <c> loop nucleation → breakaway growth.
  - Deformed material (cold worked) results in high growth at low fluence.
- What helps <c> loops nucleate?
  - Alloy chemistry affects growth
  - Fe enrichment around SPP acts as nucleation sites for <c> loops?



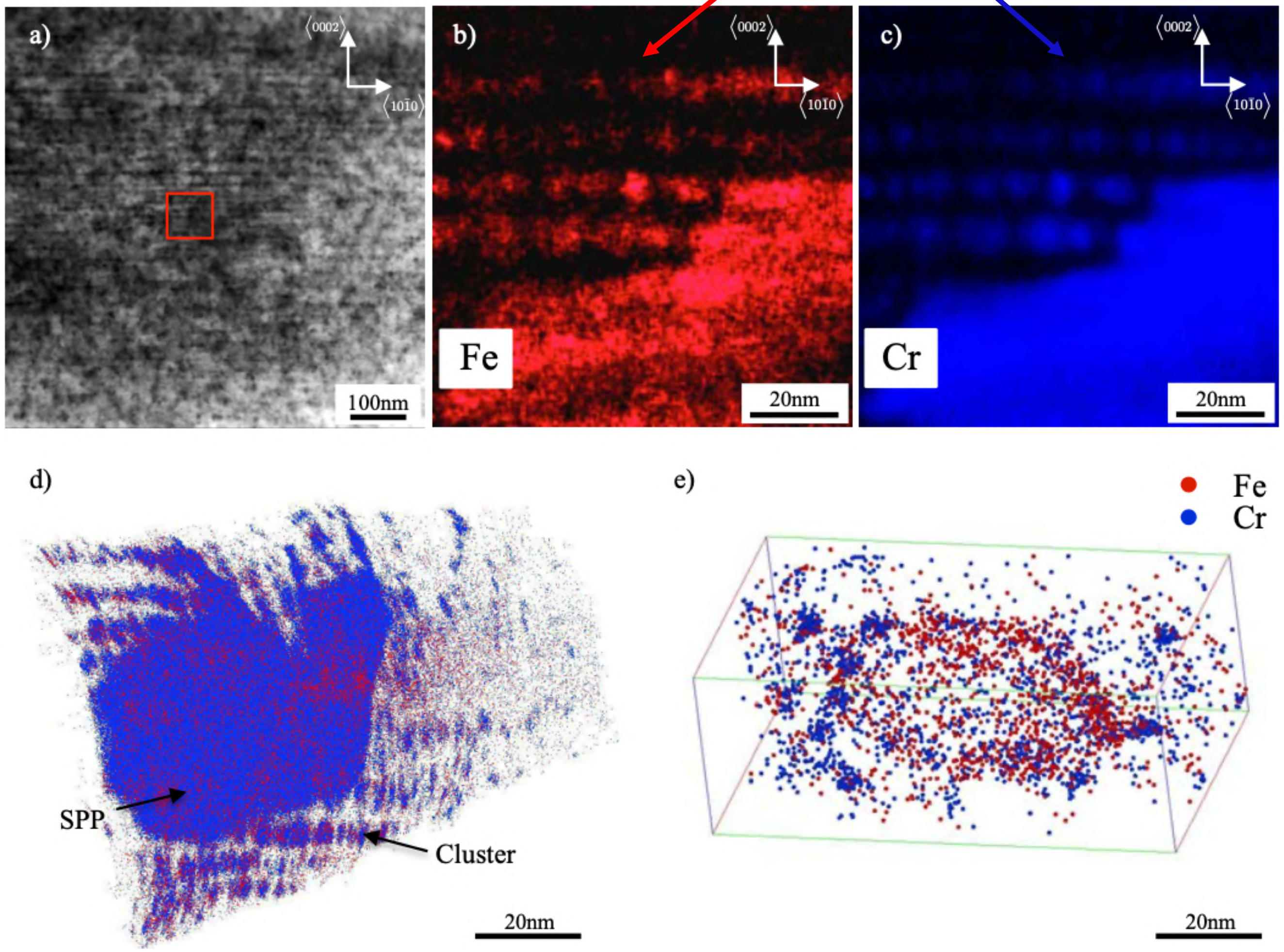


Dissolution of SPPs

- Intermetallic precipitates are affected by neutron irradiation

1. Crystalline → amorphous *(non-crystalline)* transformation.
2. Amorphisation from outside to inside
