

Fuel Chemistry

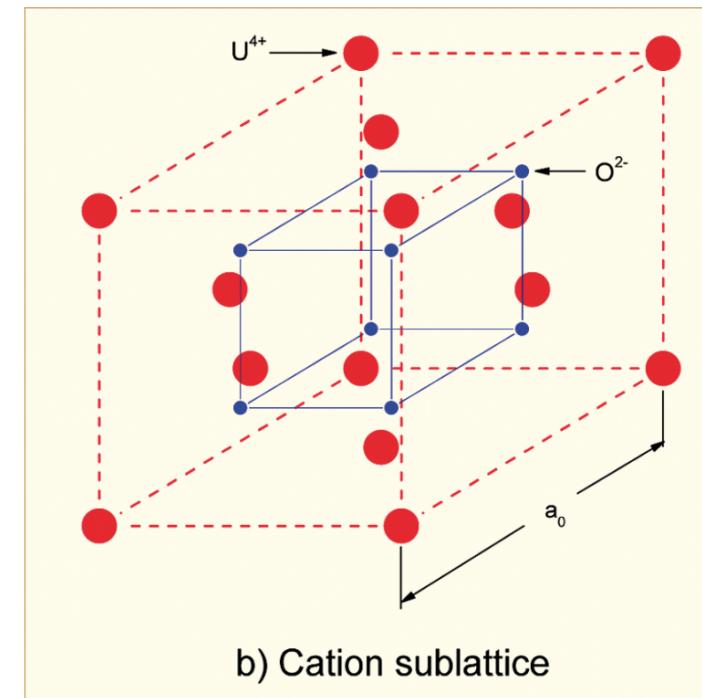
NE 591

Last Time

- Basic materials science overview
 - Crystal structures
 - Point defects, dislocations, grain boundaries, etc.
- Began fuel chemistry
 - UO₂ stoichiometry

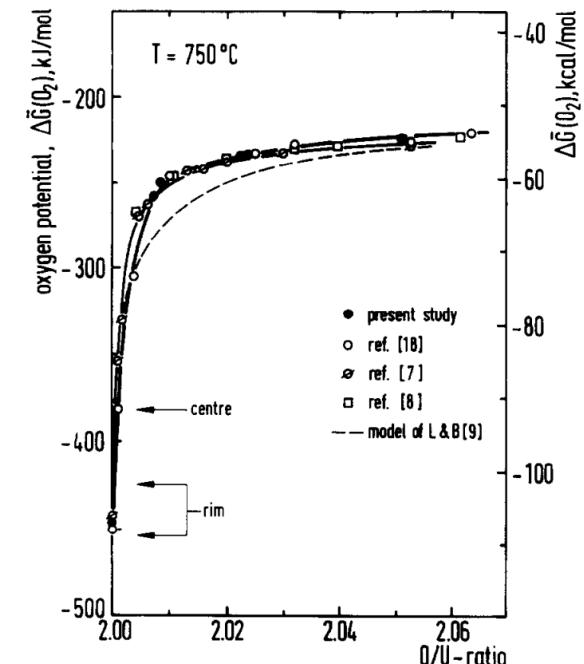
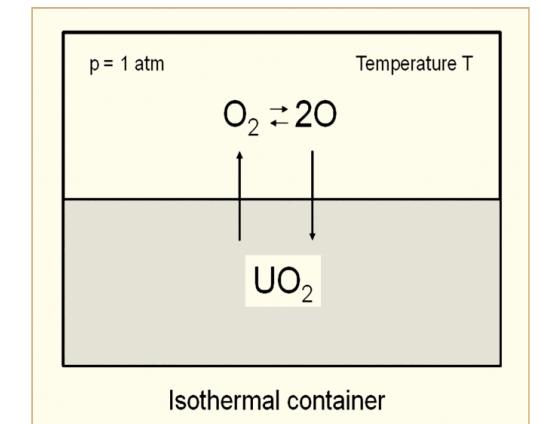
Incorporation of Fission Products

- As fission products form, the valence state of the uranium can change
- Typical valence of soluble fission products is M^{3+}
- The uranium valence state changes to compensate
 - Oxygen liberated by fission
 - Fission products produced with M^{3+} valence state incorporated in fuel lattice
 - Uranium oxidizes from U^{4+} to U^{5+} or U^{6+} to maintain local electrical neutrality



