

Nuclear Fuel Performance

NE-533
Spring 2023

Notes

- MOOSE project part 1 recap:
 - Generally pretty good
 - No one mentioned my mistake in listing LHR in the wrong units
 - I provided one transient equation in class, and a different one in Moodle: my fault
 - For those that had issues, verify that your code is working properly and you can get the right results before moving to part 2
 - All should perform some convergence testing on your meshes and timestep, if you haven't done so

Paper assignment

- I will have assign each of you a paper to read and review by tomorrow
 - if you have a preference on topic, please let me know ASAP
- We will have 15 minute presentations from each person on April 11 and March 11 summarizing and analyzing their respective paper
- Papers available on Moodle
- Everyone will upload their slides into Moodle by 11:59 pm April 10

Last Time

- The average grain size in UO_2 impacts fuel behavior and performance
- The material lowers energy by having large grains grow at the expense of small grains
- Fuel densification is driven by reduction in surface area of pores – continuation of sintering process
- Five families of fission products which uniquely change the fuel behavior
- Fission gas is released in three stages
 1. Fission gas production and diffusion to grain boundaries
 2. Grain boundary bubble nucleation, growth, and interconnection
 3. Gas transport through interconnected bubbles to free surfaces
- Fission gas release is measured using post-irradiation annealing and/or in pile experiments

Fission Gas Release

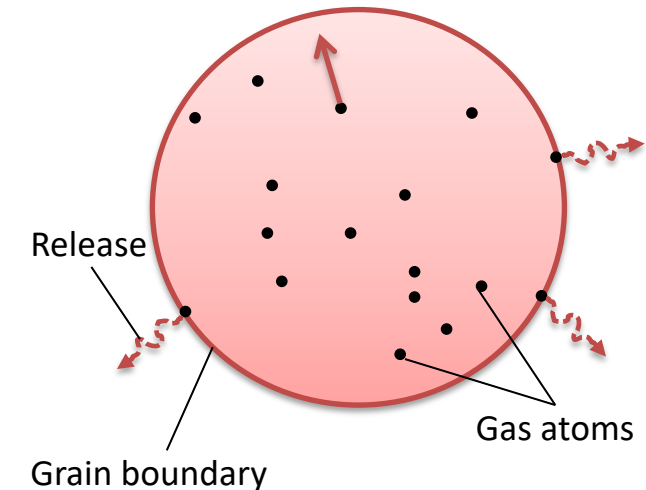
- Fission gas release models attempt to predict the rate at which gas is released from the fuel
- To model fission gas release, ideally, we must model all three stages of gas release
 - Diffusion of gas atoms to grain boundaries
 - Growth and interconnection of grain boundary bubbles
 - Transport of gas atoms through interconnected bubbles to free surfaces
- The earliest models only considered Stage 1
- Most models now consider stage 1 and 2
- There are no models that consider all three stages, but some are under development

Booth Model

- The Booth model is the earliest model of fission gas release and only considers stage 1
- A grain is considered as a simple sphere
- Gas atoms are released at the grain boundary
- The model solves the diffusion equation in 1D spherical coordinates
- Assumptions
 - $c_g(r, t)$
 - All grains are spheres of radius a
 - D is constant throughout the grain
 - Gas is produced uniformly throughout the grain
 - Gas is released once it reaches the grain boundary

$$\dot{c}_g = k_{c_g} + \nabla \cdot D \nabla c_g$$

$$\dot{c}_g = k_{c_g} + D \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial c_g}{\partial r} \right)$$



ICs and BCs

$$c_g(r, 0) = 0$$

$$c_{g,r}(0, t) = 0$$

$$c_g(a, t) = 0 \text{ (release)}$$

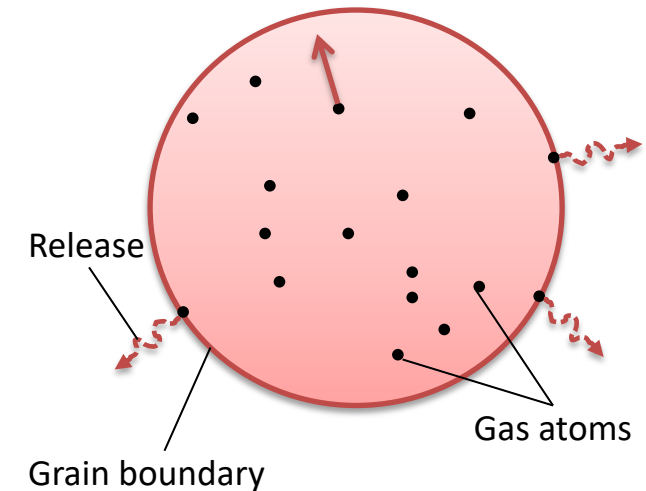
Modeling post-irradiation annealing

- The initial gas concentration is c_g^0
- No gas is produced

$$\dot{c}_g = D \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial c_g}{\partial r} \right)$$

- Solving this equation tells us the value of c_g at any radius or time
- However, we want to know the fraction of gas atoms that have made it to the grain boundary
- We use the flux at the grain boundary

$$J_a = -D \left(\frac{\partial c_g}{\partial r} \right)_a \quad f = \frac{4\pi a^2 \int_0^t J_a dt}{4/3\pi a^3 c_g^0} = \frac{3}{ac_g^0} \int_0^t J_a dt$$



ICs and BCs

$$c_g(r, 0) = c_g^0$$

$$c_{g,r}(0, t) = 0$$

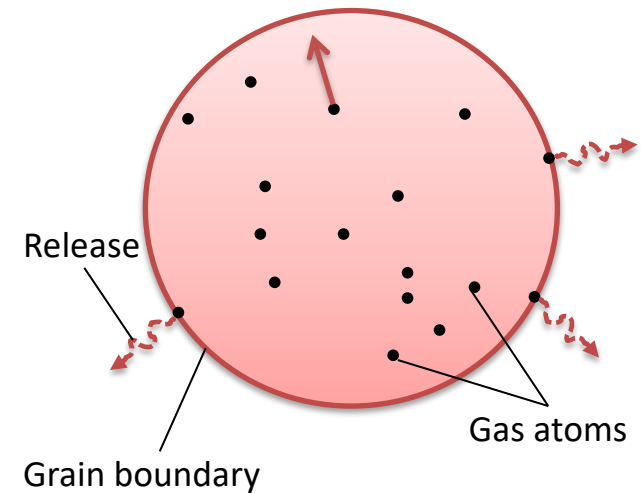
$$c_g(a, t) = 0 \text{ (release)}$$

Solving the Booth Model

- This equation is solved using a Laplace transform after nondimensionalization
- Will not go through the derivation (shown in Olander)
- $\tau = D \times t / a^2$

$$f = 6\sqrt{\frac{Dt}{\pi a^2}} - 3\frac{Dt}{a^2} \quad \tau < \pi^2$$

$$f = 1 - \frac{6}{\pi^2} e^{-\pi^2 \frac{Dt}{a^2}} \quad \tau \geq \pi^2$$



Booth Example

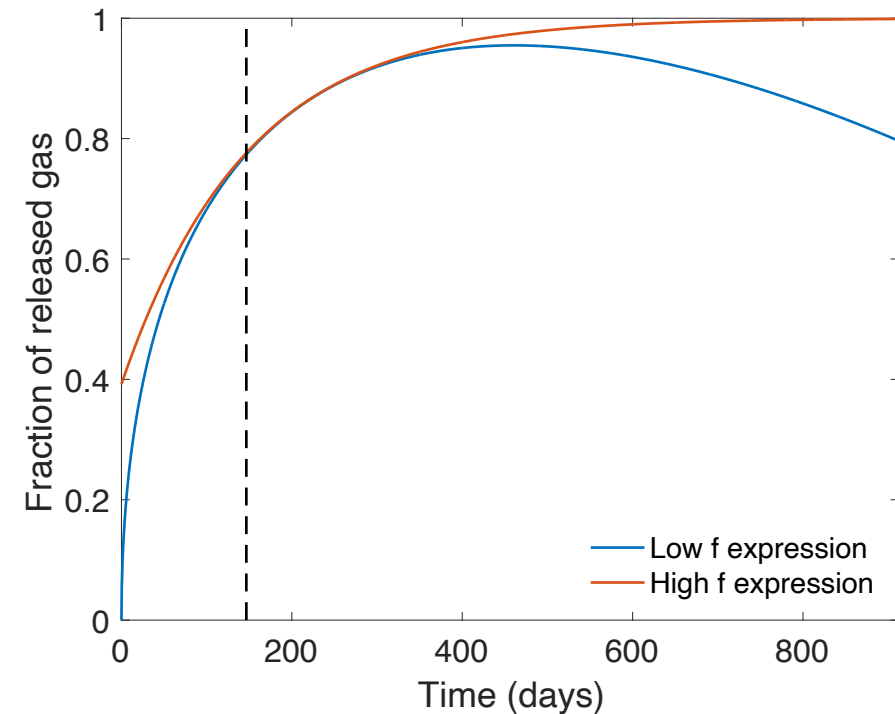
- For a diffusion coefficient for Xe of $D = 8\text{e-}15 \text{ cm}^2/\text{s}$, what fraction of the fission gas trapped in an post-irradiation annealed fuel pellet has escaped after one hour? It has an average grain size of 10 microns
 - $D = 8\text{e-}15 \text{ cm}^2/\text{s}$
 - $a = 10\text{e-}4 \text{ cm}$
 - $t = 3600 \text{ s}$
- Which f ? $\tau = D \times t/a^2 = 2.88\text{E-}4 < \pi^{-2} = 0.101$

$$f = 6\sqrt{\frac{Dt}{\pi a^2}} - 3\frac{Dt}{a^2}$$
 - $f = 6*\text{sqrt}(8\text{e-}15*3600/(\text{pi}*(10\text{e-}4)^2)) - 3*8\text{e-}15*3600/(10\text{e-}4)^2 = 0.0181$