3. Fe diffuses out from amorphous particles, Cr concentration in particles stays constant.
4. After precipitates become amorphous, dissolution accelerates.
5. Fe diffuses further away than Cr.

Fe and Cr depletion along basal planes



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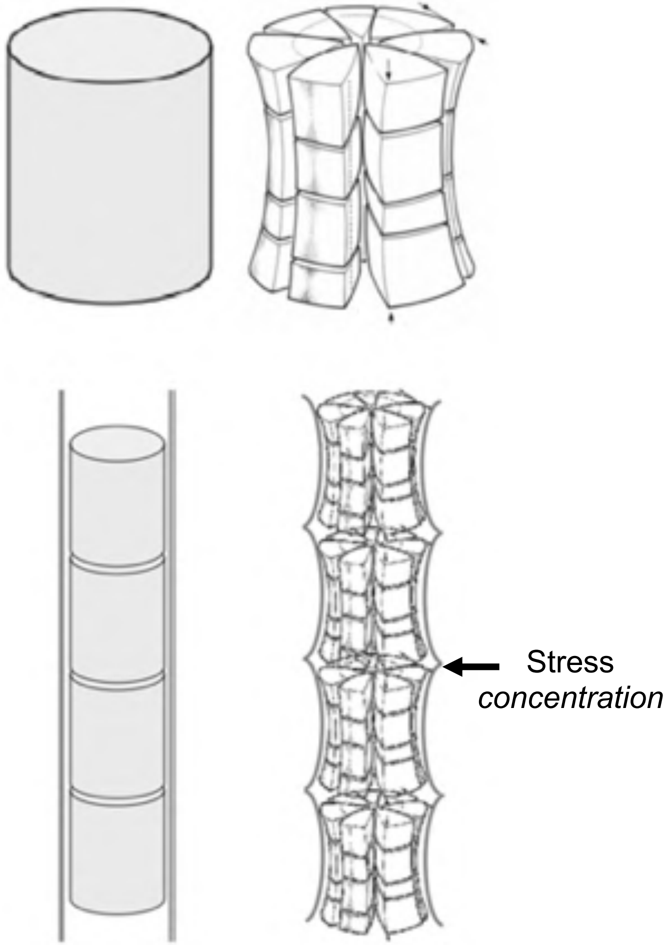


Ur fuel pellets at the start and end of service, showing stress concentrations forming on the Zr cladding, which act as sites for PCI.