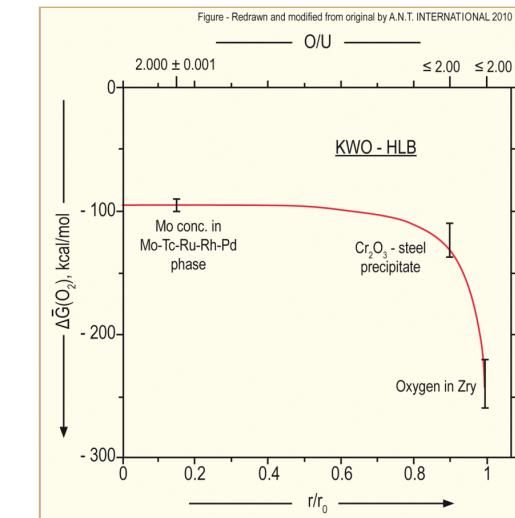
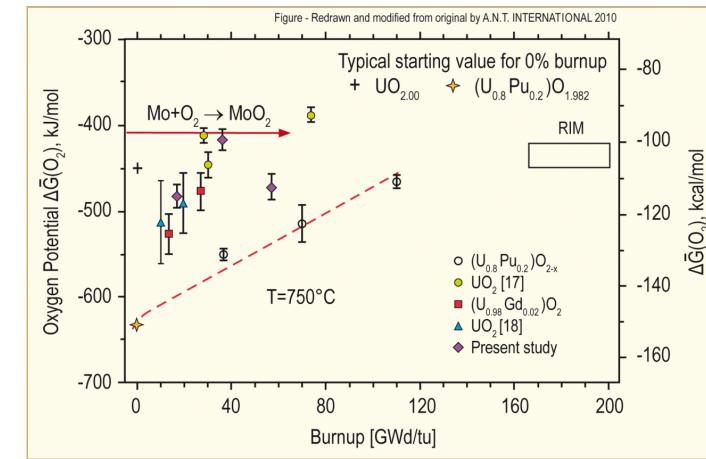
Oxygen potential

- The oxygen potential is a measure of how free the oxygen is to escape/move around
- Oxygen potential is defined as $\Delta\bar{G}_{O_2} \equiv RT \ln(p_{O_2})$
or, equivalently $\Delta\bar{G}_{O_2} = 2\mu_{O_{solution}} - G_{O_2}^\circ$
 - With $\mu_{O_{solution}}$ = Chemical potential of oxygen in solution
 - $G_{O_2}^\circ$ = Gibbs free energy of gaseous oxygen at temperature T and a standard pressure (1 atm)
- It is possible to determine the stoichiometry from the oxygen potential



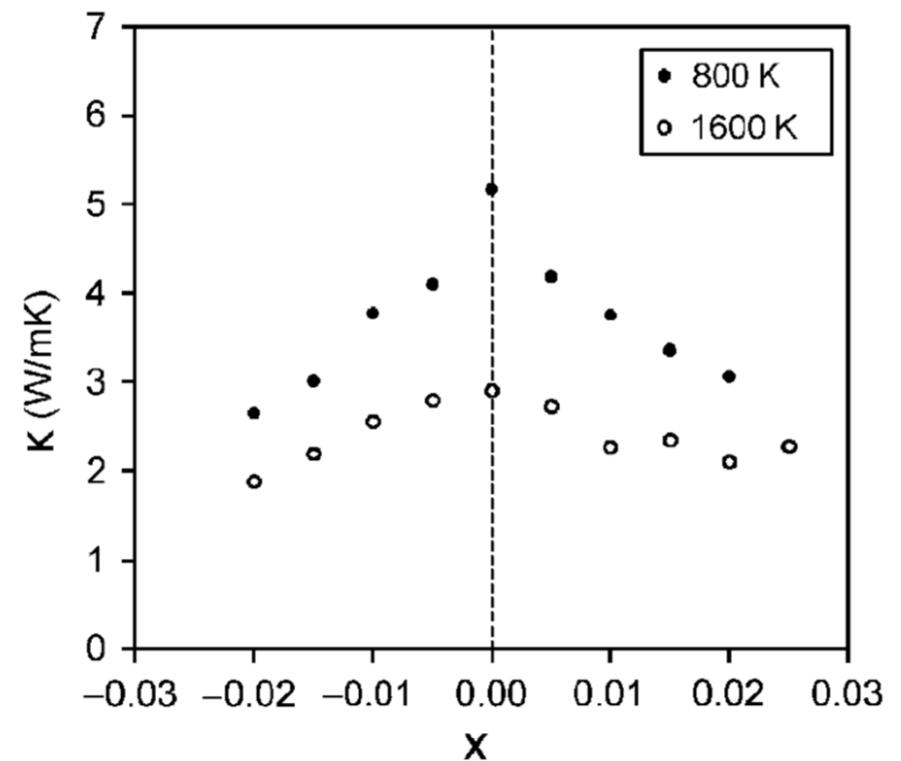
Oxygen potential

- The oxygen potential changes during irradiation, indicating change in the O/M ratio
- Oxygen potential changes during irradiation due to
 - Liberation of oxygen by fission
 - Generation of fission products
 - Conversion of uranium to plutonium
 - Reaction of oxygen with U, Pu, fission products, and cladding
- Oxygen potential across pellet radius observed to be constant at the approximate value of Mo/MoO₂ reaction (from calculations)
- Oxygen potential is low near the cladding, because the oxygen enters the cladding