Different expressions for fission gas release

- Given the data from the previous example, can plot both

$$\begin{aligned} - \tau < \pi^{-2} & \quad f = 6\sqrt{\frac{Dt}{\pi a^2}} - 3\frac{Dt}{a^2} \\ - \tau > \pi^{-2} & \quad f = 1 - \frac{6}{\pi^2}e^{-\pi^2 \frac{Dt}{a^2}} \end{aligned}$$



Modeling in-pile release

- The initial gas concentration is 0
- Gas is produced due to fission, where y is the chain yield ($y = 0.3017$ for Xe and Kr) and the fission rate

$$\dot{F} = qN_U\sigma_f{}_{235}\phi_{th}$$

- Gas can also decay, where λ is the decay constant
 - If we only consider stable stable products, $\lambda = 0$
- For in pile release, the fraction is equal to

$$f = \frac{3}{ay\dot{F}t} \int_0^t J_a dt$$

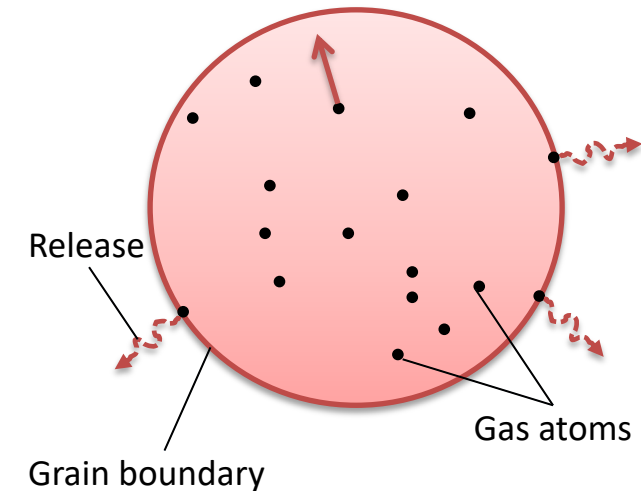
- After solving with with a Laplace transform

$$f = 4\sqrt{\frac{Dt}{\pi a^2}} - \frac{3}{2} \frac{Dt}{a^2} \quad \tau < \pi^2$$

$$f = 1 - \frac{0.0662}{\frac{Dt}{a^2}} \left(1 - 0.93e^{-\pi^2 \frac{Dt}{a^2}}\right) \quad \tau \geq \pi^2$$

- The total gas production is $y\dot{F}t$ gas atoms/cm³

$$\dot{c}_g = y\dot{F} + D \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial c_g}{\partial r} \right) - \lambda c_g$$



ICs and BCs

$$c_g(r, 0) = 0$$

$$c_{g,r}(0, t) = 0$$

$$c_g(a, t) = 0 \text{ (release)}$$

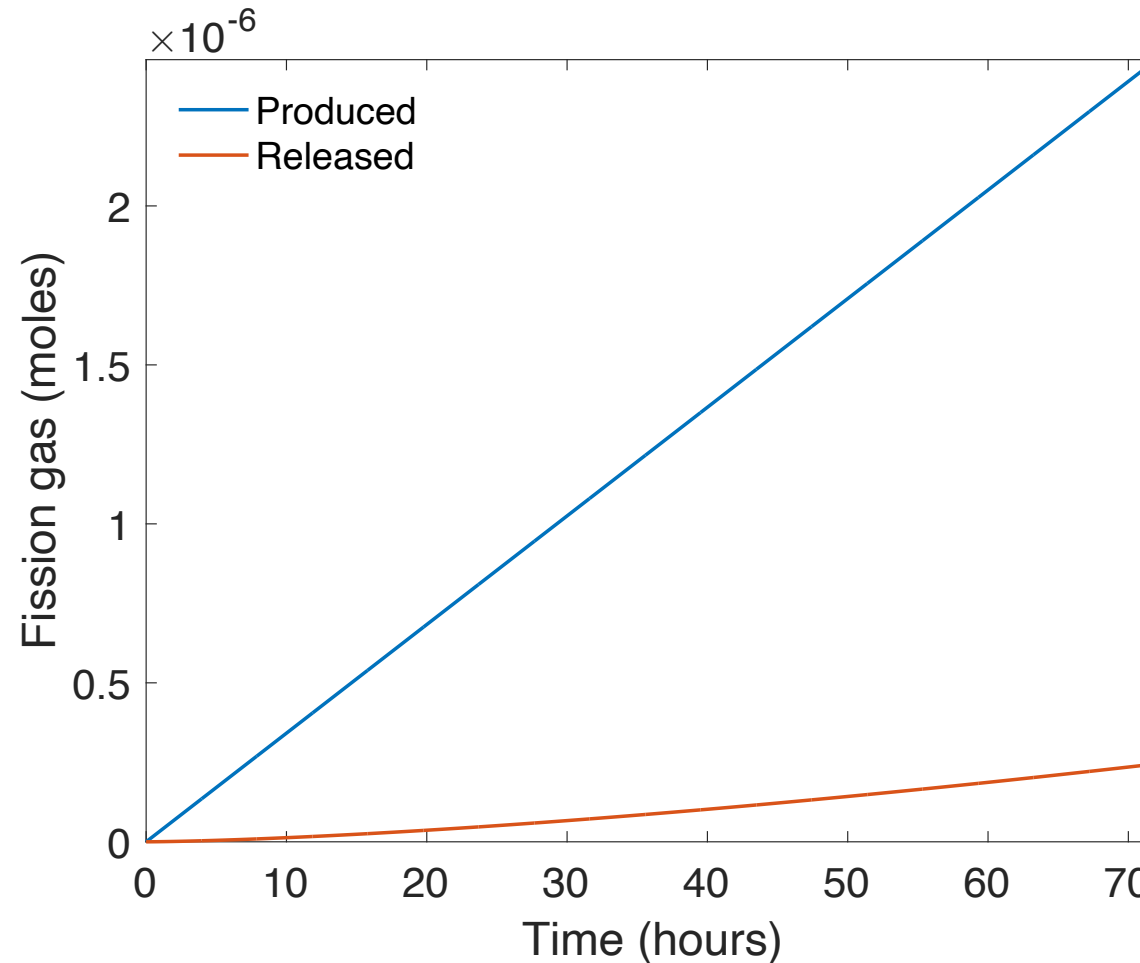
Example

- For a diffusion coefficient for Xe of $D = 8\text{e-}15 \text{ cm}^2/\text{s}$, what fraction of the fission gas trapped in an in-pile fuel pellet has escaped after one hour? It has an average grain size of 10 microns.
 - $D = 8\text{e-}15 \text{ cm}^2/\text{s}$
 - $a = 10\text{e-}4 \text{ cm}$
 - We have a short time ($t=3600 \text{ s}$), so we can use:

$$f = 4\sqrt{\frac{Dt}{\pi a^2}} - \frac{3}{2} \frac{Dt}{a^2}$$

- $f = 4*\text{sqrt}(8\text{e-}15*3600/(\text{pi}*(10\text{e-}4)^2)) - 3/2*8\text{e-}15*3600/(10\text{e-}4)^2 = 0.0121$

As time progresses, both the fraction released and the produced gas increase



Forsberg-Massih model

- The Booth model ONLY considers stage one of fission gas release
- Two stage Forsberg-Massih mechanistic model
 - Considers intragranular diffusion diffusion to grain boundaries (stage 1)
 - Also, grain boundary gas accumulation, resolution back into grain, saturation (stage 2)
 - Assumes that once the bubbles on the grain face are interconnected, it is released (no stage 3)

