PennState
College of Engineering

NucE 497: Reactor Fuel Performance

Lecture 32: Cladding oxidation

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Most material taken from 409 slides by Adi Shivprasad

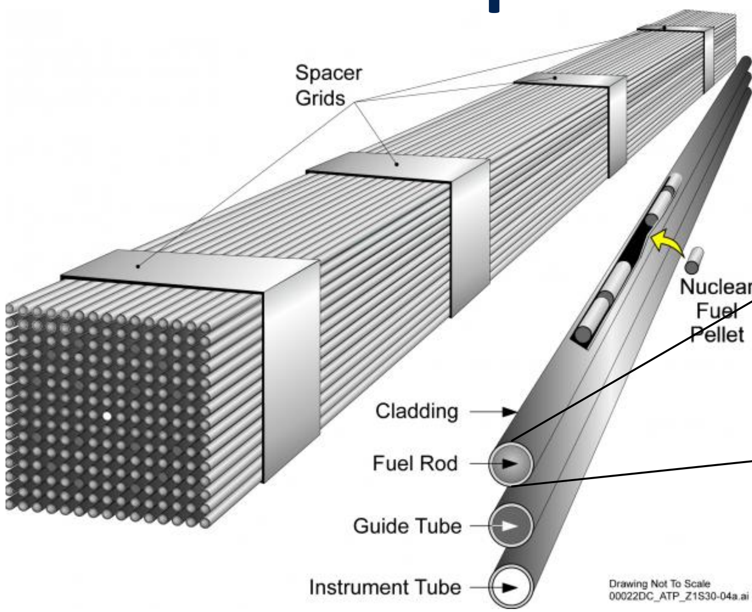
Today we will discuss oxidation of the cladding

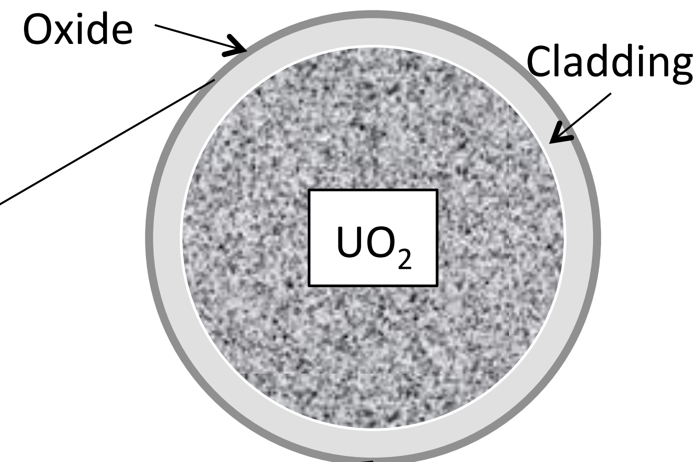
- Module 1: Fuel basics
- Module 2: Heat transport
- Module 3: Mechanical behavior
- Module 4: Materials issues in the fuel
- Module 5: Materials issues in the cladding
  - Zirconium alloys and fabrication
  - Cladding creep and growth
  - Mechanical behavior
  - **Oxidation**
  - Hydride formation
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

Here is some review from last time

- Irradiation hardening in zircaloy cladding results primarily from
  a) Interstitial loop formation on prism planes
  b) Vacancy loop formation on basal planes
  c) Void formation throughout the material
  d) Dislocation formation due to deformation
- PCCI stands for
  a) Pellet clad corrosive intrusion
  b) Pellet chemical corrosion inspection
  c) Pensacola Christian College
  d) Pellet clad chemical interaction

Corrosion of zirconium is the largest concern for LWR fuel operation

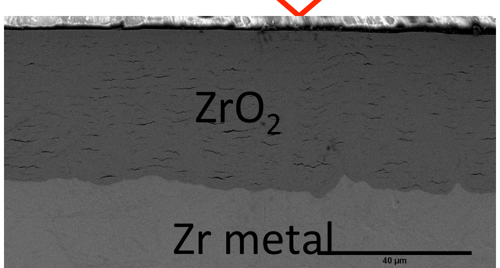


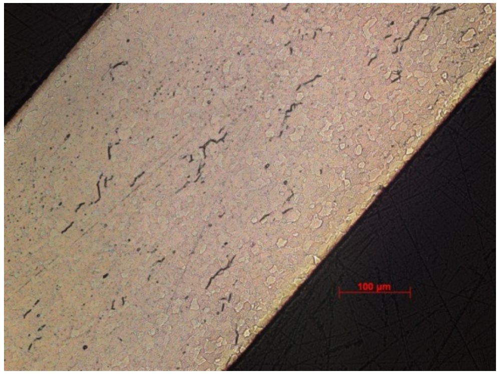


Corrosion reaction:

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

Hydrogen pick-up

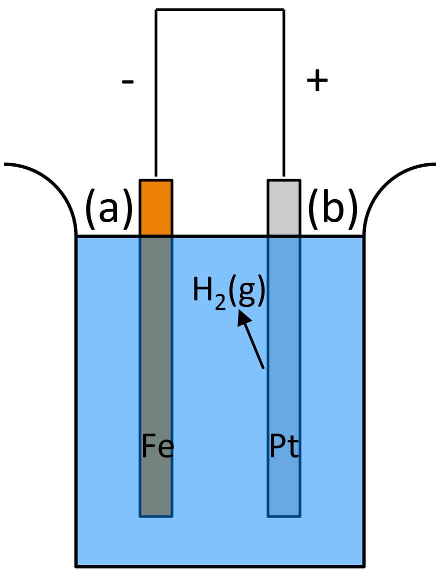




What is corrosion?

- Corrosion is the degradation of a material and its properties under the action of the surrounding environment
- Corrosion reactions require the following:
  - Oxidant
  - Electric current
- A corrosion reaction is composed of an oxidation reaction and a reduction reaction.

First we will consider iron as an anode in an electrochemical cell



$$\mathrm{Fe(s) + 3\,H_2O(\ell) \rightleftharpoons Fe_2O_3(s) + 3\,H_2(g)}$$

Anodic reaction: oxidation

$$\text{(a)}\ \mathrm{Fe(s) \rightleftharpoons Fe^{3+}(aq) + 3\,e^-}$$

$$\mathrm{2\,Fe^{3+}(aq) + 3\,H_2O(\ell) \rightleftharpoons Fe_2O_3(s) + 6\,H^+(aq)}$$

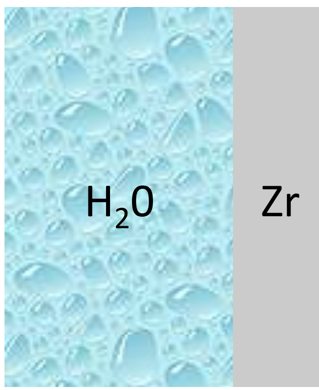
Cathodic reaction: reduction

$$\text{(b)}\ \mathrm{2\,H^+(aq) + 2\,e^-} \overset{Pt}{\rightleftharpoons} \mathrm{H_2(g)}$$

What prevents everything from corroding to oblivion?