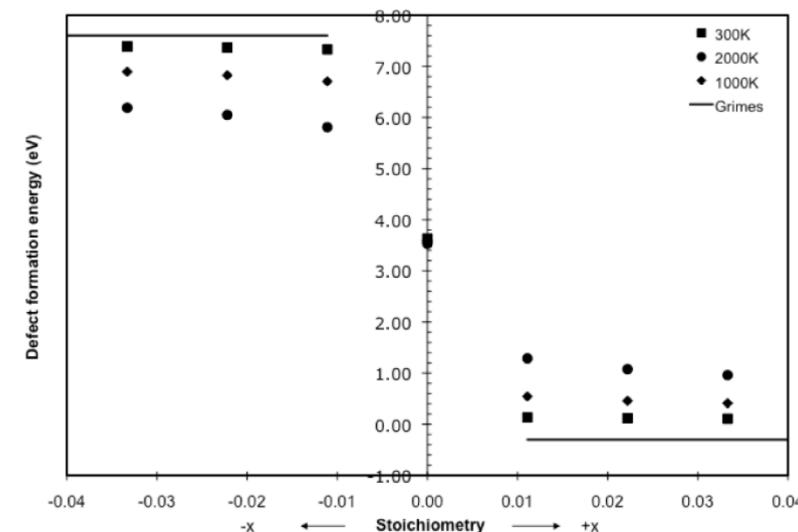
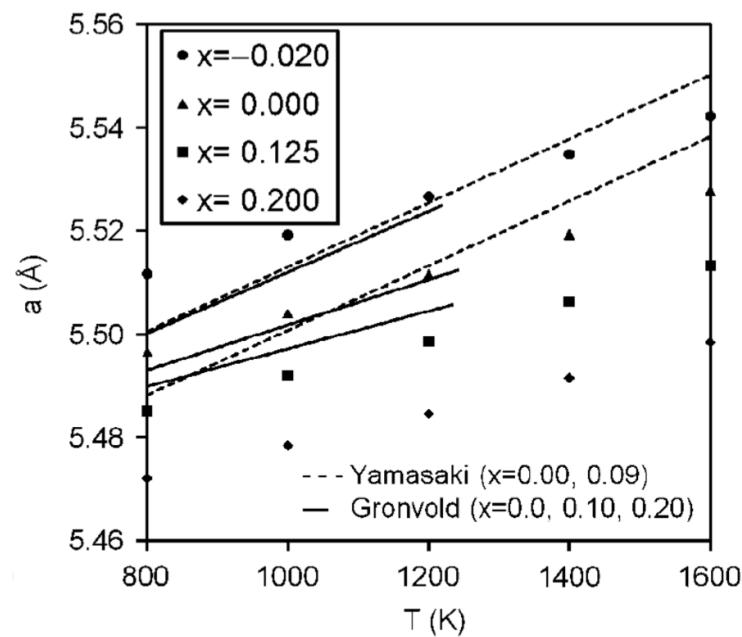
Fuel Stoichiometry/Properties

- The stoichiometry of the fuel directly impacts the fuel performance
- Stoichiometry impacts
 - Melting temperature
 - Thermal conductivity
 - Processes dependent on diffusion
 - Grain growth
 - Fission gas release
 - Creep
 - Chemical state and behavior of fission products
 - Chemical reactions at inner cladding surface
- Thermal conductivity is highest for stoichiometric UO₂