Fission gas is released once the GB coverage reaches a predetermined threshold

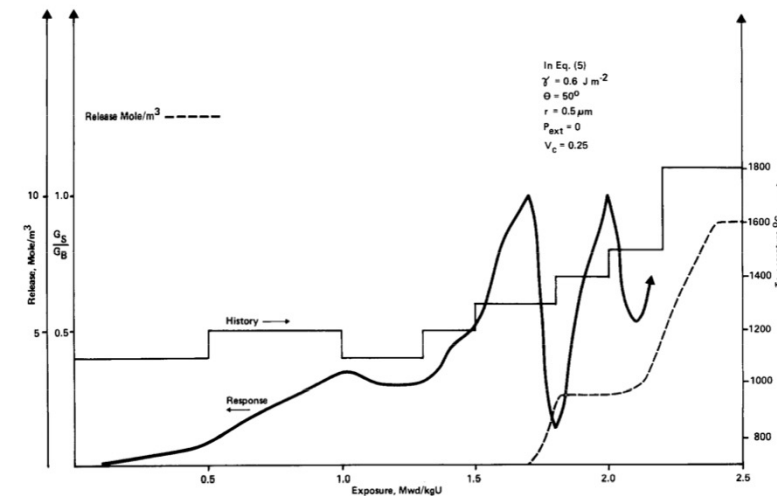
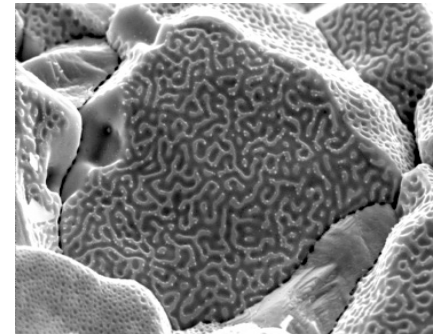
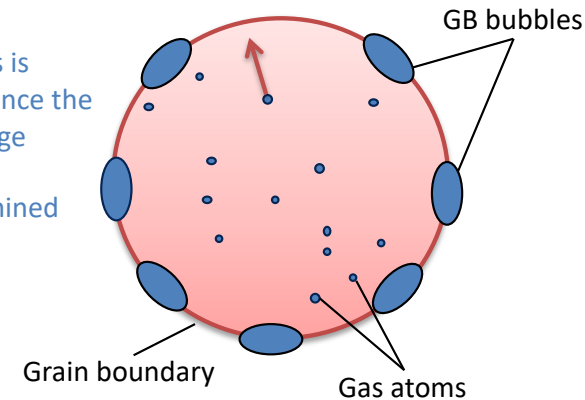
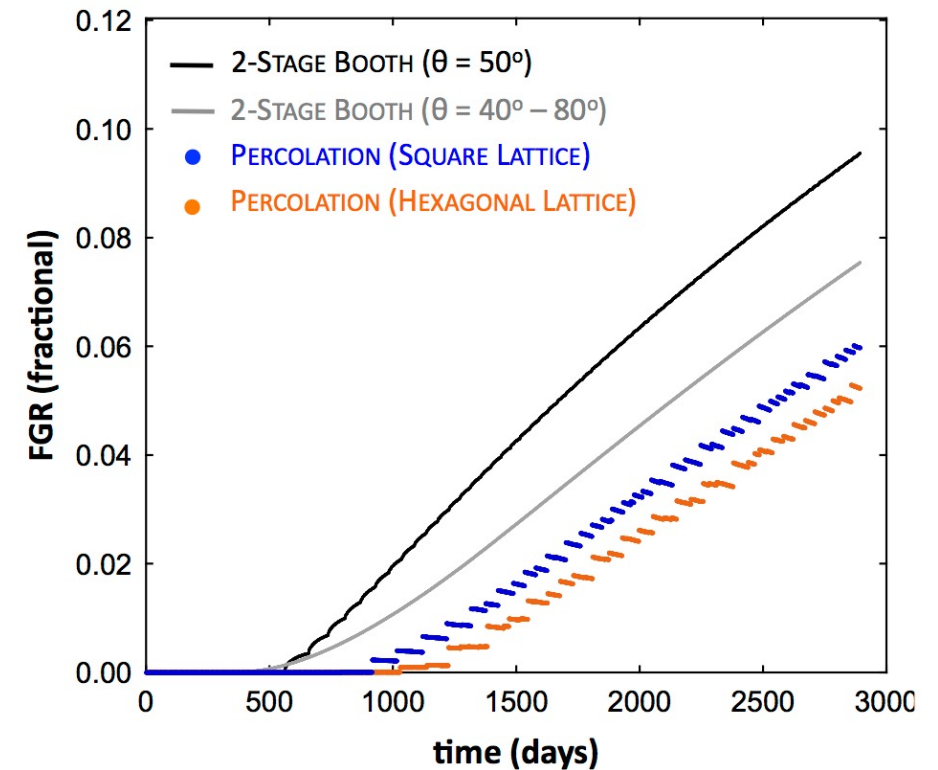
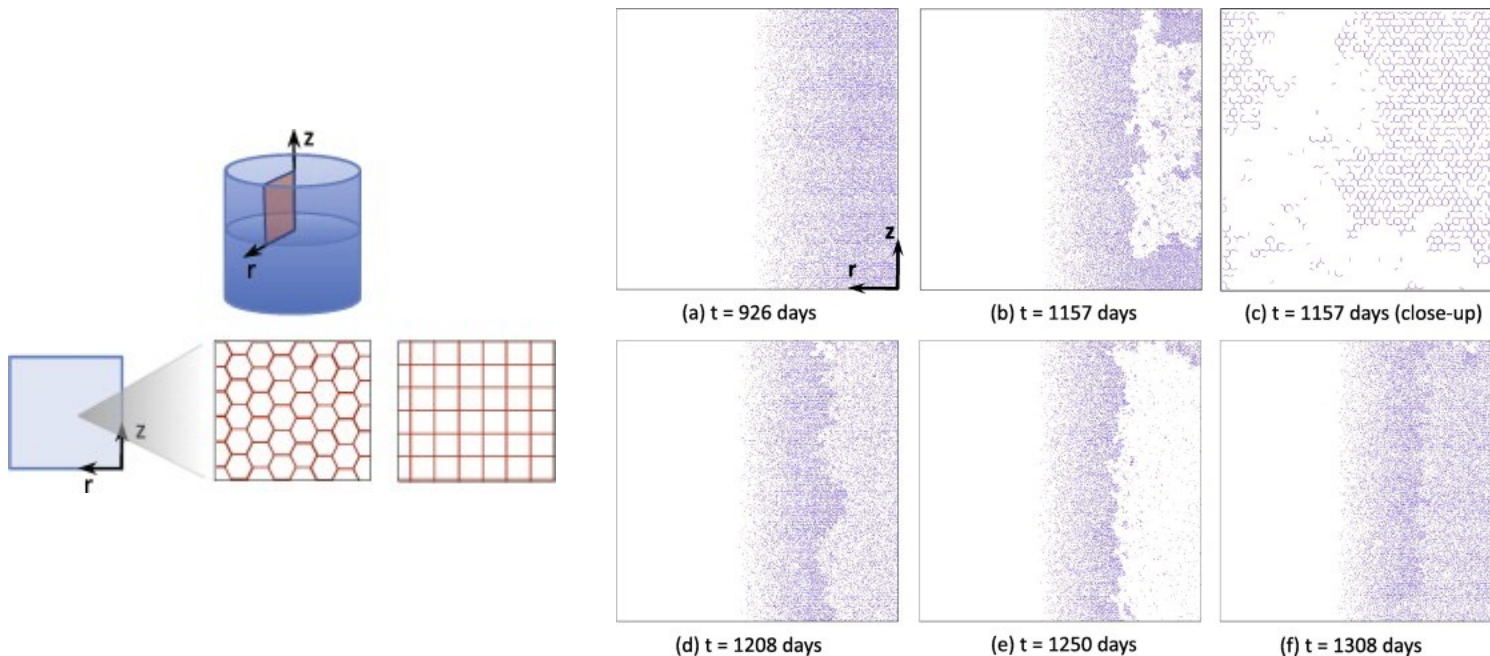


Fig. 1. Fraction of gas atoms on grain boundary, G_g/G_b , as a function of exposure for downward fuel cascading temperature history. γ is the bubble surface tension, 2θ is the angle where two free surfaces meet at a grain boundary, r is average bubble radius, V_c is the fractional coverage of the grain boundaries at saturation and the grain radius is taken to be $5 \mu\text{m}$.

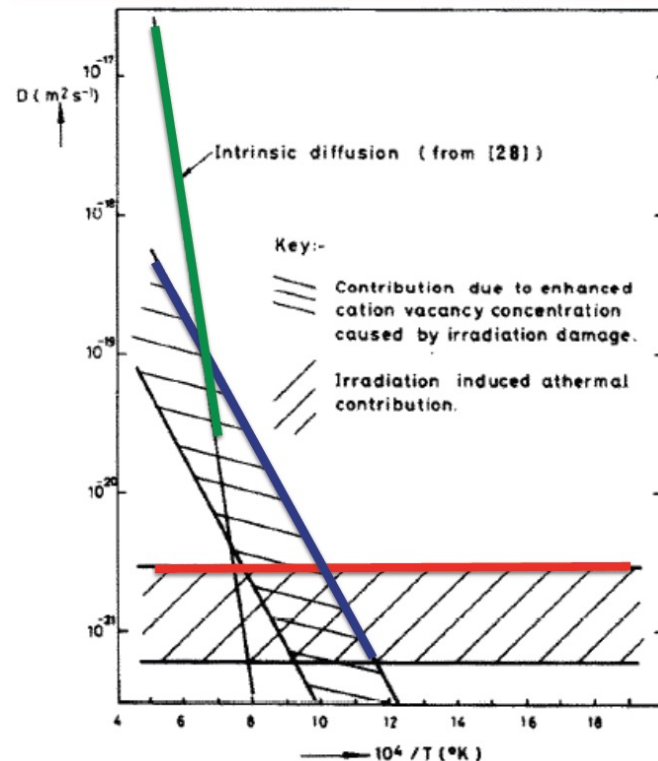
Forsberg-Massih model

- 2-stage F-M model over-predicts gas release because it neglects grain boundary bubble percolation (Stage 3)



Gas diffusion

- The diffusivity of the fission gas depends on temperature and on irradiation
- Experimental data shows three different regimes for the diffusivity