- 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

Now we will consider the reaction taking place in the cladding



Oxidation reaction:

$$\mathrm{Zr(s)} \rightarrow \mathrm{Zr^{4+}(aq)} + 4\mathrm{e}^-$$

$$\mathrm{Zr(aq)^{4+}} + 2\mathrm{H_2O(l)} \rightarrow \mathrm{ZrO_2(s)} + 4\mathrm{H^+(aq)}$$

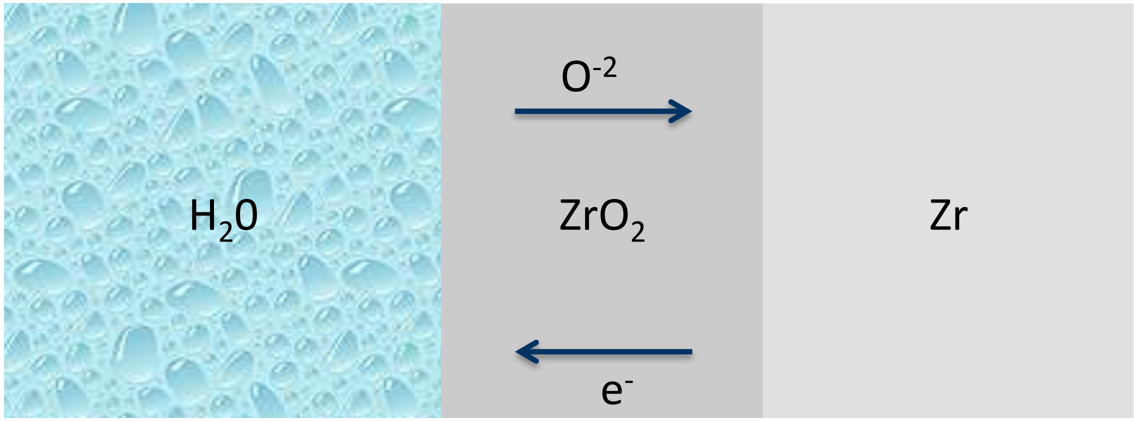
Reduction reaction:

$$4\mathrm{e}^- + 4\mathrm{H^+(aq)} \rightarrow 2H_2$$

Once the oxide layer forms, more steps are required for oxidation

$$2\mathrm{H_2O(l)} \rightarrow 2\mathrm{O(aq)}^{-2} + 4\mathrm{H^+(aq)}$$

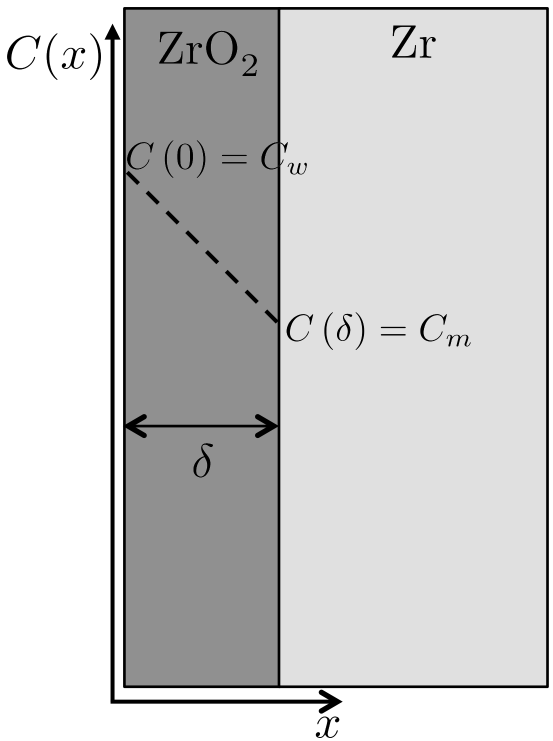
$$\mathrm{Zr}^{4+} + 2\mathrm{O}^{-2} \rightarrow \mathrm{ZrO_2} + 4\mathrm{e}^-$$



$$4\mathrm{e}^- + 4\mathrm{H^+(aq)} \rightarrow 2H_2$$

1. Dissociation of water at oxide/water interface
2. Absorption of oxygen into oxide layer
3. Diffusion of oxygen through oxide layer
4. Reaction of oxygen with zirconium
5. Diffusion of electrons through oxide layer
6. Reduction of hydrogen

Because the rate limiting steps are diffusion, we can model the oxidation rate using diffusion



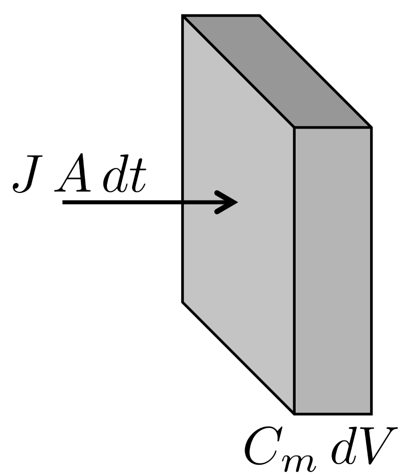
Assumptions:

- 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

$$\mathbf{J} = -D\,\nabla C$$

$$\frac{\partial C}{\partial t} = -\left(\nabla \cdot \mathbf{J}\right) = D\,\nabla^2 C$$

$$C = \frac{C_m - C_w}{\delta}\,x + C_w$$



$$D\,\frac{C_w - C_m}{C_m}\int \mathrm{d}t = \int \delta\,\mathrm{d}\delta$$

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

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

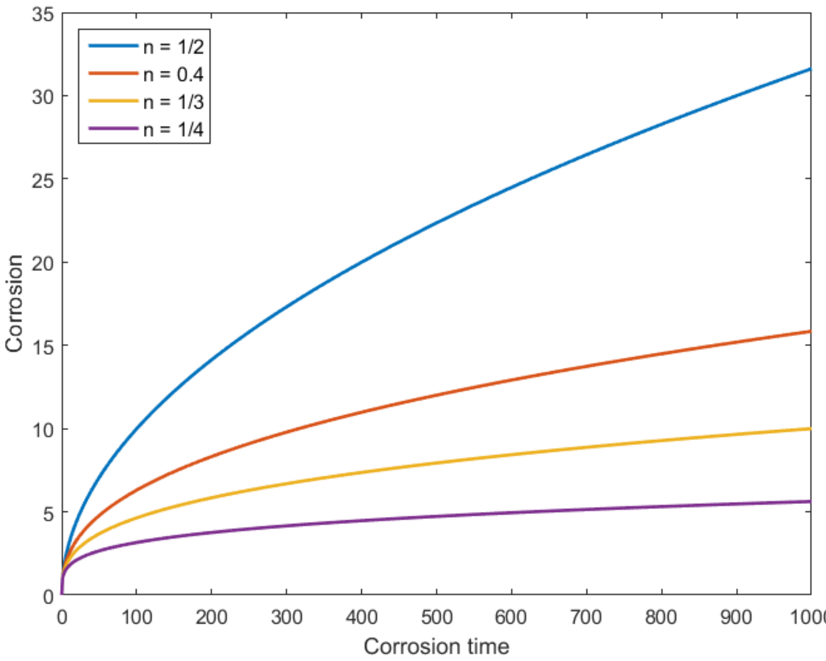
Observed kinetics are slower than parabolic

Parabolic kinetics

- Diffusion of species across the oxide

Sub-parabolic kinetics

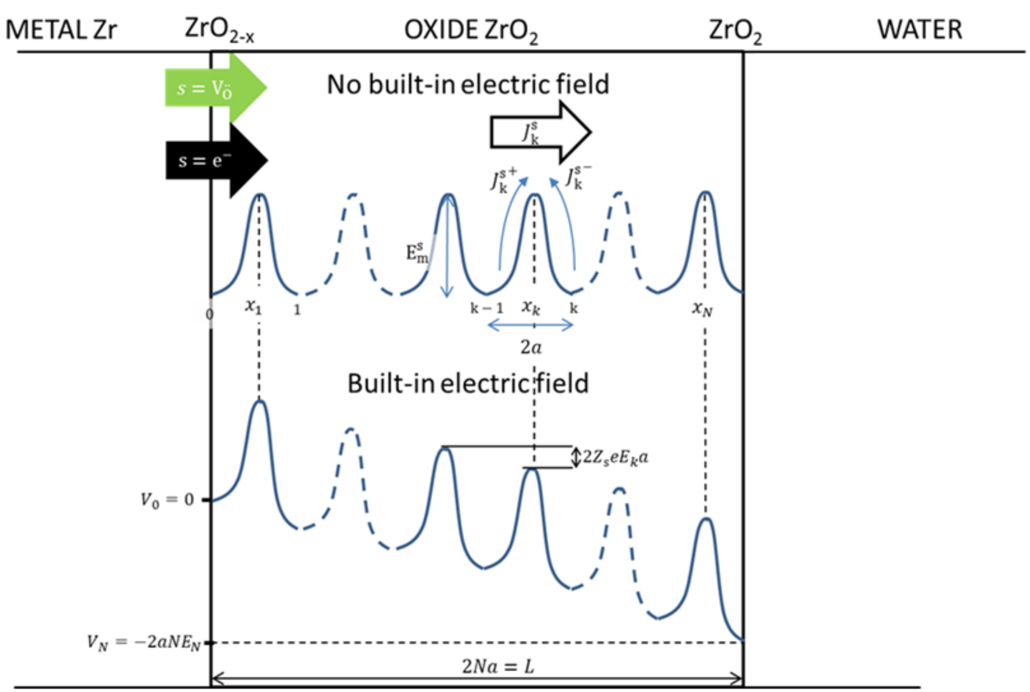
- Development of cracks in oxide
- Additional ions in oxide
- Non-uniform electric field in oxide layer