Fuel Stoichiometry/Properties

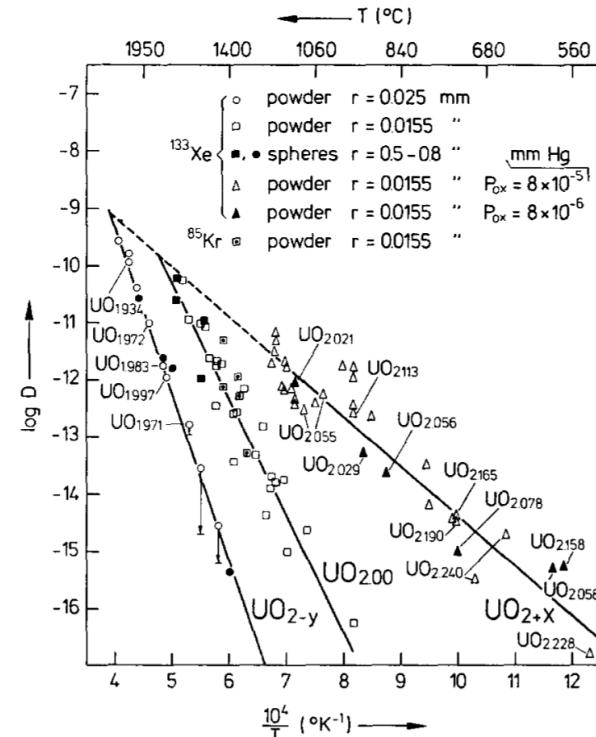
- The lattice constant of the material decreases with increasing stoichiometry
- The vacancy formation energy also changes with stoichiometry



Fuel Stoichiometry/Properties

- The solution energy of Xe, Cs, and Sr in UO_2 depends on stoichiometry as well
- The coefficient defining Xe diffusion also changes with stoichiometry
- Though stoichiometry matters, most fuel performance codes ignore it**

Fission product	$\text{UO}_{1.97}$	UO_2	$\text{UO}_{2.03}$
Xe	3.88 eV	3.88 ev	2.61 eV
Cs	1.7 eV	-0.04 eV	-3.29 eV
Sr	-3.71 eV	-6.03 eV	-9.55 eV



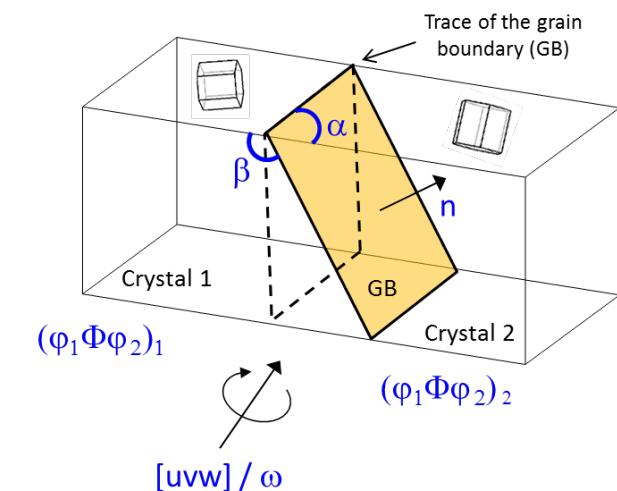
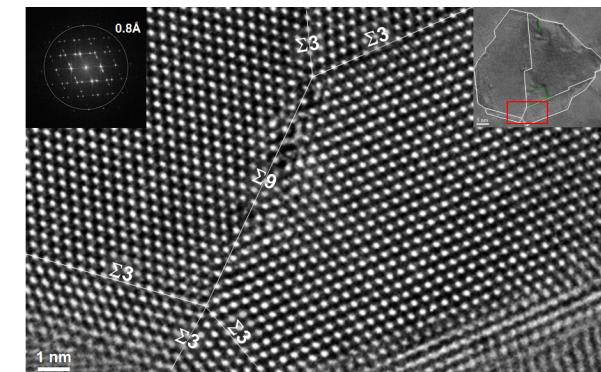
Fuel Chemistry Summary

- UO_2 has a cubic fluorite structure that is very stable
- The charges are balanced with a U^{4+} valence state
- However, the ratio of oxygen to uranium can change. We call this the stoichiometry and abbreviate it as O/M ratio
- The O/M ratio changes during reactor operation, but it is complicated
- The O/M ratio impacts many properties of the fuel