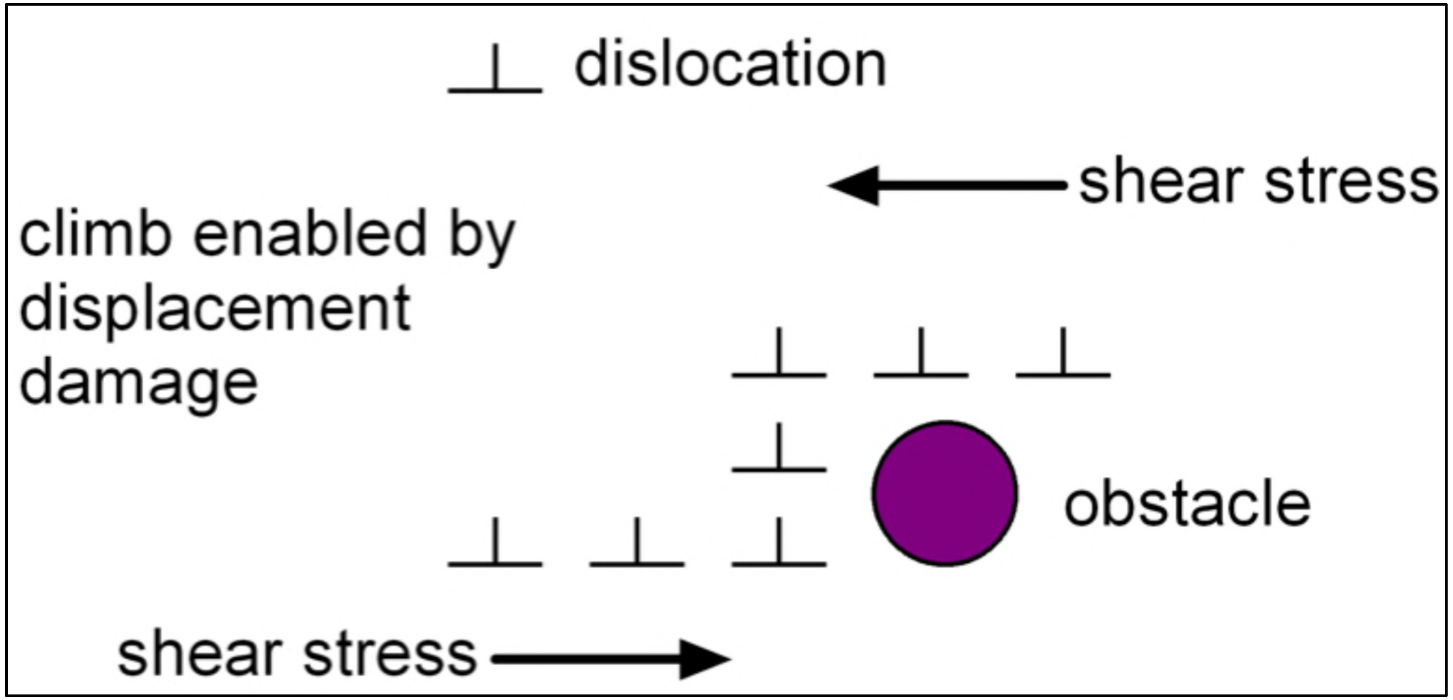
Irradiation Enhanced Creep

- ***What is creep?***
  - ***Creep is tendency of material to deform plastically under applied stress.***
  - ***Usually occurs over long time period.***
  - ***Creep is more severe at high temperature.***
  - ***Irradiation increases creep rates.***

- ***Irradiation Enhanced Creep:*** Displacement damage from irradiation + applied stress causes creep of Zr alloys *in-service*.
- Even without irradiation, Zr cladding will creep due to internal pressure/temperature of the cladding.
- In Zr, irradiation creep is anisotropic due to texture.

Irradiation Enhanced Creep

- A number of mechanisms have been proposed.
- In the case of Zr:
  - Climb enabled glide (CEG) – climb rate limiting
  - Elasto diffusion (ED) – stress induced