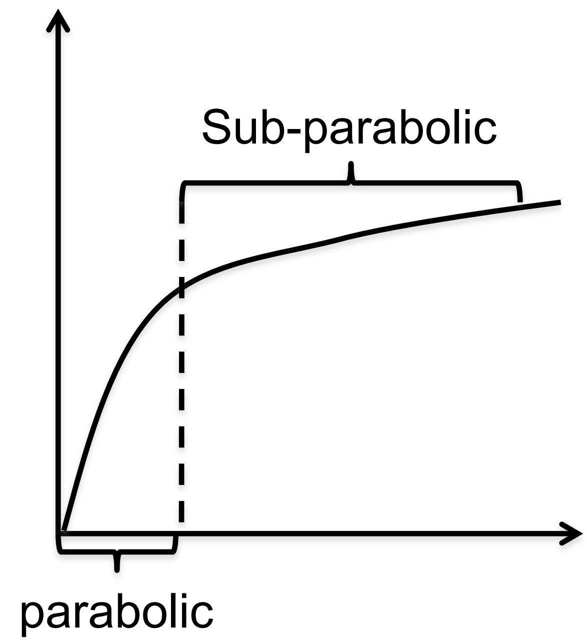


The growth start parabolic and then slows down

Sub-parabolic kinetics have the form

$$w = k\, t^n \quad n < 0.5$$

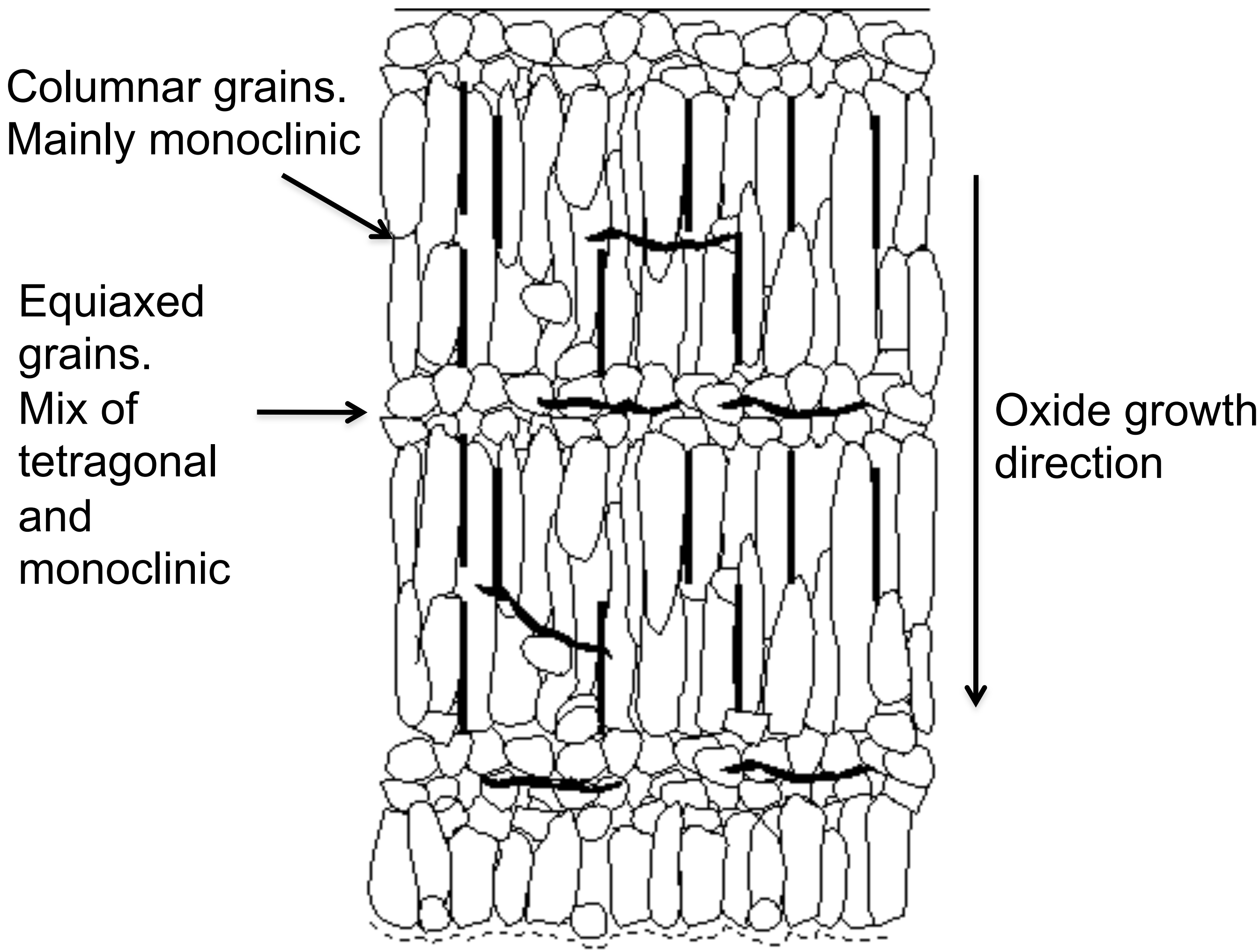




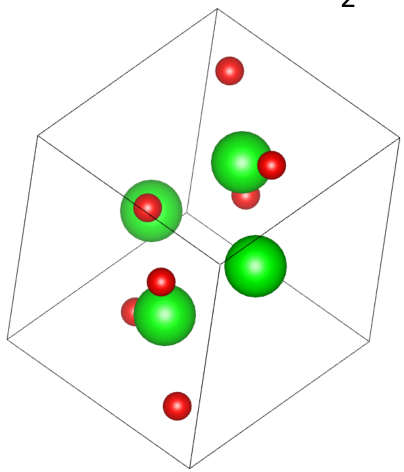
Once a nonhomogeneous electric field arises, the corrosion rate decreases to the sub-parabolic rate due to inhibition of transport of charged species.

Couet, A. Ph.D. Thesis. 2014.