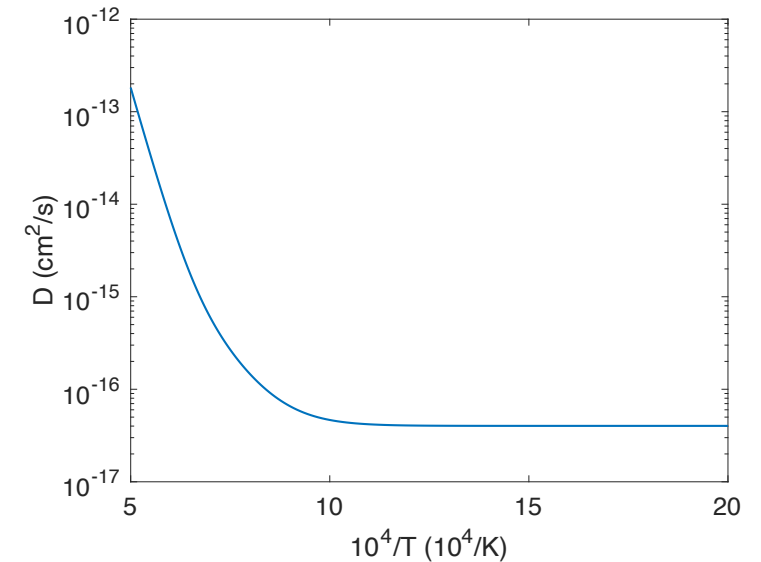


$$D = D_1 + D_2 + D_3 \text{ cm}^2/\text{s}$$

$$D_1 = 7.6 \times 10^{-6} e^{-\frac{3.03 \text{ eV}}{k_b T}}$$

$$D_2 = 1.41 \times 10^{-18} e^{-\frac{1.19 \text{ eV}}{k_b T}} \sqrt{\dot{F}}$$

$$D_3 = 2.0 \times 10^{-30} \dot{F}$$



Gas diffusion

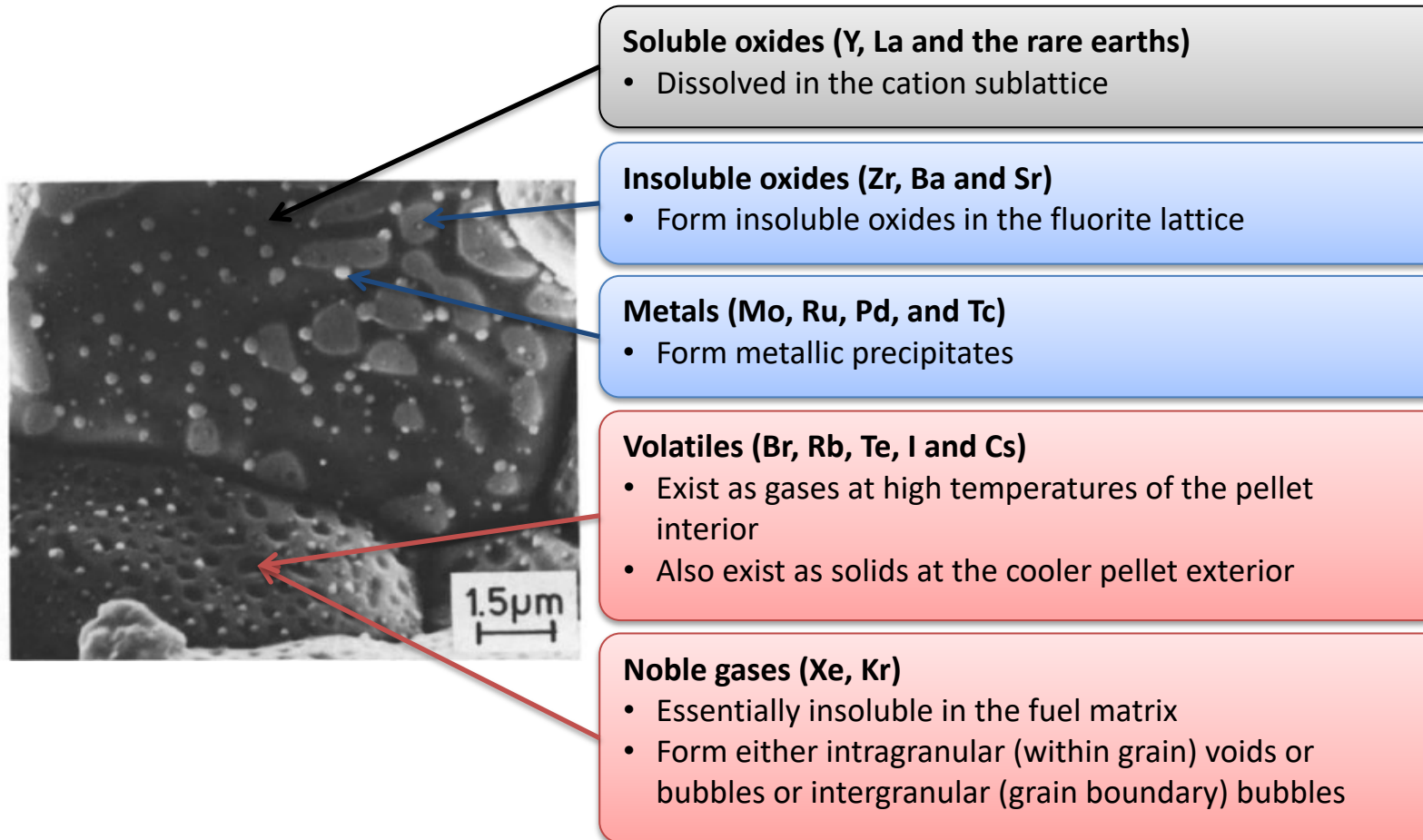
- The effective fission gas diffusivity is slower due to trapping by intragranular bubbles
- As the gas atoms diffuse towards the grain boundary, some are trapped by the small intragranular bubbles
- Some are later knocked out by energized particles (called resolution)
- The effective diffusion constant depends on the trapping rate r_t and the resolution rate r_r

$$D_{eff} = \left(\frac{r_r}{r_r + r_t} \right) D$$

Summary

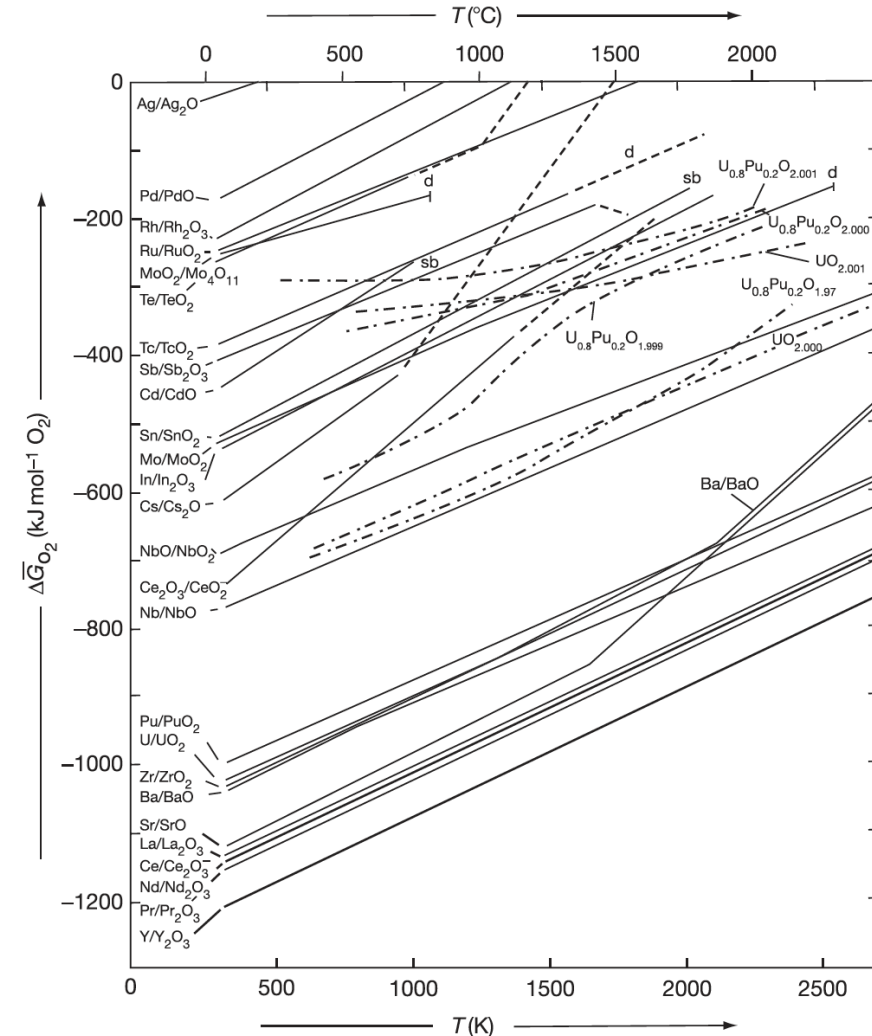
- Fission gas release models are used to understand fission gas experiments and to predict gas release for fuel performance codes
- Spherical grain models predict a fraction of gas release for post-irradiation annealing or for in-pile gas release
- There are models which include 2nd and 3rd stages of fission gas release
- Fission gas diffusivity behavior changes with temperature and fission rate

There are various types of fission products that form in the fuel



Oxide Formation

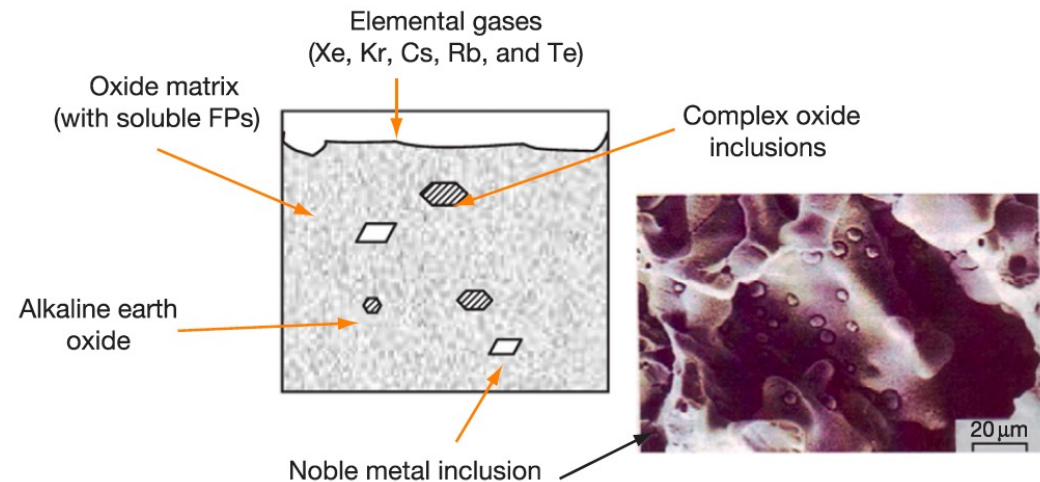
- With burnup, the liberated oxygen will associate with U, Pu, and La but may not be in sufficient supply to combine with Pd and other less oxidizing elements
- If the Gibbs energy of formation of the given fission product lies below the fuel oxygen potential, the element will be capable of forming an oxide
- If the fission product point is above the chemical potential in the fuel, the fission product will exist as an element in the fuel (in a separate metallic phase)