Grain Growth

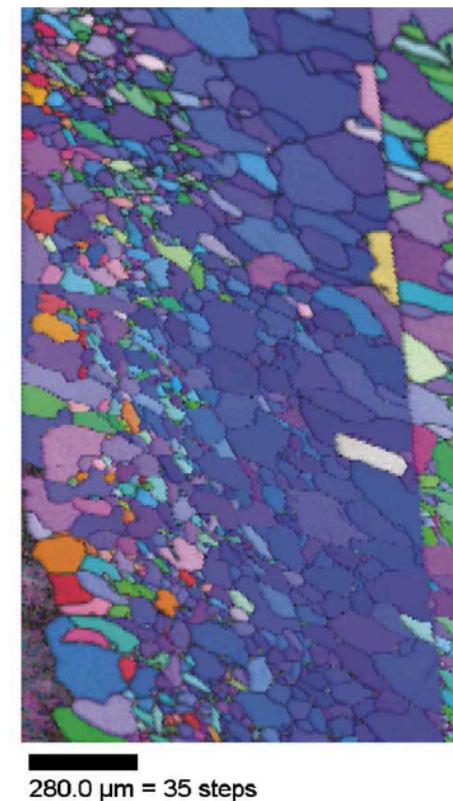
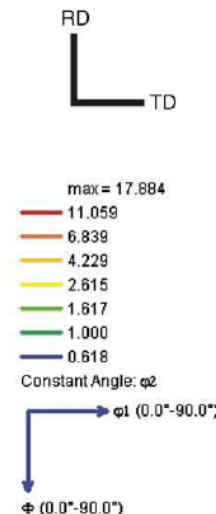
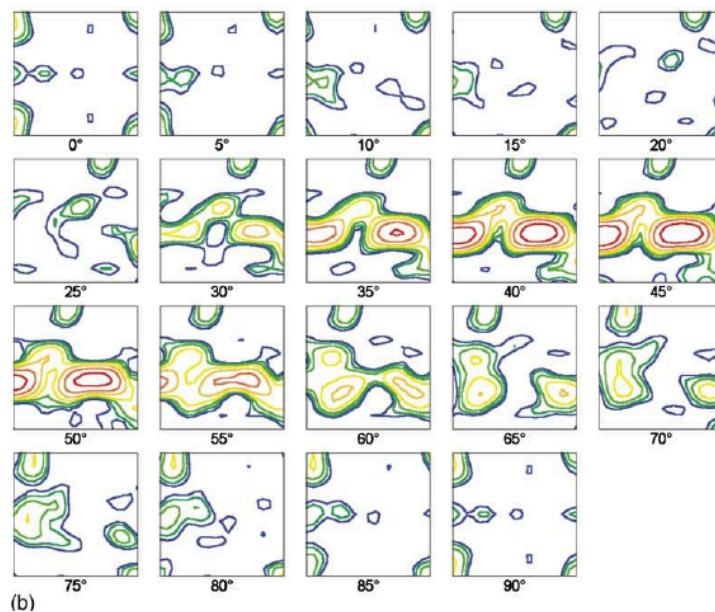
Grain Growth in UO₂

- Materials are typically composed of various regions where the crystal lattice is oriented differently
- When two grains meet, there is a plane of atoms that do not follow the crystal lattice called a **grain boundary**
- Grain boundaries add energy to the material that is a function of their structure
- A grain boundary's energy is determined by its:
 - Inclination** – the orientation of the 2D grain boundary plane (2 degrees of freedom)
 - misorientation** – the rotation required to align one grain with the other (3 degrees of freedom)

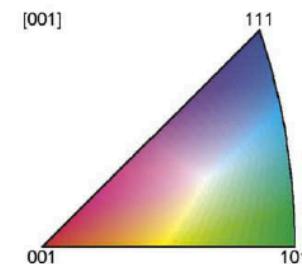


Texture

- The orientation of all the grains in a material is called the texture

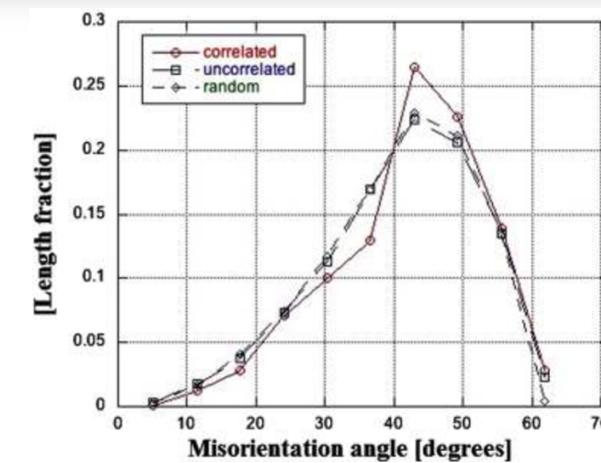
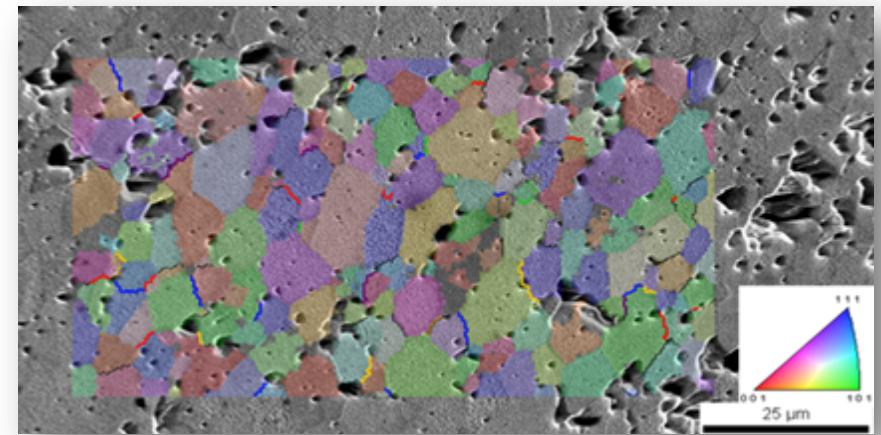