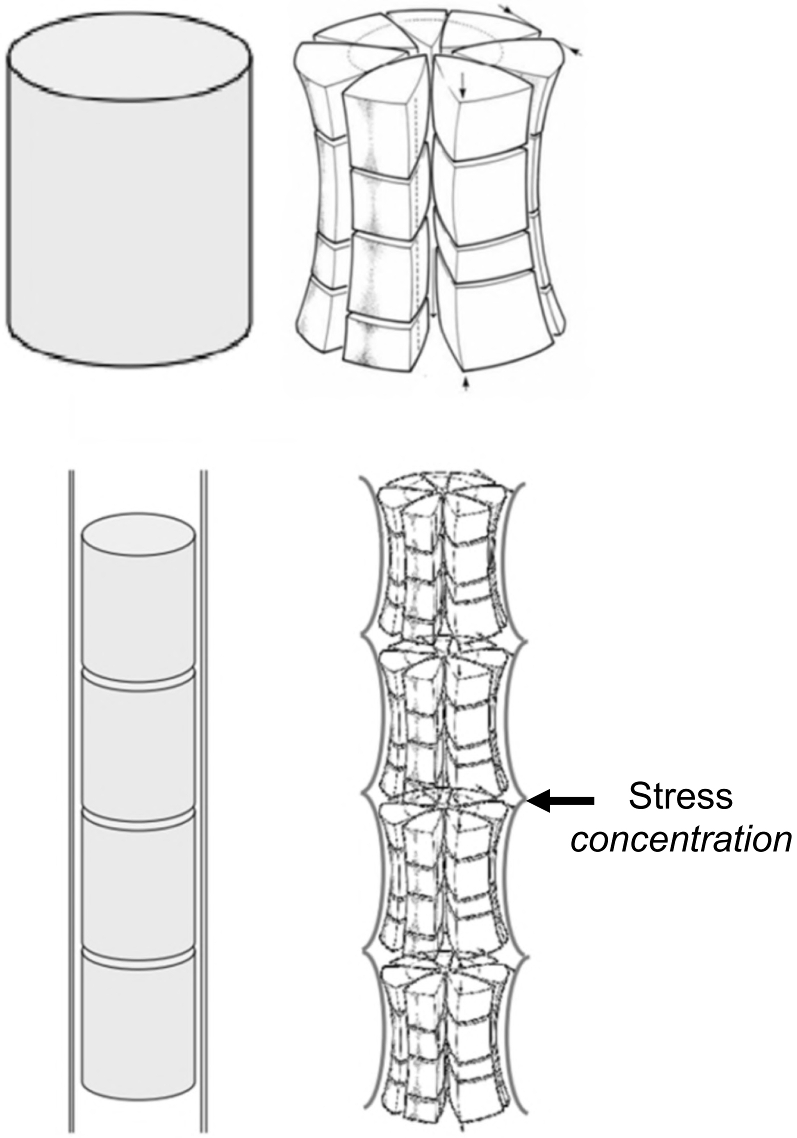
Issues with Growth and Creep

- Possible to design for reasonable elongation of fuel assemblies.
- Problem arises when some cladding rods start to grow faster than others.
- Potentially, assemblies could buckle → makes it difficult to insert control rods.
- Handling distorted assemblies also very difficult.

Fuel assembly buckling

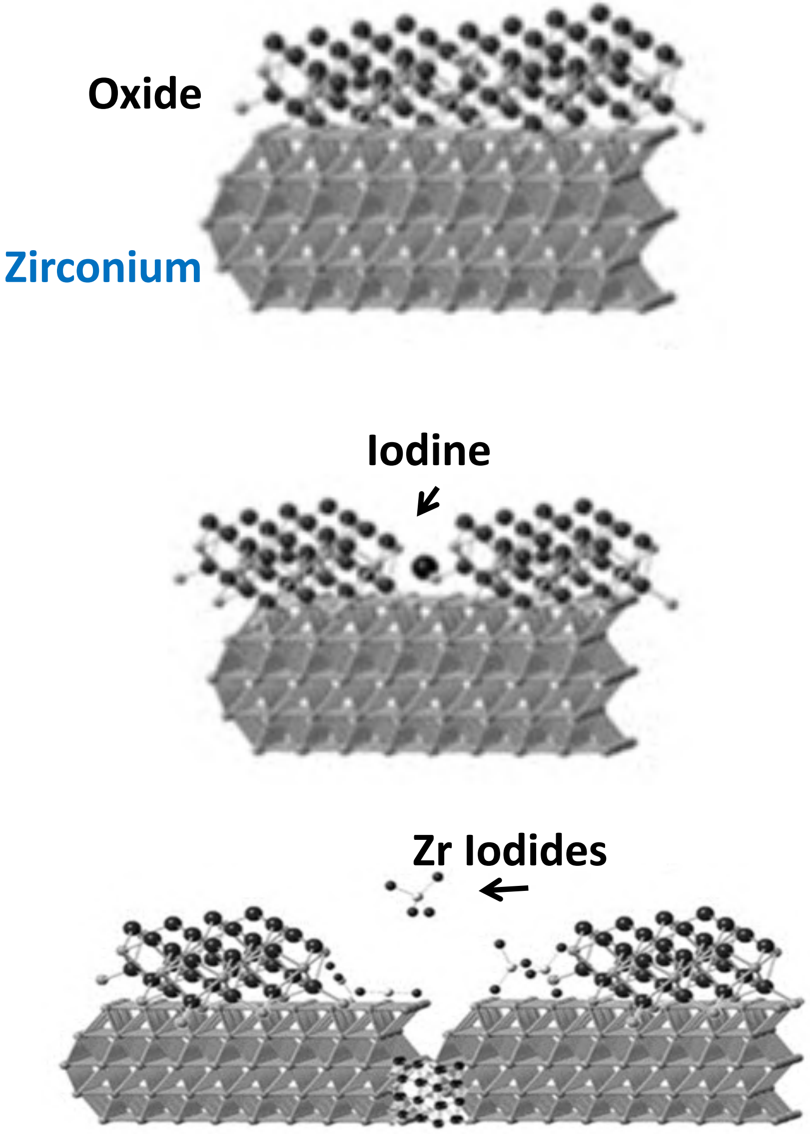
Pellet Cladding Interaction (PCI)