Soluble/Insoluble Fission Products

- When a 4+ valence fission product (e.g., Zr^{4+}) enters the lattice, there is no change in the electrical neutrality
- If the charge of the fission-product cation is lower than U^{4+} , the site occupancy of the lattice is altered to achieve electrical neutrality
- The alkaline earth cations Ba^{2+} and Sr^{2+} have large ionic radii and form a separate oxide phase
- Fission products that have limited solubility in UO_2 will segregate to the grain boundaries and voids


| Chemical group | Physical state | Probable valence |
|--------------------|---|------------------|
| Zr and Nb | Oxide in fuel matrix; some Zr in alkaline earth oxide phase | 4 + |
| Rare earths | Oxide in fuel matrix | 3 + |
| Ba and Sr | Alkaline earth oxide phase | 2 + |
| Mo | Oxide in fuel matrix or element in metallic inclusion | 4 + or 0 |
| Ru, Tc, Rh, and Pd | Elements in metallic inclusion | 0 + |
| Cs and Rb | Elemental vapor or separate oxide phase in cool regions of fuel | 1 + or 0 |
| I and Te | Elemental vapor; I may be combined with Cs and CsI | 0 or 1 - |
| Xe and Kr | Elemental gas | 0 |





Volatile Fission Products


- Xe release occurs at the central region of the pellet where the highest temperatures were achieved during irradiation
- Volatile FPs are released from the fuel matrix similar to that of the noble gases
- Volatile fission products in the gap can react among themselves, resulting in a changing chemical speciation
- The kinetics of formation/decomposition of CsI and Zr iodides are possible factors in the mechanism of SCC

| ← A | | T | | | | | | | | | | B → | | | | | | | | | |
|-----|------|-------|------|-----|------|-------|----|------|----|-----|------|-------|------|-----|------|-------|----|--|--|--|--|
| I A | II A | | | | | | | | | | | III B | IV B | V B | VI B | VII B | | | | | |
| Li | Be | | | | | | | | | | | B | C | N | O | F | Ne | | | | |
| Na | Mg | III A | IV A | V A | VI A | VII A | | VIII | | I B | II B | Al | Si | P | S | Cl | Ar | | | | |
| K | Ca | Sc | Ti | V | Cr | Mn | Fe | Co | Ni | Cu | Zn | Ga | Ge | As | Se | Br | Kr | | | | |
| Rb | Sr | Y | Zr | Nb | Mo | Tc | Ru | Rh | Pd | Ag | Cd | In | Sn | Sb | Te | I | Xe | | | | |
| Cs | Ba | La | Hf | Ta | W | Re | Os | Ir | Pt | Au | Hg | Tl | Pb | Bi | Po | At | Rn | | | | |
| Fr | Ra | Ac | | | | | | | | | | | | | | | | | | | |
| | | Ce | Pr | Nd | Pm | Sm | Eu | Gd | Tb | Dy | Ho | Er | Tm | Yb | Lu | | | | | | |
| | | Th | Pa | U | Np | Pu | Am | Cm | Bk | Cf | Es | Fm | Md | No | Lr | | | | | | |

 Volatile fission product

 Metallic precipitates (alloys)

 Ceramic precipitates (oxides)

 Oxides dissolved in the fuel

Fission Product Segregation

- Fission products can be segregated because of their migration to specific locations such as intragranular segregations, grain boundaries, or pellet surfaces
- Metallic inclusions are commonly observed in ceramographs from irradiated samples
- They are formed by isotopes of Mo, Tc, Ru, Rh, Pd, Ag, Cd, In, Sn, Sb, and Te
- These inclusions are found at the surface of the grain boundaries and are associated, in general, with grain boundary and intragranular bubbles
- Some of the components of these precipitates can be oxidized or reduced forming other compounds of high volatility that can be released from the fuel matrix
- Cs, Ru, Te, and Ba have been consistently found at the cracks in the pellet and on the clad inner surface
- The white inclusions are metallic precipitates, which are composed of Mo, Tc, Rh, Ru, and Pd, form a quinary alloy in an hcp structure
- A “gray oxide phase” perovskite structure containing different combinations of Ba, Cs, Zr, Mo, and U can also form

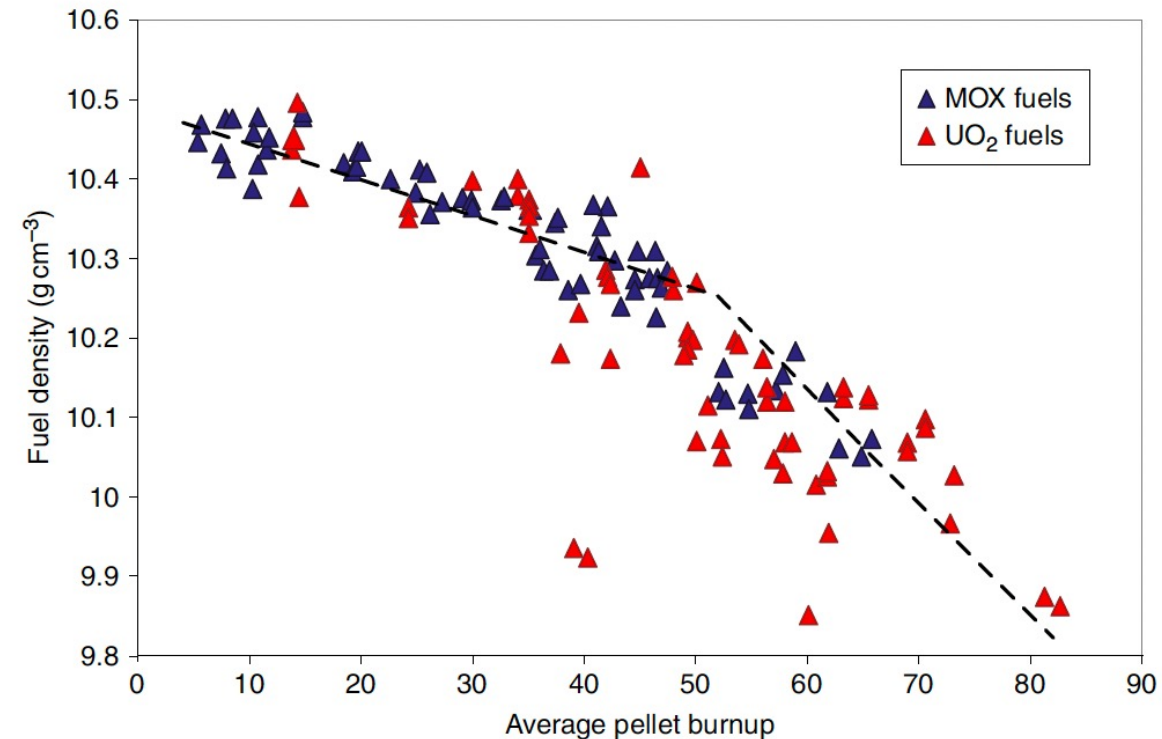
FP Interaction with Zr Cladding

- Fission fragments will deposit on the inner surface of the cladding
- Some of these species can diffuse into the cladding, while others can attack the cladding thereby initiating cracks that can later progress with the formation of through-wall cracks
- Oxygen will diffuse into the cladding and contribute to its oxidation state
- Measurements have shown deposits of Sr, Cs, Pu, and Am
- The corrosion behavior of zirconium by Te has been reported
- The chemical reaction between some corrosive fission products and the cladding can lead to PCI
- Fission products such as Cs, Cd, or I can attack the cladding inducing crack initiation, which then progress through the cladding by intragranular and transgranular cracking modes

FUEL SWELLING/DIMENSIONAL CHANGE

Fuel changes size and shape under reactor operation

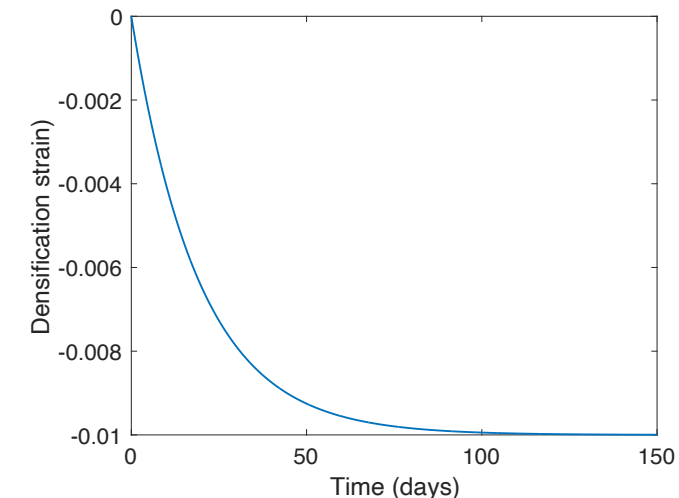
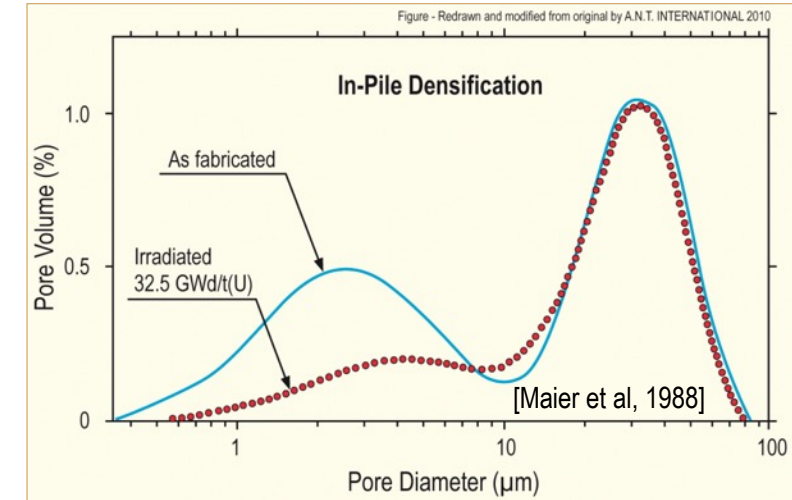
- Thermal expansion:
 - increase in volume, decrease in density, caused by increasing temperature
- Densification:
 - Decrease in volume, increase in density, caused by shrinking of porosity left after sintering
- Swelling:
 - Increase in volume, decrease in density, caused by fission products
- Irradiation Creep:
 - Change in shape, constant density, occurs with applied stress less than σ_y