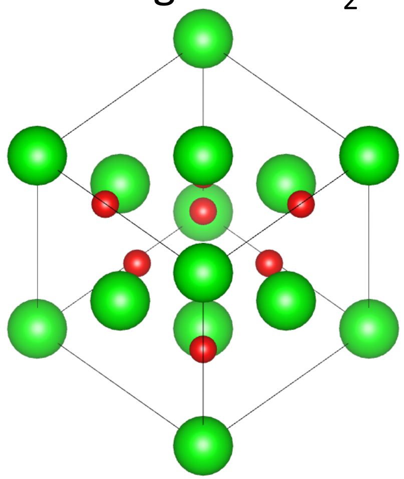
Microstructural basis for oxide growth



Monoclinic ZrO_2



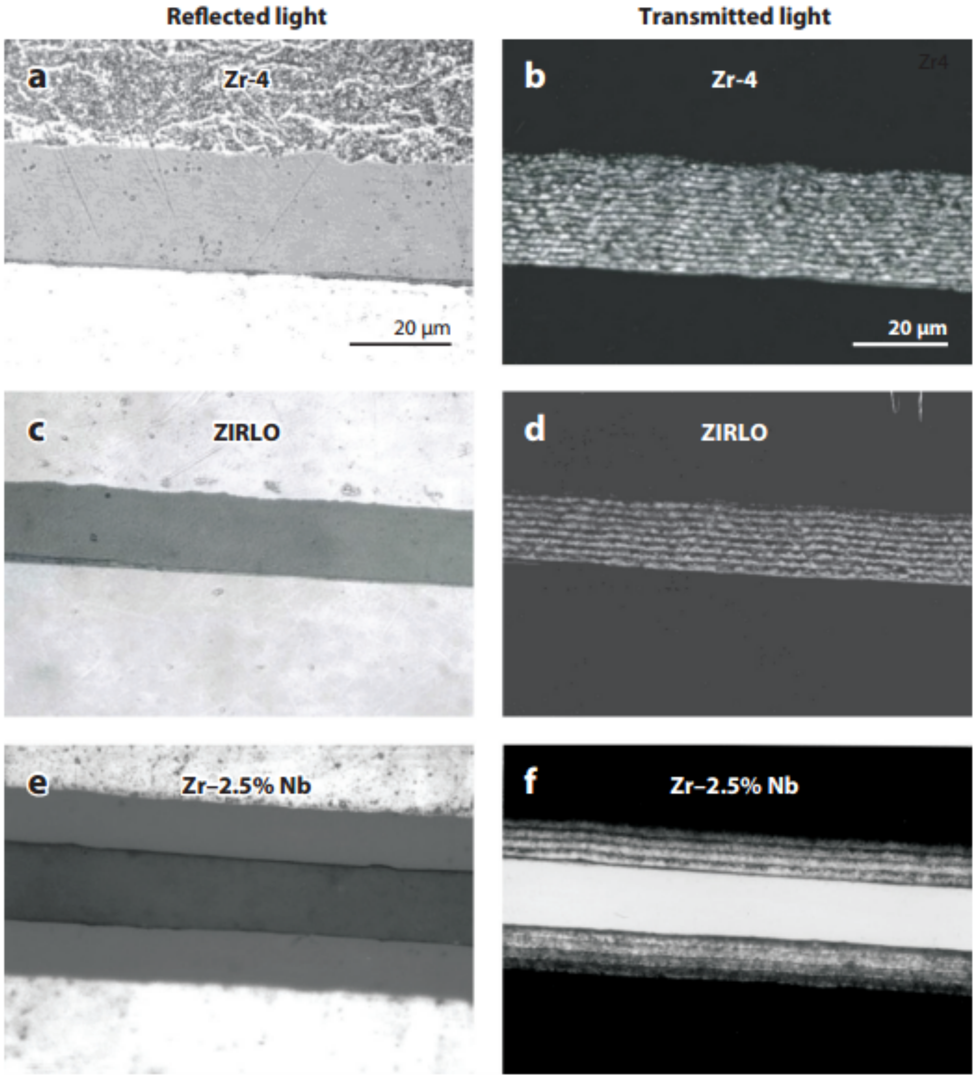
Tetragonal ZrO_2



Source unknown

Loss of and subsequent recovery of oxide protectivity is called transition

- In zirconium-based alloys, oxide recovers and reforms the protective layer and repeats the process in cycles



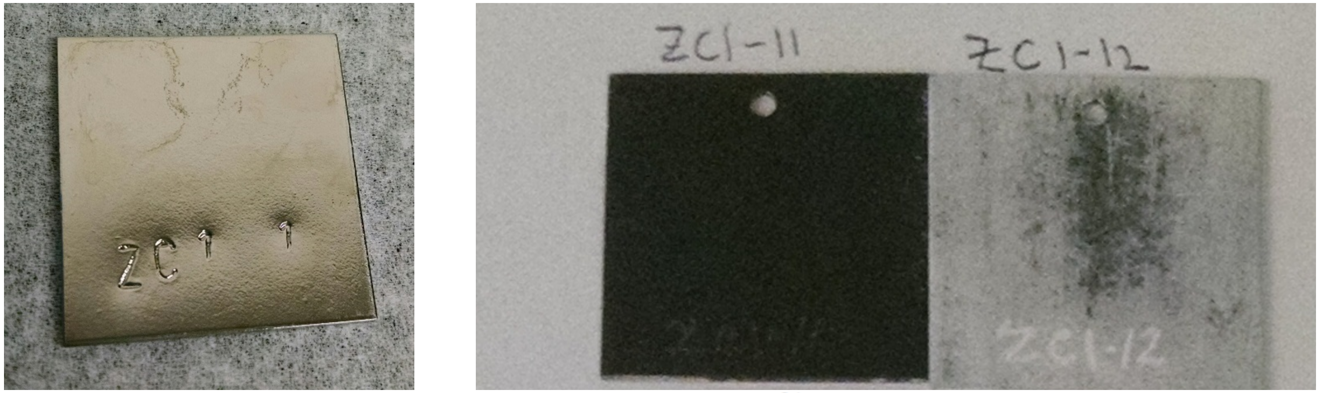
Images courtesy of G.P. Sabol. Westinghouse Electric Co.

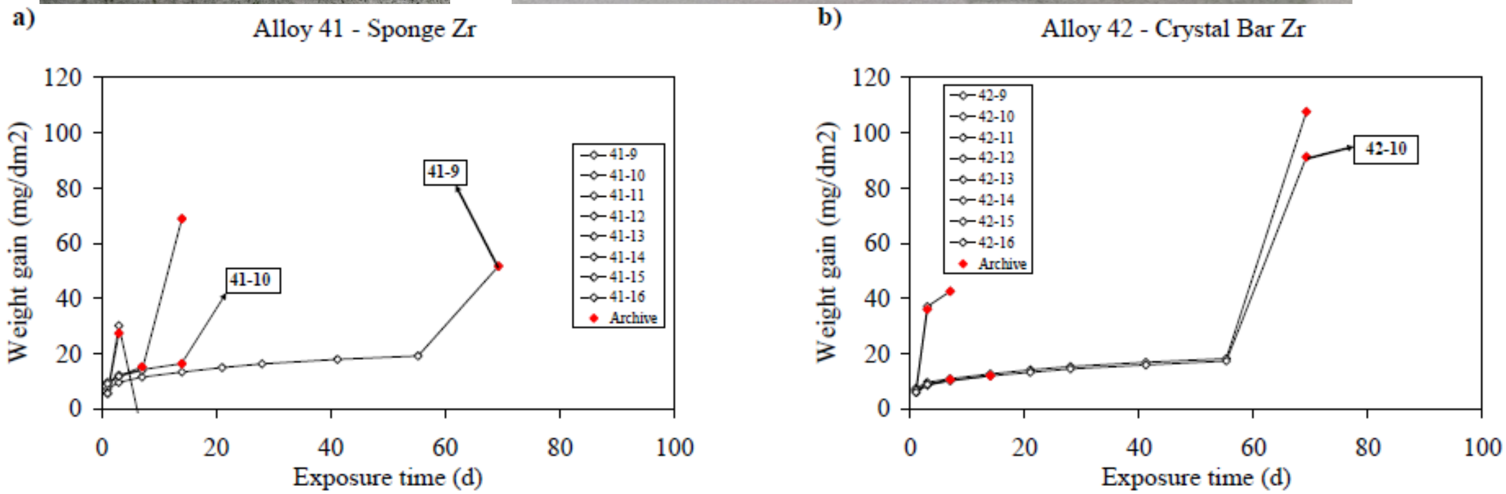
Previously we talked about break away corrosion in pure Zirconium