- Over time, UO_2 pellet expands and cracks into wedge-shaped blocks.
- Different thermal expansion of UO_2 and Zr → local stresses on cladding.

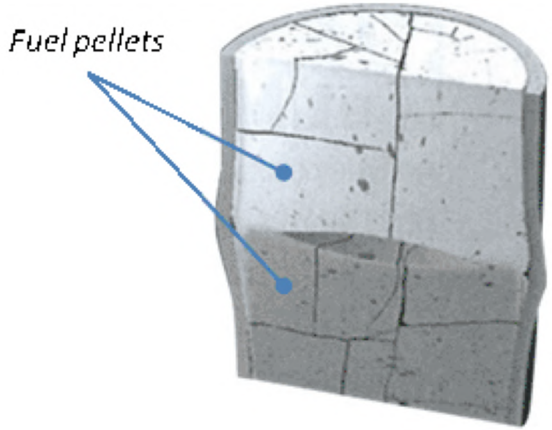


Pellet Cladding Interaction (PCI)

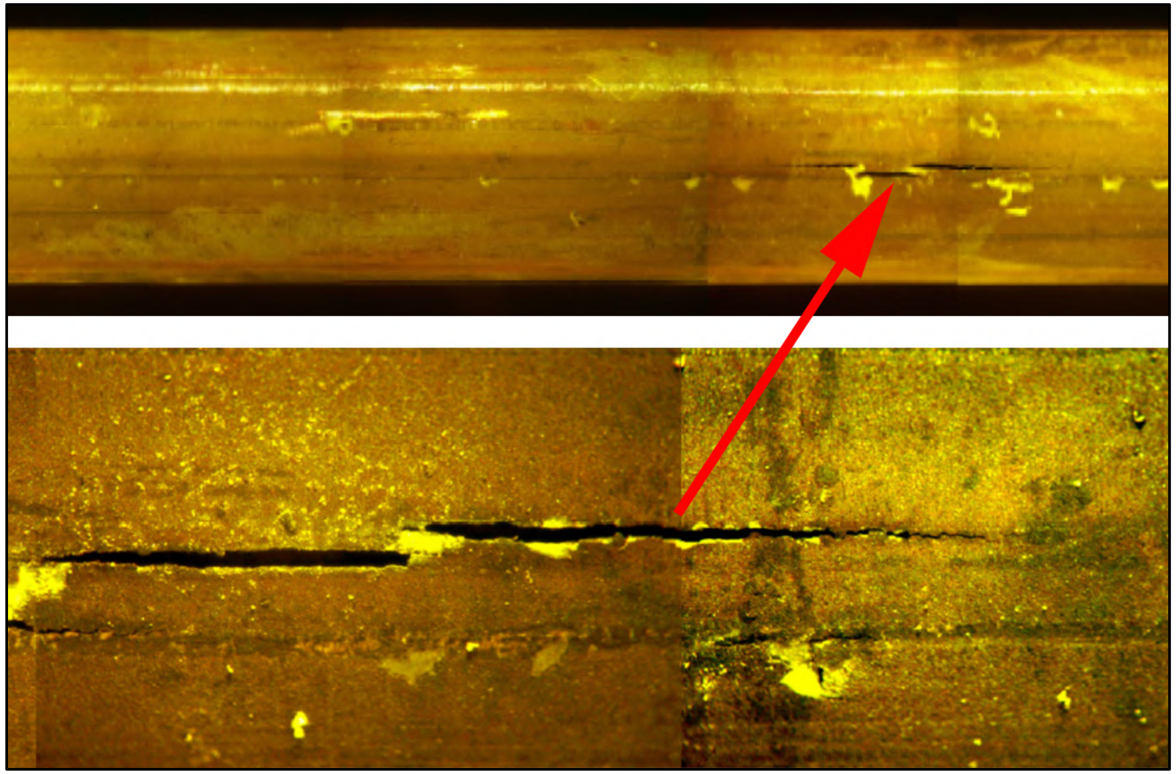
- Over time, UO_2 pellet expands and cracks into wedge-shaped blocks.
- Different thermal expansion of UO_2 and Zr → local stresses on cladding.
- Iodine fission gas *(a fission product from nuclear reaction)* trapped and then released from UO_2 → iodine penetrates oxide.
- Chemical reaction between Zr and iodine → pitting corrosion.