Densification

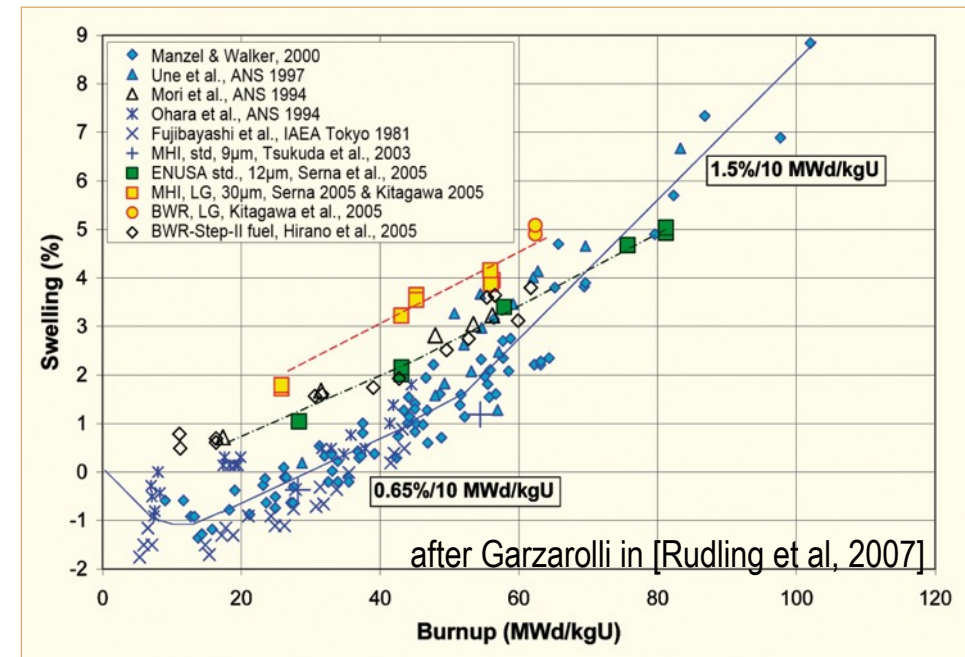
- Densification takes place during initial 5 - 10 MWd/kgU
 - Small, as-built pores close due to effects of fission spikes and vacancy diffusion
 - Large pores stable (in absence of large hydrostatic stress)
- Empirical correlation for densification is a function of
 - β - Burnup (in FIMA)
 - $\Delta\rho_0$ – Total densification that can occur (a common value is 0.01)
 - β_D – Burnup at which densification stops (a common value is 5 MWD/kgU)
 - $C_D = 7.235 - 0.0086 (T(^{\circ}\text{C}) - 25)$ for $T < 750^{\circ}\text{C}$ and $C_D = 1$ for $T \geq 750^{\circ}\text{C}$

$$\epsilon_D = \Delta\rho_0 \left(e^{\frac{\beta \ln 0.01}{C_D \beta_D}} - 1 \right)$$



Fission product induced swelling

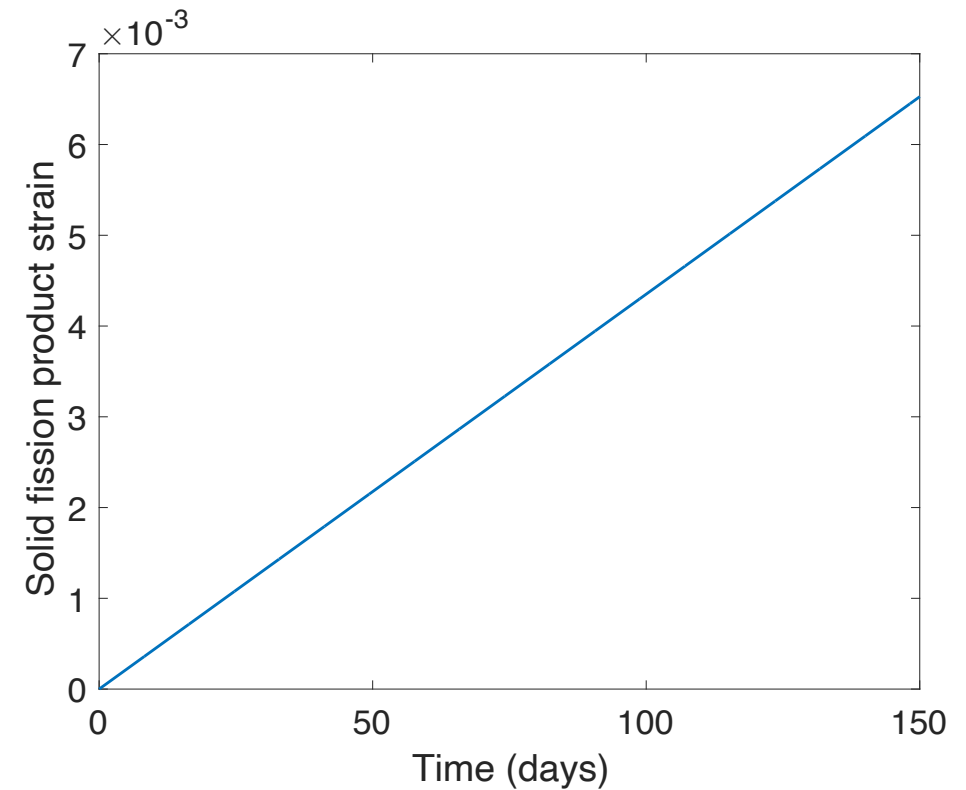
- Fission product swelling results from three changes in the fuel microstructure
 - Solid swelling: Accumulation of soluble and insoluble fission products in fuel matrix
 - Gaseous swelling: Accumulation of gaseous and volatile fission products in intragranular and intergranular pores
 - High burnup swelling: Restructuring of pellet rim with the accumulation of fission gas in a large number of small pores



Solid fission product swelling

- The solid fission product swelling model is a function of:
 - B – Burnup (in FIMA)
 - ρ – Initial UO_2 density (g/cm^3)

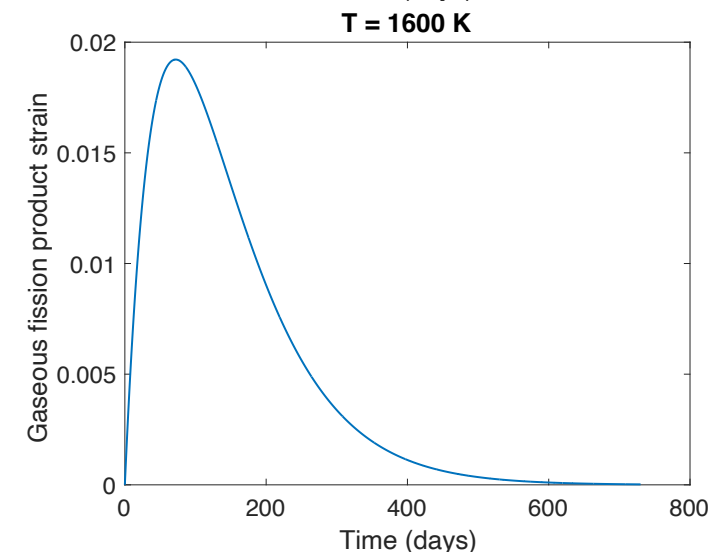
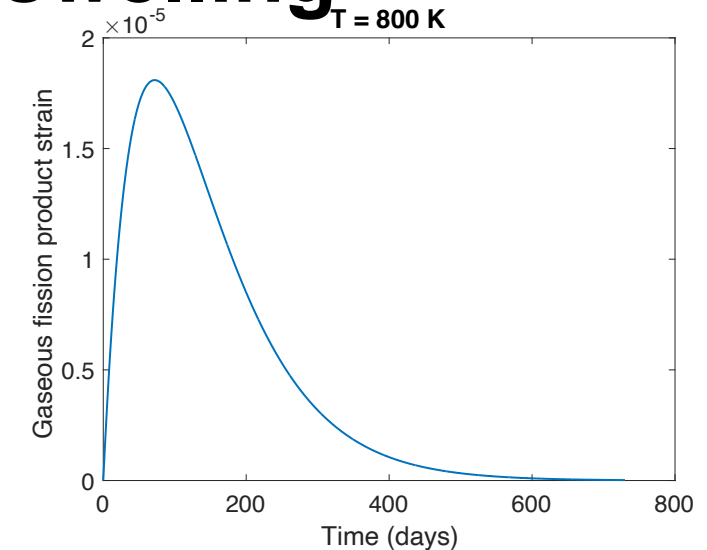
$$\epsilon_{sfp} = 5.577 \times 10^{-2} \rho \beta$$