Electron back scatter diffraction map for cubic crystal structure



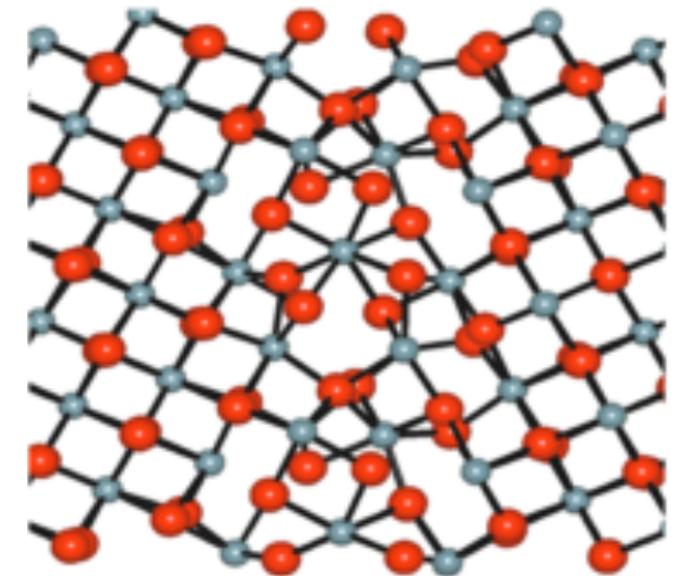
Grain size

- In a polycrystal, there is also a distribution of grain sizes
- The average grain size of the fuel has a significant impact on its behavior
- Typical LWR fuel has an initial average grain size of about 10 microns
- The average grain size impacts
 - Fission gas release
 - Swelling
 - Thermal conductivity
 - Creep