Breakaway corrosion is an unpredictable loss of oxide protection

Crystal bar zirconium

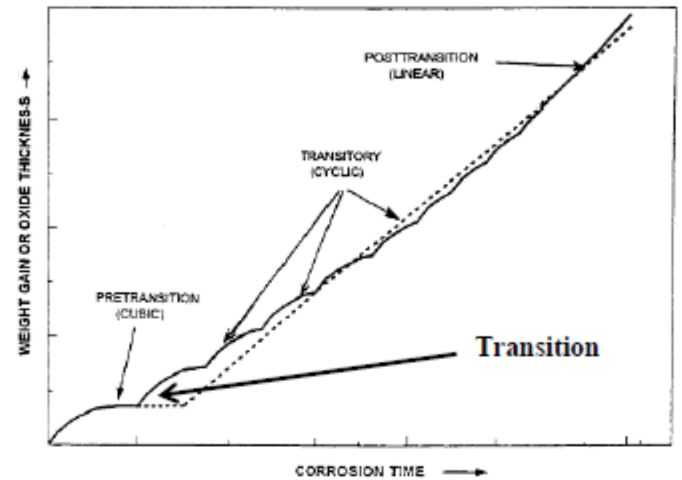
0 d | 10 d in 360 °C water

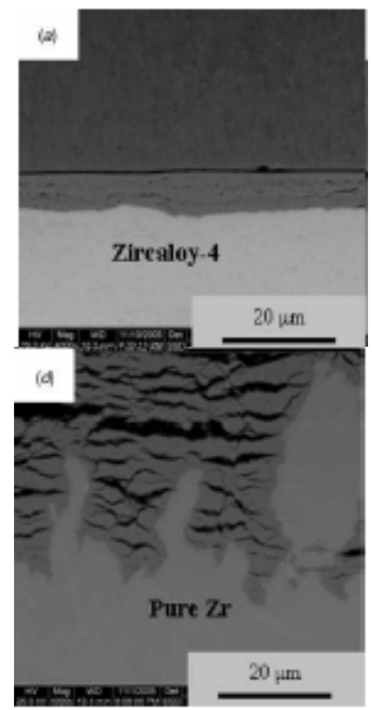




Unstable oxide growth

- Oxide grows in vertical direction to accommodate stress associated with volume expansion (PBR ~ 1.56)
- Oxide layer is protective and hinders oxygen diffusion in the pre-transition regime
- At transition oxide will lose protectivity, allowing water access to the metal

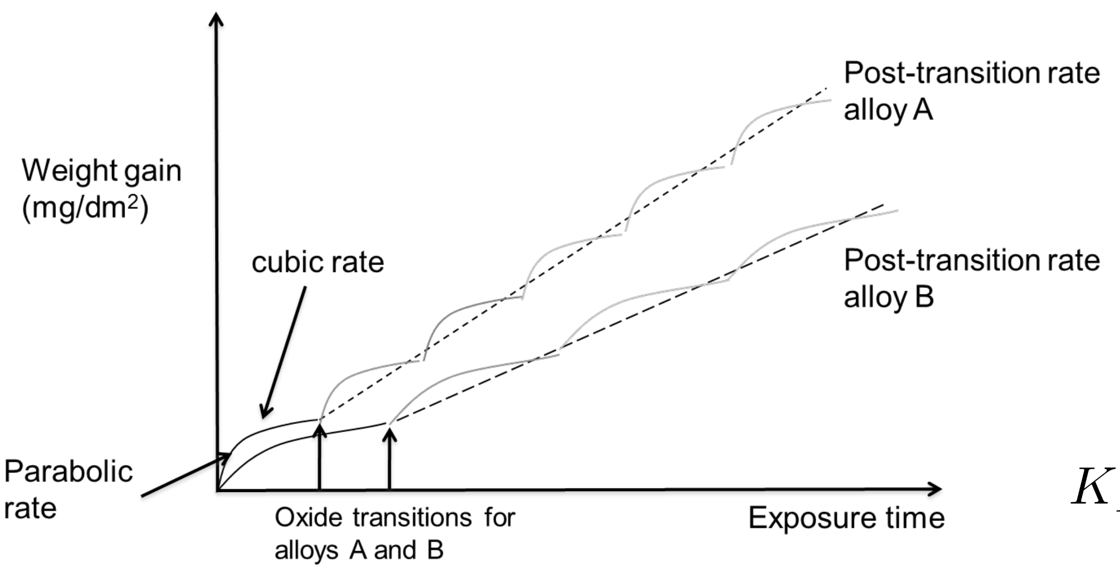




Hillner, E., et al. *Journal of Nuclear Materials*. 2000.

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

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

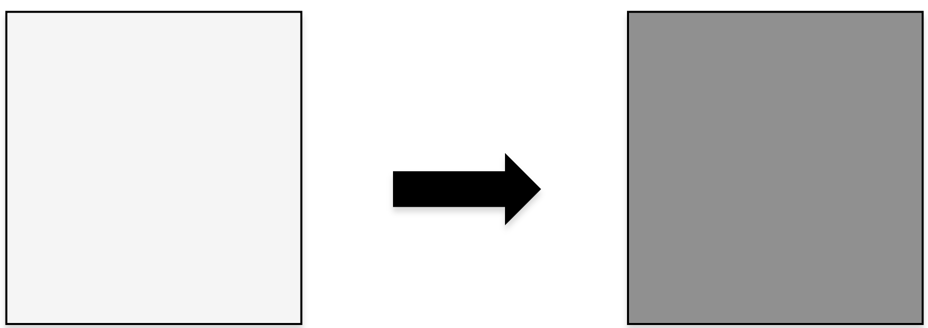
$$K_L\left(\frac{\mu\mathrm{m}}{\mathrm{d}}\right) = 7.48\times10^{6}\exp\frac{-12500}{T}$$

* Constants given apply to ZIRLO

Corrosion is measured by sample weight gain

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

$$\boxed{W = (m_2 - m_1)/S}$$



<u>Original coupon</u>:
Weight m_1
Surface S

<u>corroded coupon</u>:
Weight $m_2 > m_1$
Surface S

Dividing by the surface enables comparison between samples

<u>Approximation weight gain – oxide thickness for Zr</u>:

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

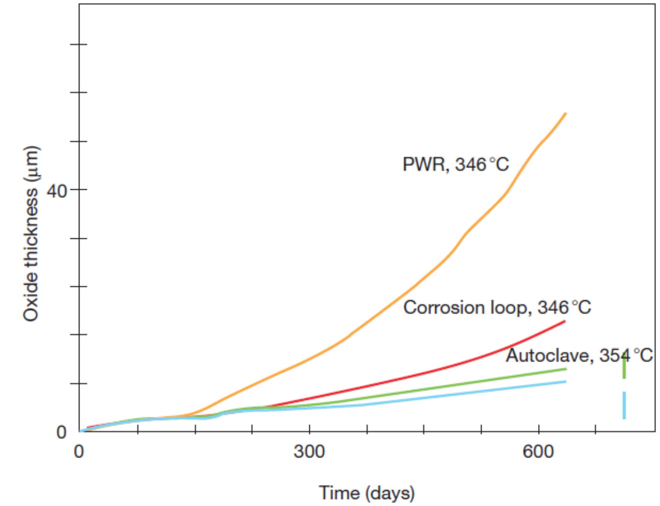
We will now work a problem

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

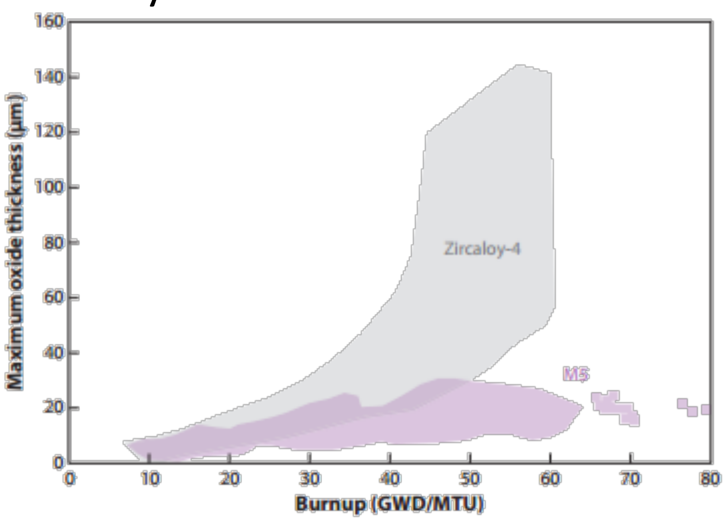
The presence of irradiation can alter corrosion properties