- Stress + corrosion can lead to cladding failure.
- *PCI limits power maneuvering (load following) of nuclear power stations. (Important for National Grid and renewable energy sources).*



How can we prevent Pellet Cladding Interaction (PCI)?



- Change fuel pellet shape
- Fuel pellet additives
- Cladding liner
- Modify cladding microstructure
- Control operating procedure to keep stress below empirically derived threshold



Fuel can splitting via PCI.

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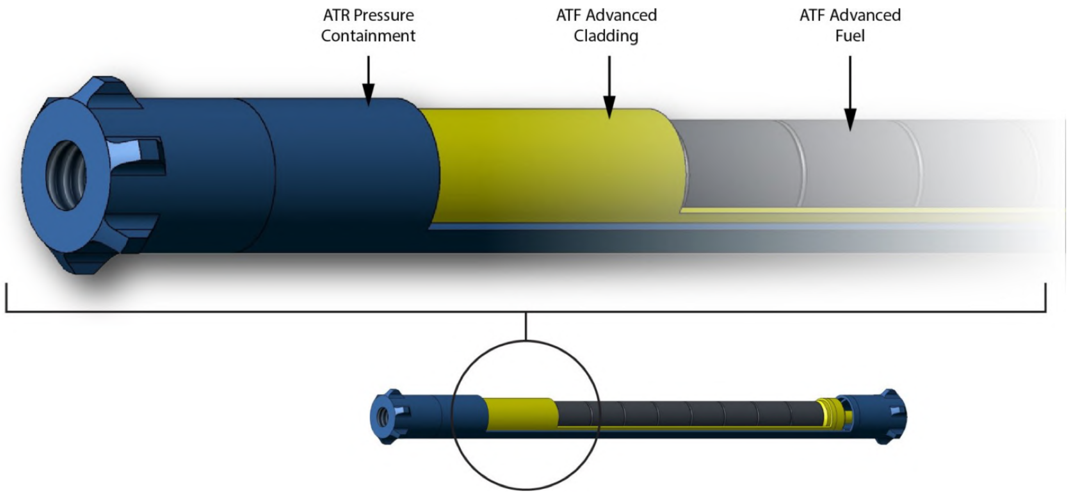


The future design of cladding tubes?