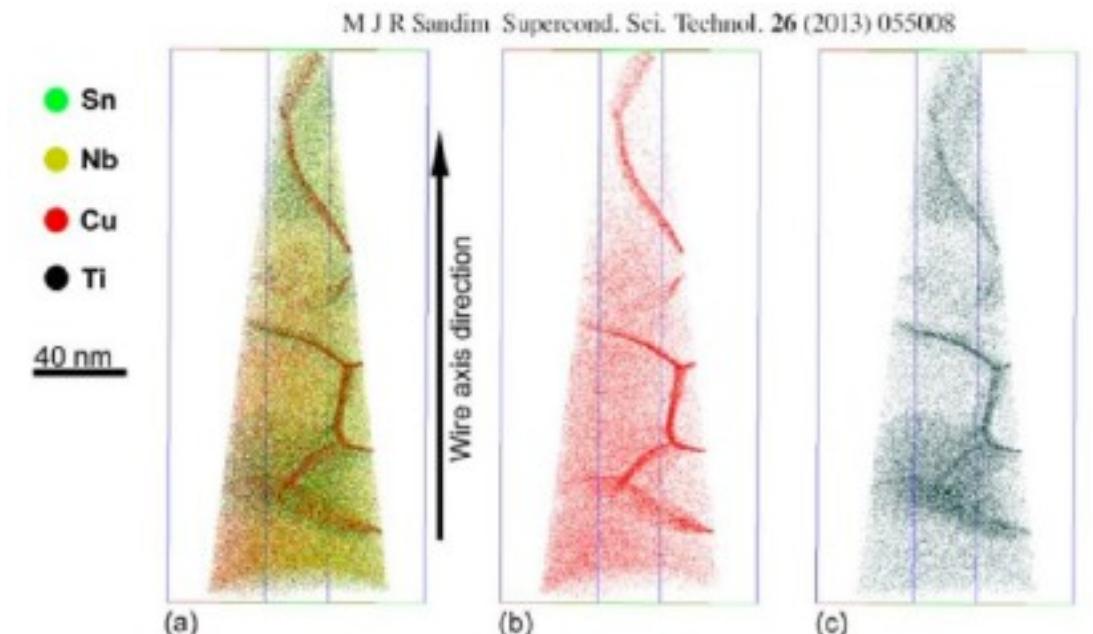
Grain boundary diffusion

- Diffusion often occurs faster along grain boundaries than in the perfect crystal
- Grain boundaries have more space than the perfect lattice
- So, atoms diffuse faster along grain boundaries than through the perfect lattice
- This means that grain boundary, or intergranular, diffusion increasingly dominates bulk (intragranular) diffusion as the temperature is reduced
- Grain boundary vacancy diffusion has a large impact on creep



Grain boundary segregation

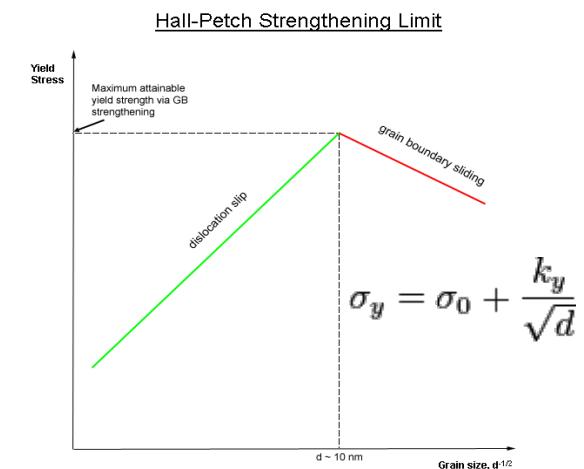
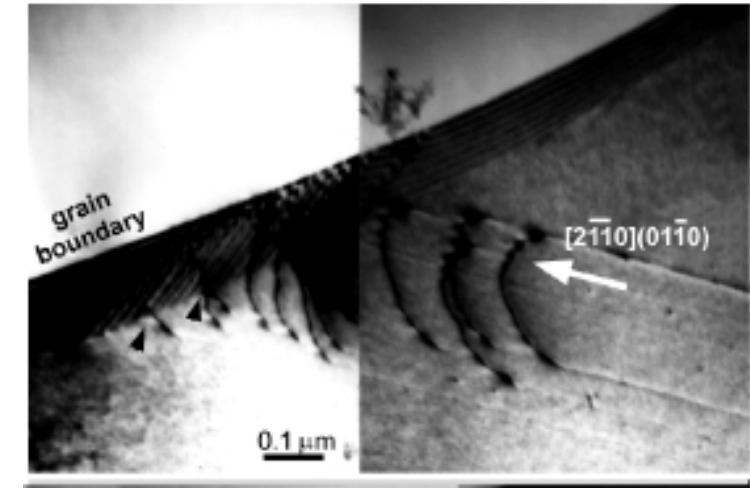
- Impurity atoms (such as fission gas) and other defects move to grain boundaries
- Due to grain boundaries having more open space, impurity atoms have a lower energy when they are on grain boundaries.
- This is called **grain boundary segregation**



APT reconstruction : (a) elements mapped in the sample and (b) and (c) show only Cu and Ti

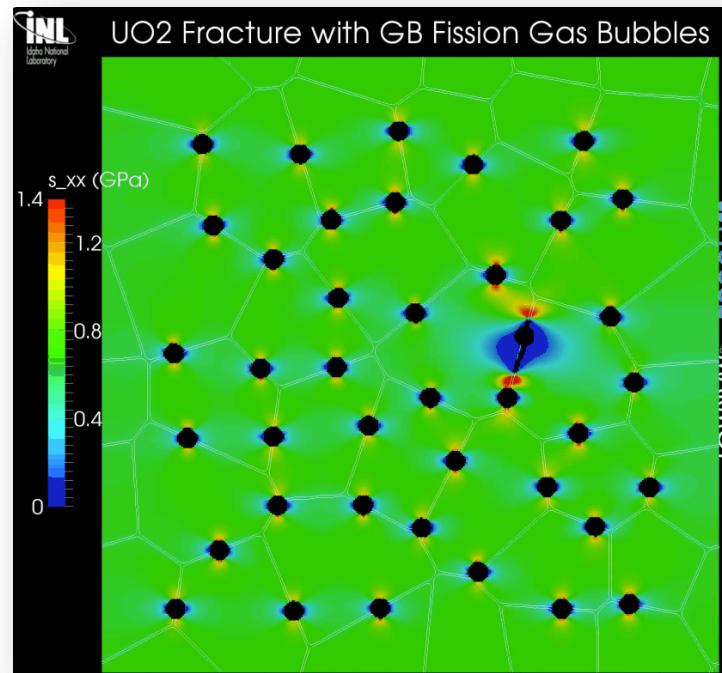
Dislocation interaction with grain boundaries