Gaseous fission product swelling

- Gaseous swelling varies strongly with temperature, fission rate and stress
- $T < 1000\text{K}$
 - Fission gas atoms remain in fuel matrix or collect in small, isolated, intragranular pores (<1 nm)
 - Intragranular pore size limited by fission spikes that drive gas back into fuel matrix
 - Gaseous swelling constrained by fission gas release
- $T = 1000$ to 1700 K
 - Swelling takes place at hot interior of pellet
 - Gas atoms in fuel matrix diffuse to grain boundaries and collect in pores
 - Gas pressure causes bubbles to increase in size and to coalesce into larger pores
 - Gaseous swelling opposed by applied stress
 - Gaseous swelling also constrained by fission gas release

$$\epsilon_{gfp} = 1.96 \times 10^{-28} \rho \beta (2800 - T)^{11.73} e^{-0.0162(2800 - T)} e^{-17.8 \rho \beta}$$

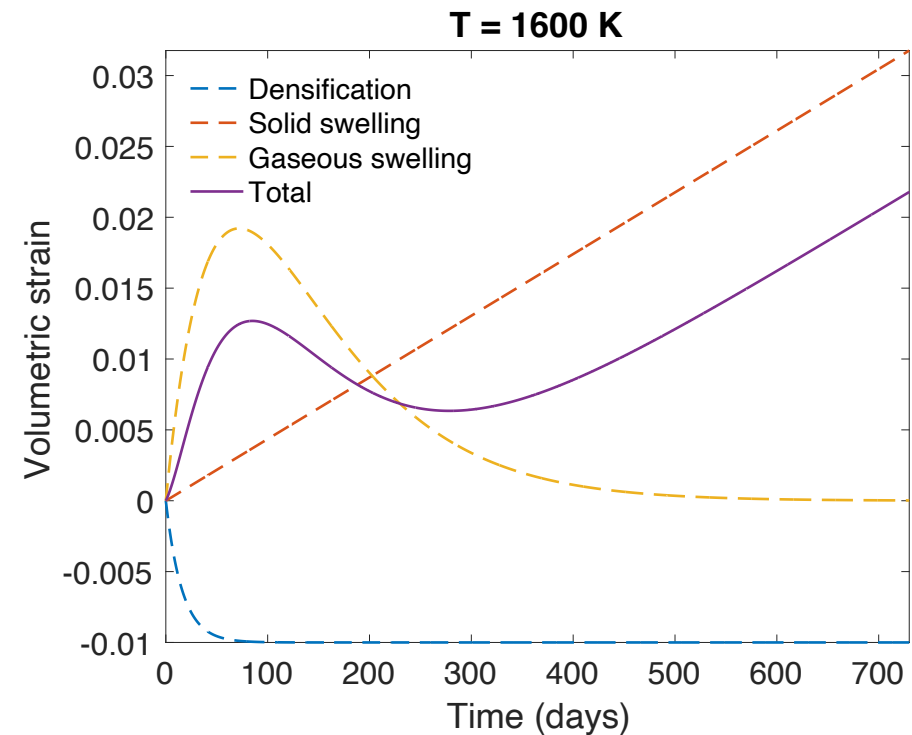
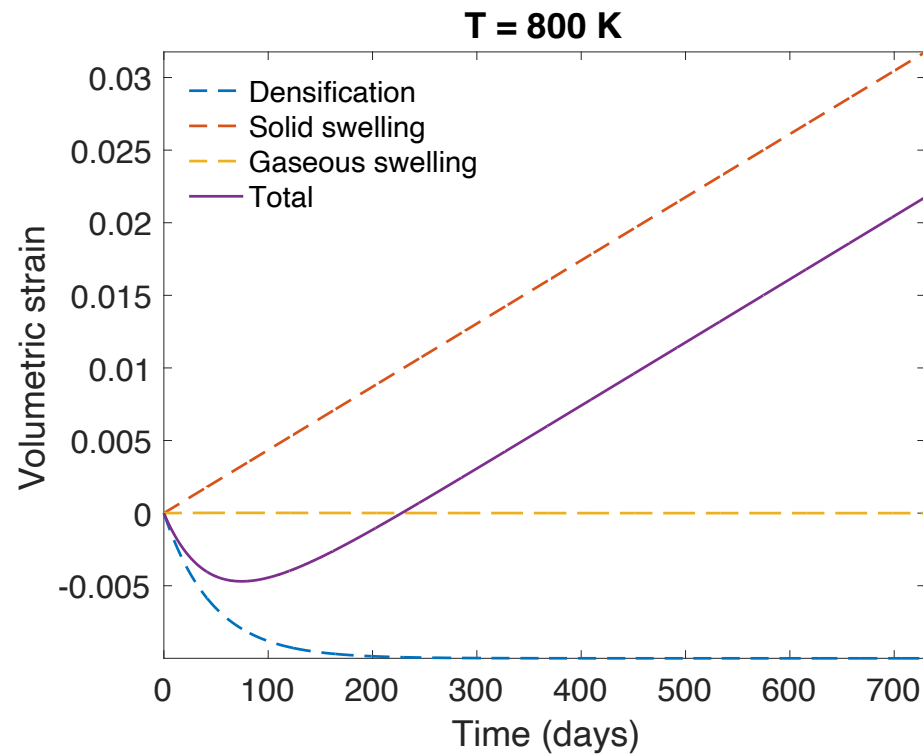


Total change in volume

- The total change in volume is found by adding all components of dimensional change
 - $\epsilon_{\text{tot}} = \epsilon_{\text{th}} + \epsilon_{\text{D}} + \epsilon_{\text{sfp}} + \epsilon_{\text{gfp}}$
- Example:
 - fission rate = $2.5 \times 10^{13} \text{ f}/(\text{cm}^3 \text{ s})$
 - $T(\text{fuel}) = 1400 \text{ K}$
 - $T_{\text{ref}} = 300 \text{ K}$
 - For densification: $\Delta\rho_0 = 0.01$ and $\beta_{\text{D}} = 5 \text{ MWD/kgU}$
 - Total time: 2 weeks

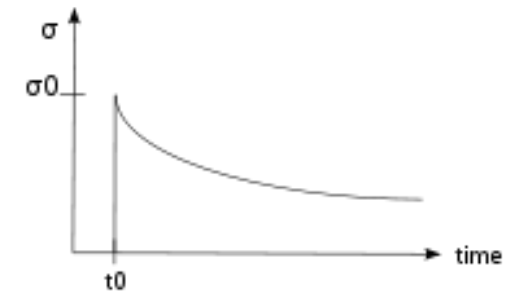
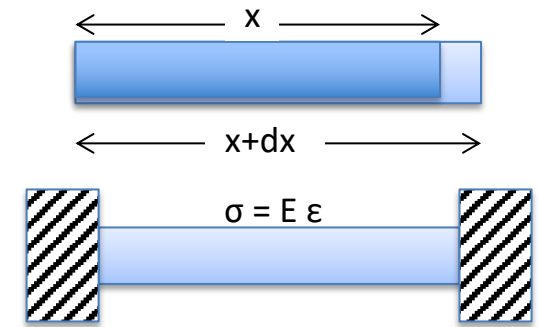
Example

The overall swelling behavior depends on temperature



Creep

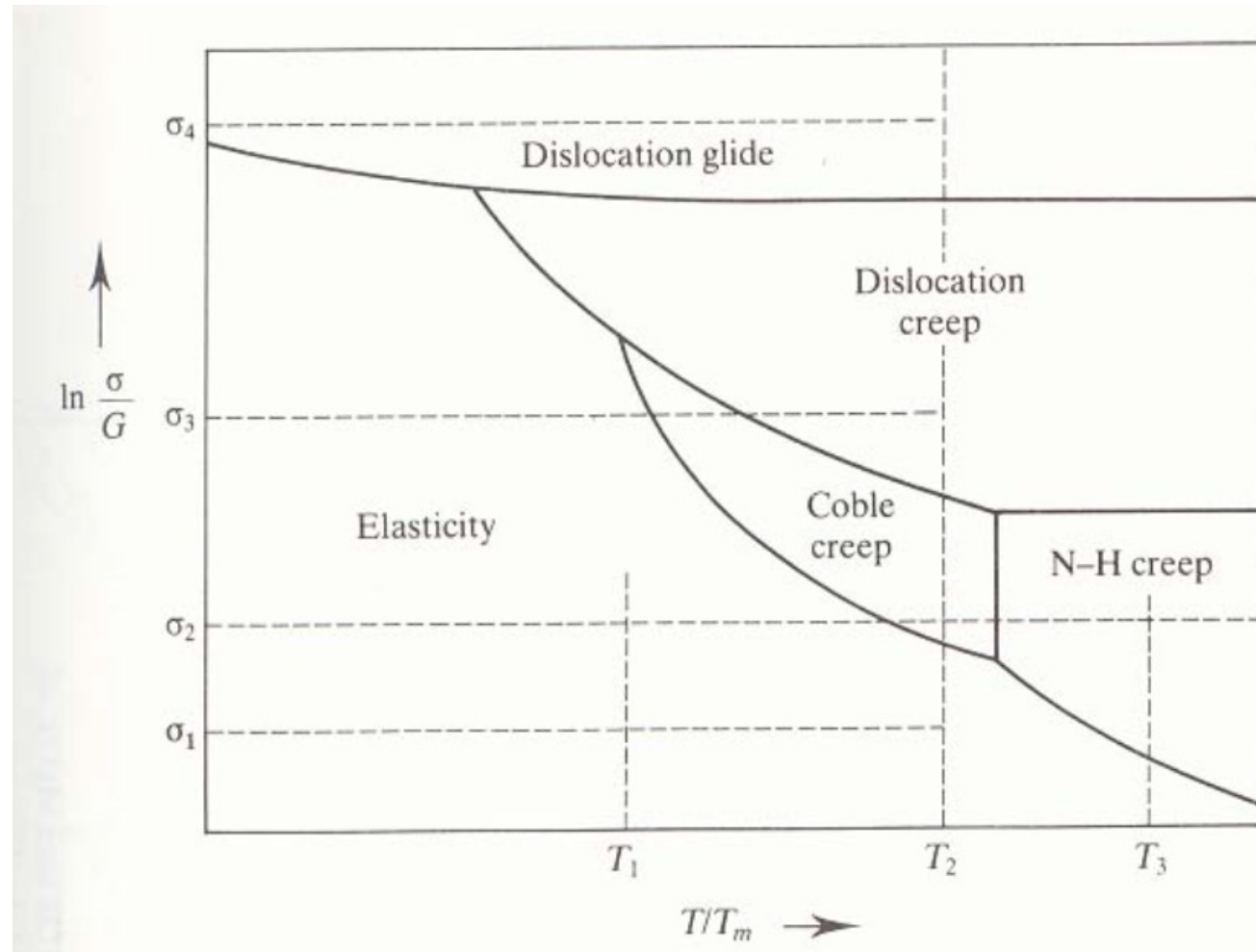
- Creep is a general mechanism for plastic deformation that occurs over time when $\sigma < \sigma_y$
- Consider a heated metal beam so it expands some distance dx
- We then fix it between two walls and let it cool down
- Because $\sigma < \sigma_y$, that stress remains constant
- In creep, defect diffusion is induced by the stress to cause permanent deformation and reduce the stress
- Therefore, creep
 - Occurs over time
 - Increases with increasing number of diffusing defects
 - High temperature (**thermal creep**)
 - Irradiation (**irradiation creep**)