Fukushima Incident

- Earthquake
- Control rods inserted
- Power Loss
- Diesel generators activated

http://edition.cnn.com/2011/WORLD/asiapcf/03/16/japan.nuclear.heroes/

- Tsunami
- Loss of generators
  (design deficiency, safety culture, lifetime extension)
- Loss of coolant

- Explosions
- Due to hydrogen build-up

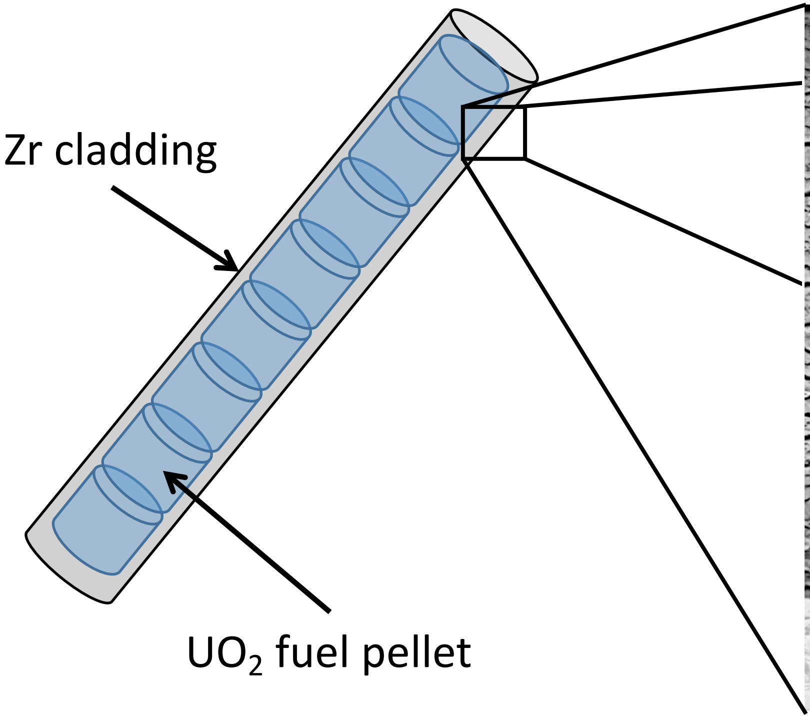
http://beforeitsnews.com/alternative/2014/05/fukushima-lives-unit-4-has-exploded-its-on-fire-video-2960558.html

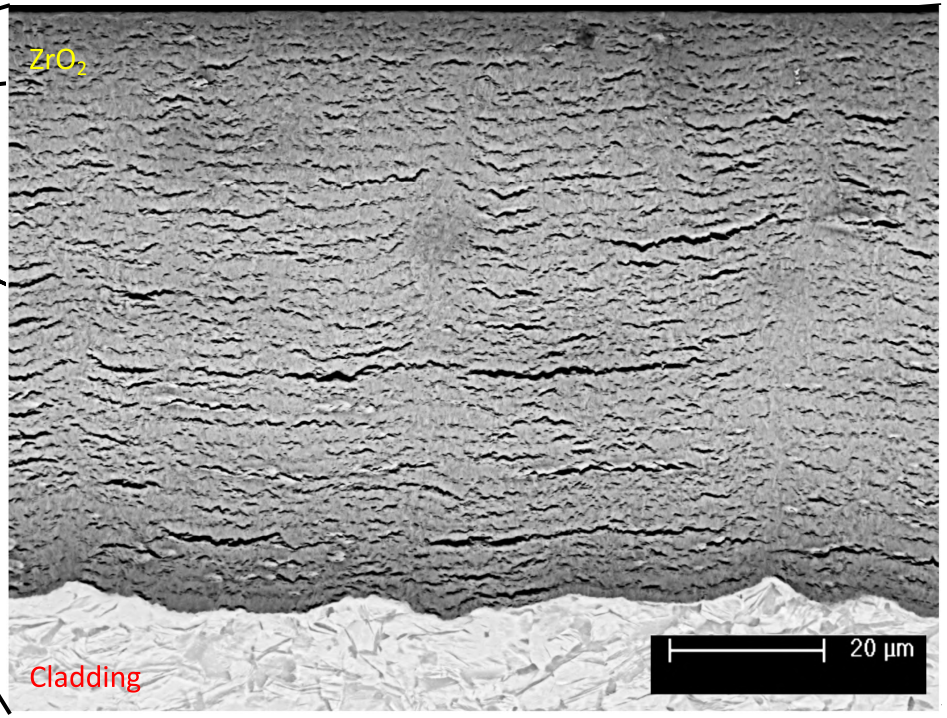
Where did the H_2 come from?