- Production of radicals through radiolysis
- Radiation damage to the metal
- Radiation damage to oxide

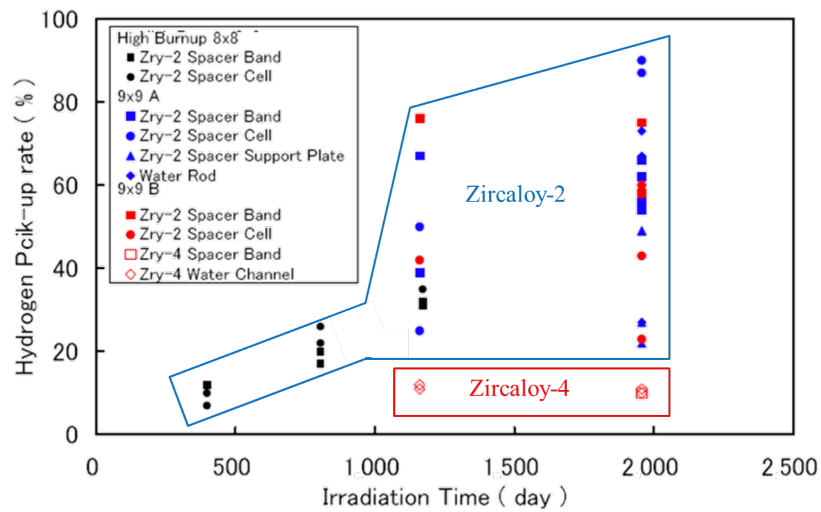
Zircaloy-4 corroded under different conditions



Zircaloy-4 and ZIRLO corroded in PWR



Zircaloy-2 and Zircaloy-4 corroded in BWR

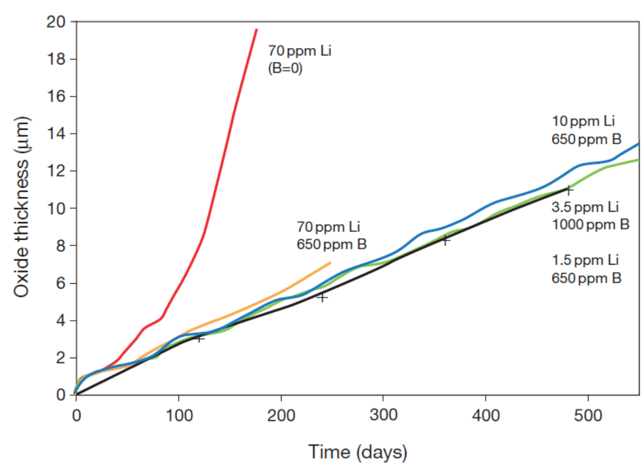


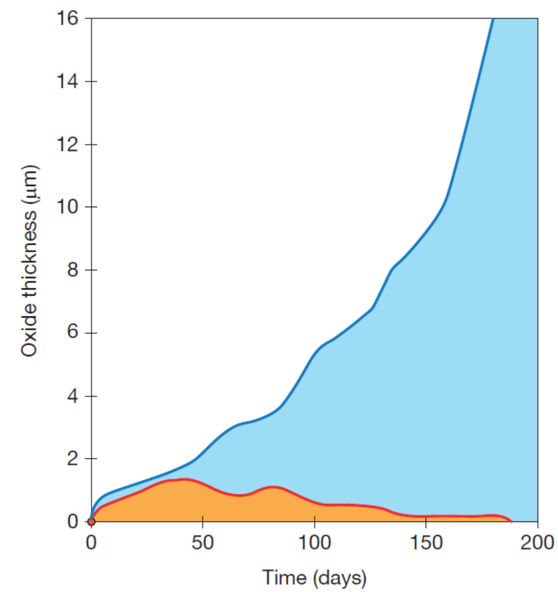
Motta, A.T., et al. *Annual Review of Materials Research*. 2015. Comprehensive Nuclear Materials. 2011. Miyashita, T. *Top Fuel*. 2007.

Coolant additions are added to control neutronics, corrosion, and hydrogen pick-up

- BWRs
  - Zinc to control radiation fields outside core
  - Hydrogen water chemistry and noble metal additions to reduce degradation of reactor internals
- PWRs
  - Boric acid as a chemical shim
  - Lithium hydroxide to control coolant pH

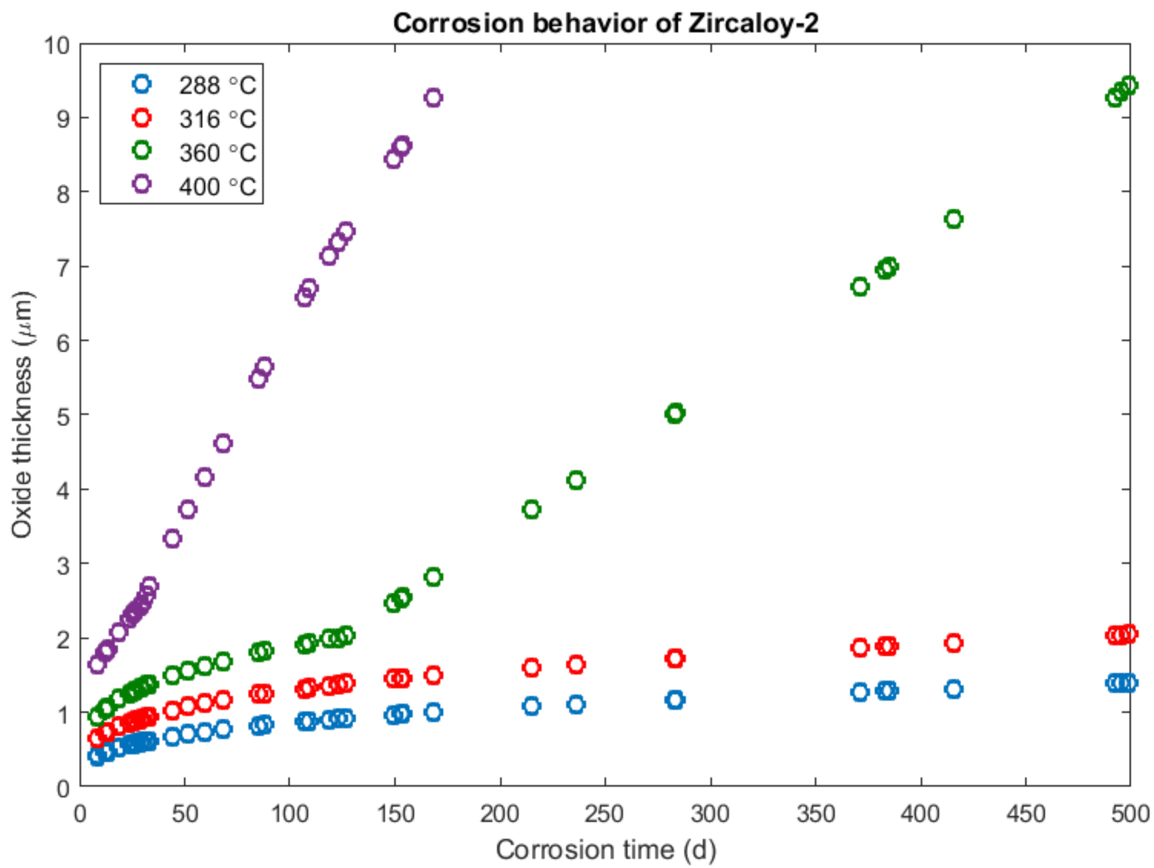
Effect of Li and B on corrosion of Zircaloy-4 in 360 °C water





Comprehensive Nuclear Materials. 2011.