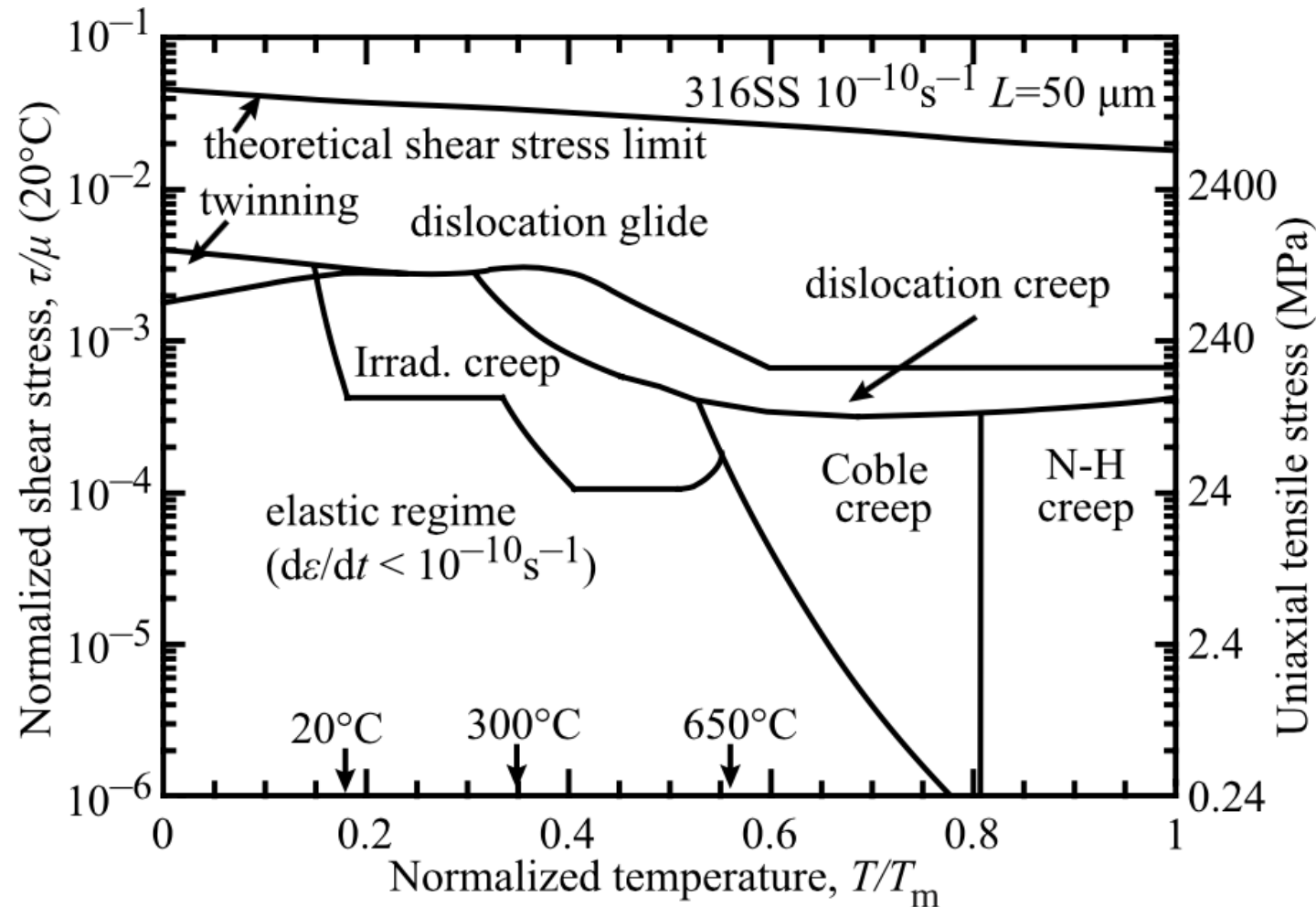
Creep

- General creep equation:
$$\dot{\epsilon} = \frac{C\sigma^m}{D_{gr}^b} e^{\frac{-Q}{k_b T}}$$
- Creep can be caused by various microstructural mechanisms
- Bulk Diffusion (Nabarro-Herring creep)
 - Atoms diffuse (high T), causing grains to elongate along the stress axis
 - $Q = Q(\text{self diffusion})$, $m = 1$, and $b = 2$
- Grain boundary diffusion (Coble creep)
 - Atoms diffuse along grain boundaries to elongate the grains along the stress axis
 - $Q = Q(\text{grain boundary diffusion})$, $m = 1$, and $b = 3$
- Dislocation creep
 - Dislocations glide under a high stress
 - Dislocations climb due to defects to avoid obstacles
 - $Q = Q(\text{self diffusion})$, $m = 4-6$, and $b = 0$

Different creep mechanisms are active for different combinations of stress and temperature



The behavior of creep changes in irradiated materials

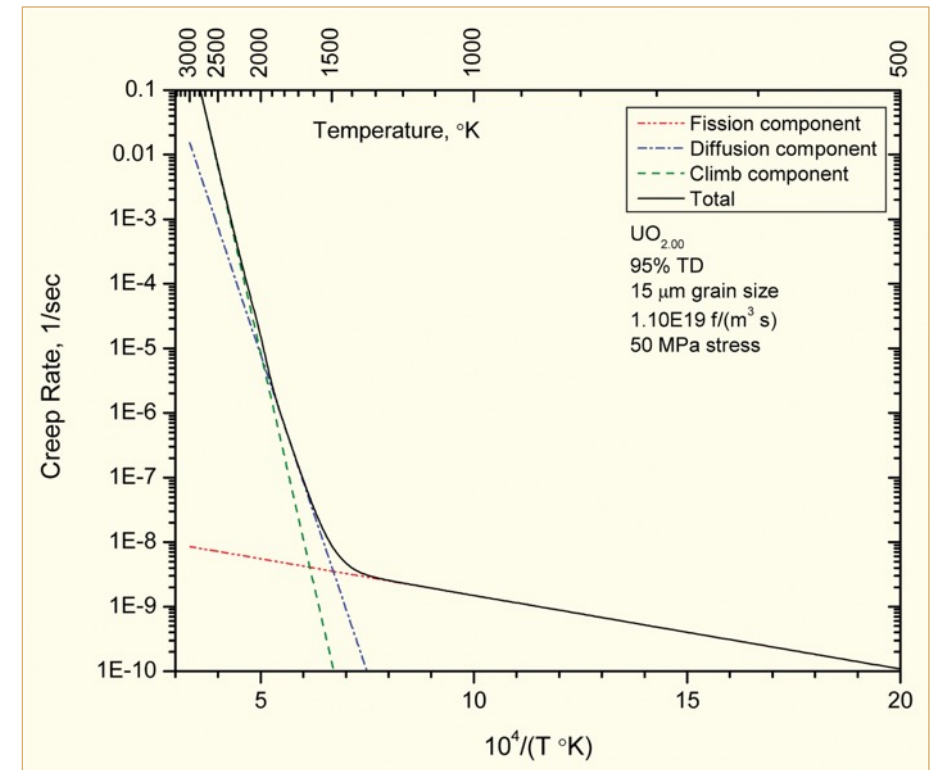


Irradiation and Creep

- Irradiation accelerates creep, causing it to be significant at lower temperatures
- Irradiation has little effect on diffusional creep, but it accelerates dislocation creep in cubic materials
- The dislocation creep rate can be written as $\dot{\epsilon} = \rho_d^m b v_d$
 - ρ_d^m is the density of mobile dislocations
 - b is the burgers vector
 - v_d is the dislocation velocity
- Gliding dislocations quickly get pinned by obstacles
- As the dislocations absorb defects created by irradiation, they climb to different slip planes to avoid the obstacles
- More interstitials are absorbed than vacancies due to the higher sink strength for interstitials

Fuel Creep

- Like other materials, the fuel also undergoes creep
- The fuel creep (In UO₂) is a combination of diffusion creep and irradiation creep
- It is expected that fuel creep plays a major role in dimensional change in metallic fuels, largely via N-H and Coble creep, but still unproven experimentally and no good creep models exist for metallic fuels



Summary

- Many materials models for fuel are empirical and correlated to burnup
- Fuel pellets change shape due to
 - Thermal expansion (increase in volume)
 - Densification (decrease in volume)
 - Swelling (increase in volume)
 - Creep (volume stays the same)
- Fracture also decreases the gap, as fractures pieces shift outward