- Zr cladding oxidation reaction:

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

- *Zr becomes highly reactive during accident conditions.*





M. Preuss, P. Frankel, S. Lozano-Perez, D. Hudson, E. Polatidis, N. Ni, J. Wei, C. English, S. Storer, B.K. Chong, M. Fitzpatrick, P. Wang, J. Smith, C. Grosvenor, G. Smith, J. Sykes, B. Cottis, S. Lyon, L. Hallstadius, R.J. Comstock, A. Ambard and M. Blat-Yrieix, Studies regarding corrosion mechanisms in zirconium alloys, J. ASTM Intl, Vol. 8, No. 9, doi: 10:1520/JAI103246, 2011, 649-681

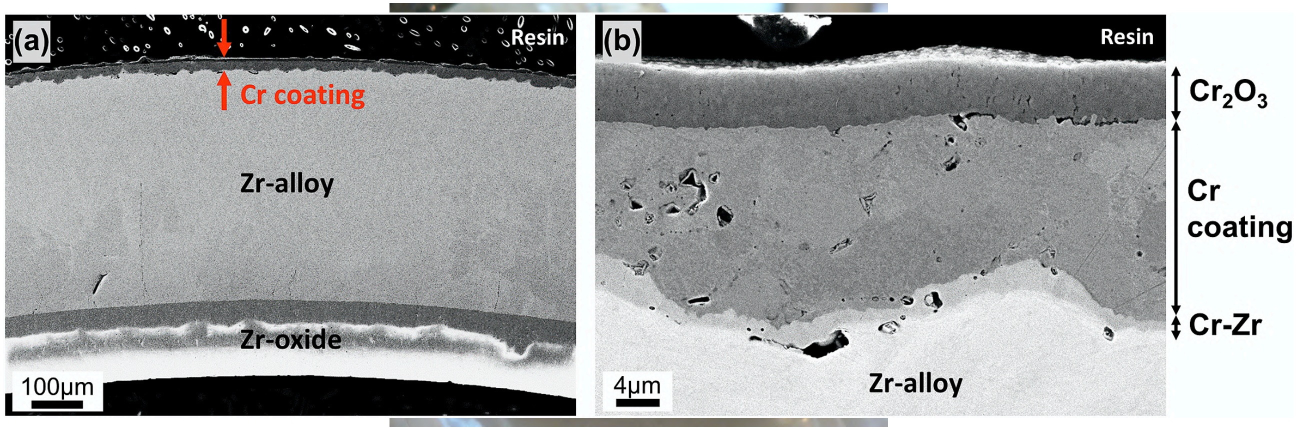
Accident Tolerant Fuels (ATFs)

Definition:

Fuels which can tolerate the loss of active cooling in the core for longer durations than the current UO_2-Zr fuels

- Improved efficiency during normal operation
- Increases in coping time that can mitigate further incidents

Accident Tolerant Fuels (ATFs) – What are the alternatives?



- SiC cladding
  - Very low neutron absorption
  - Huge manufacturing problems
  - Thermal conductivity drops during irradiation
- Coating of Zr (e.g. Cr)
  - What happens when coating fails during service?
  - Can coating sustain substrate growth and creep?
- Change from Zr to Steel
  - Higher neutron absorption
  - Would require higher enrichment
- Change from ceramic to metallic fuel
  - Higher density
  - Increased thermal conductivity