Corrosion rate depends on corrosion conditions

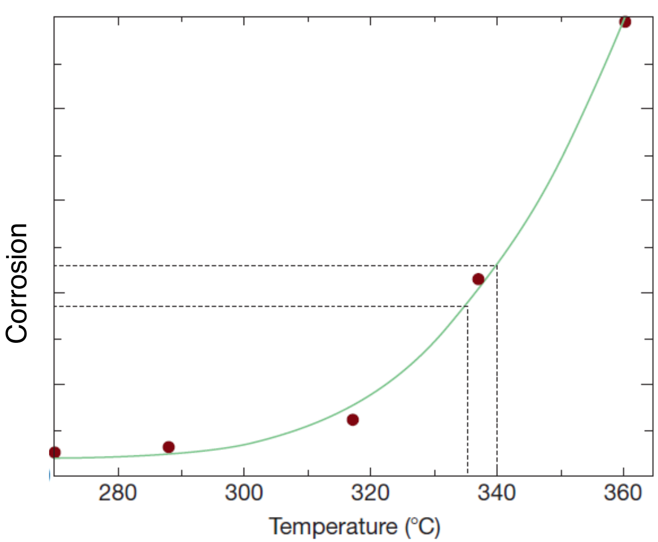


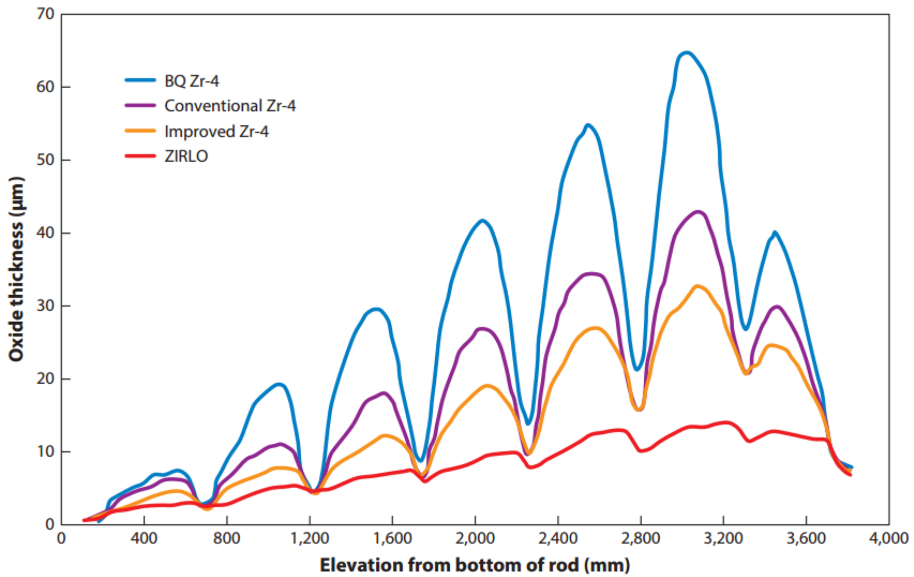
For a particular alloy, increasing corrosion temperature increases oxide thickness

Kass, S., et al. *Corrosion of Zirconium Alloys*. 1962.

Corrosion rate increases with temperature

- Oxide layer temperature depends on coolant temperature and heat flux
- Oxide layer is a thermal insulator





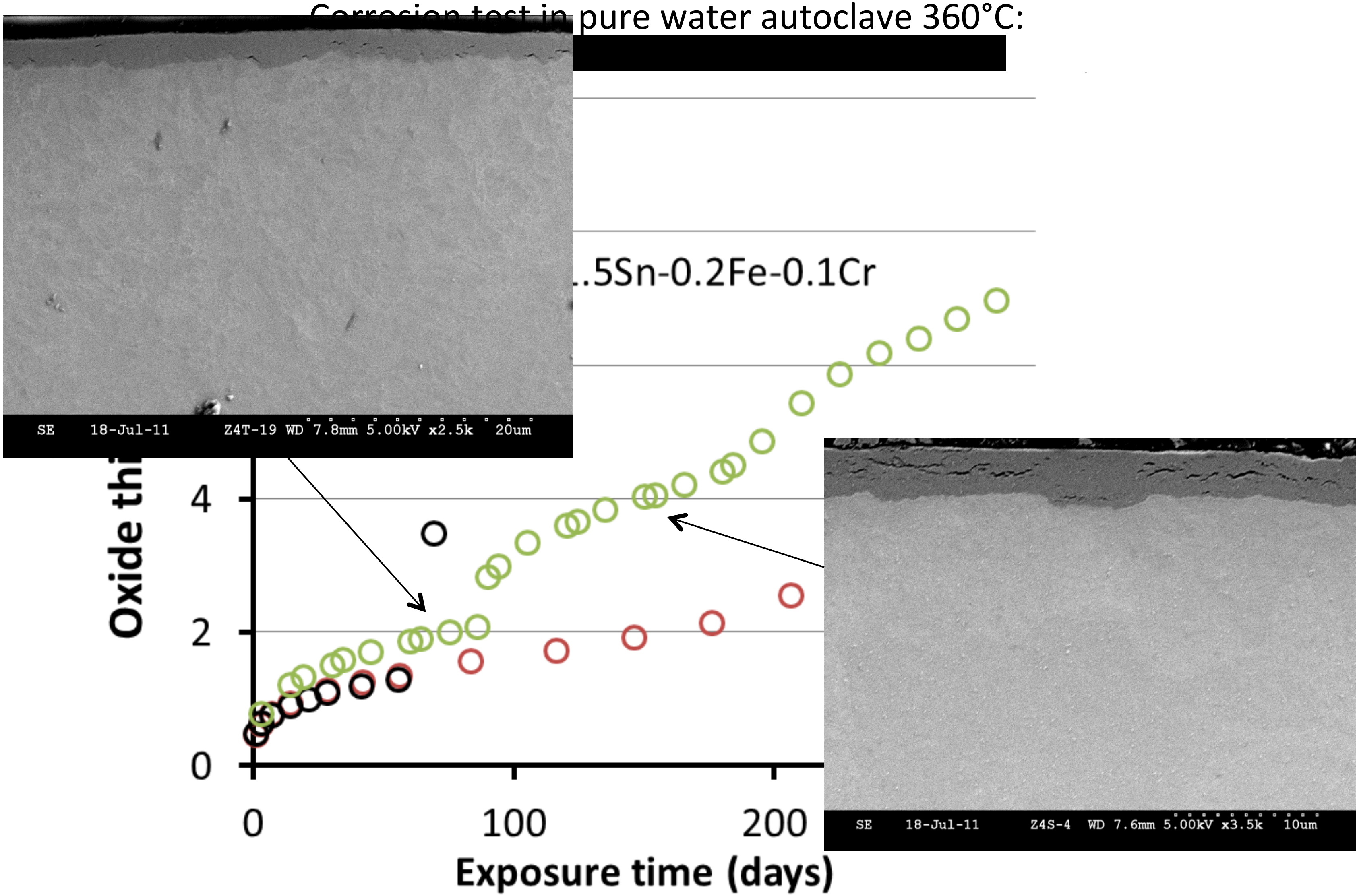
Comprehensive Nuclear Materials. 2011.

Motta, A.T., et al. *Annual Review of Materials Research*. 2015.

Different alloys corrode differently

Corrosion test in pure water autoclave 360°C:

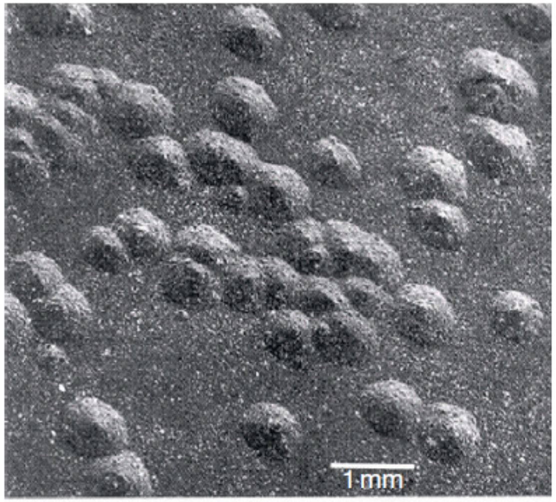
[redacted]



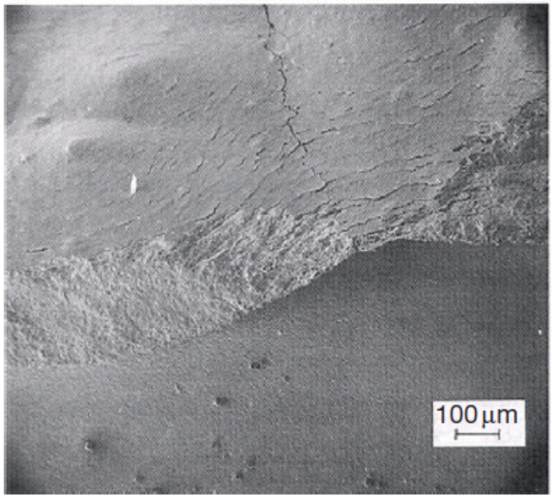
A. Couet. 2014

Consequences of second-phase precipitate distribution

(a)



(b)



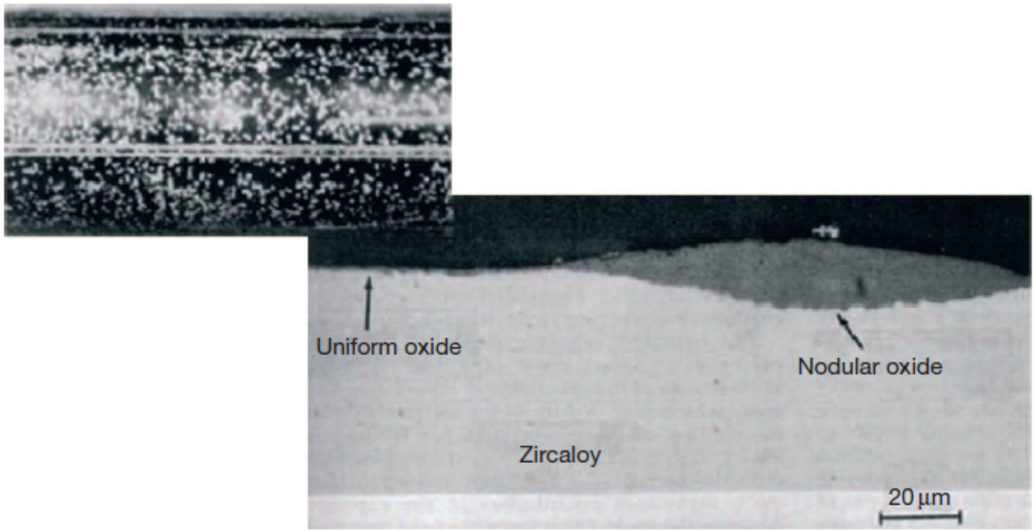
Second-phase intermetallic precipitates affect corrosion rate

Ex: Large precipitates in Zircaloy-2 cause uniform corrosion in PWRs, but cause non-uniform corrosion in BWRs

Lemaignan, C., et al. Zirconium alloys in nuclear applications. 1994.

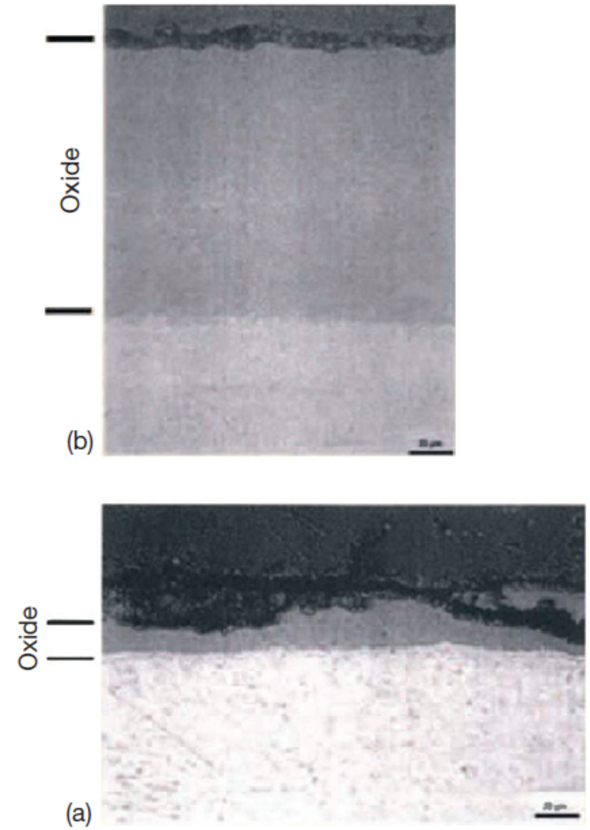
Non-uniform corrosion

Nodular corrosion



Nodular corrosion is not well understood, but is localized corrosion thought to be related to the distribution of second-phase precipitates in the metal

Shadow corrosion

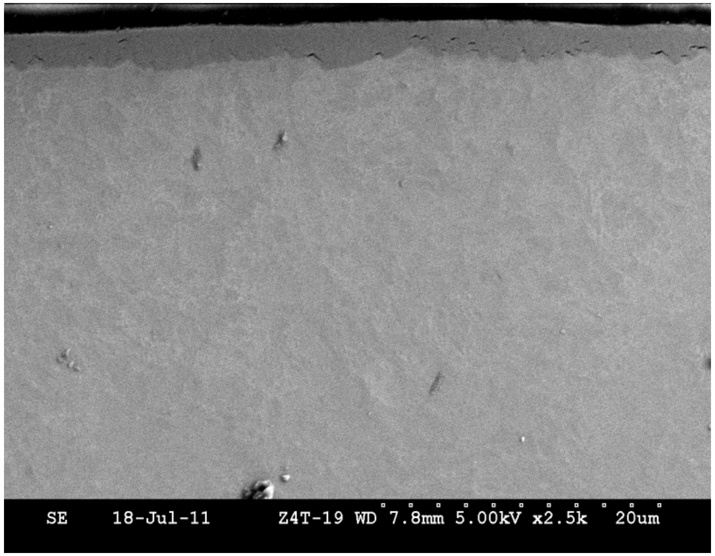


Shadow corrosion is a form of galvanic corrosion

Comprehensive Nuclear Materials. 2011.

What is the impact of oxidation on fuel performance?

- The oxide layer has a low thermal conductivity, restricting heat transport
  - For Zircaloy, k = 22 W/(mK)
  - For ZrO_2, k = 1.7 – 2.7 W/(mK)
- The oxide layer is much more brittle than the zircaloy
  - Zircaloy metal is removed as brittle oxide is added to the material
- Oxidation produces hydrogen that can enter the cladding and form brittle hydrides



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