- Grain boundaries impede dislocation motion
- The number of dislocations within a grain impacts how easily dislocations can traverse grain boundaries and travel from grain to grain.
- So, by changing grain size one can influence dislocation movement and yield strength.
- This is called the Hall-Petch effect



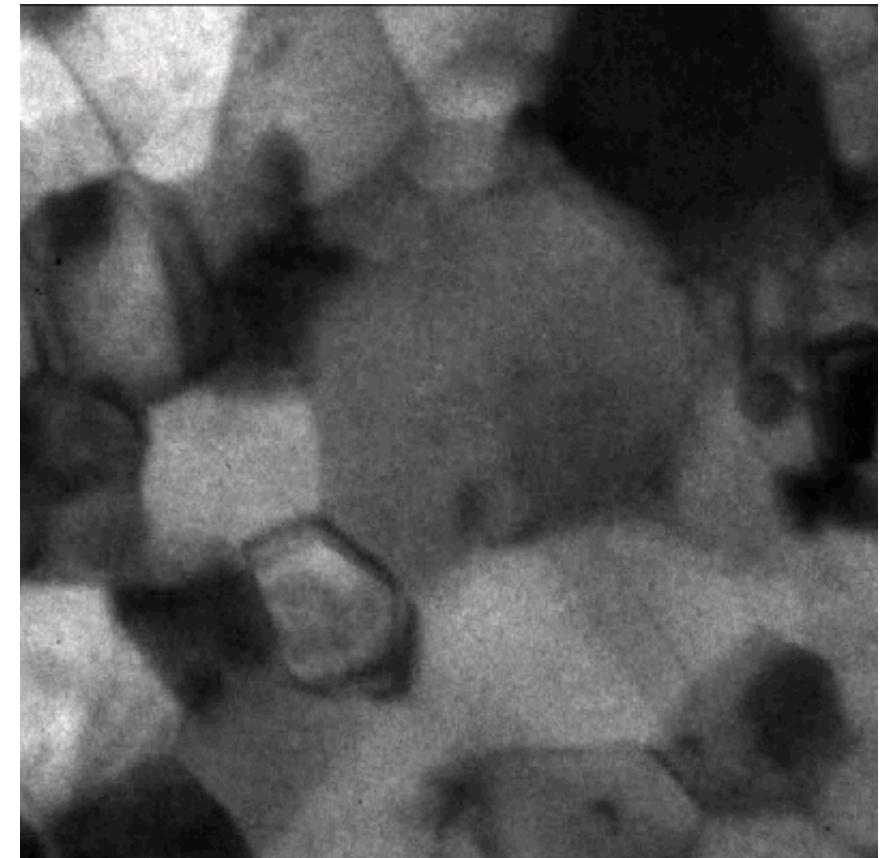
Grain boundaries and cracks

- Materials often crack along grain boundaries
- Grain boundaries can be weaker than the perfect lattice
- Thus, fracture will often occur along grain boundaries (intergranular fracture)



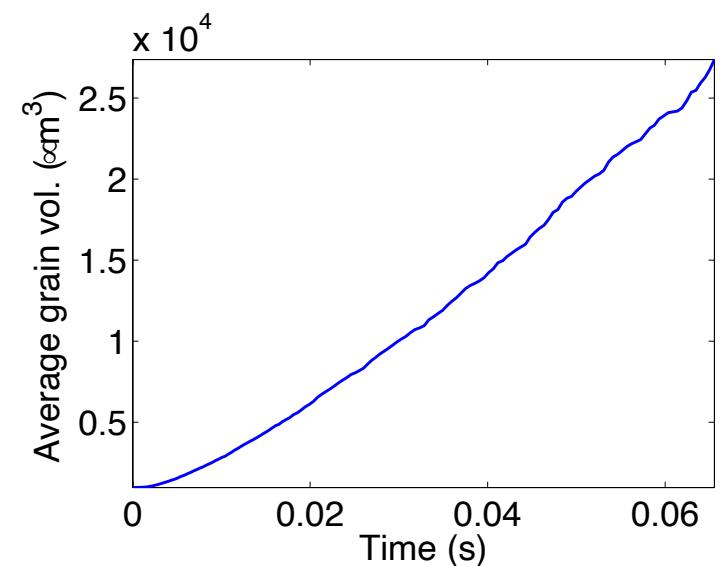
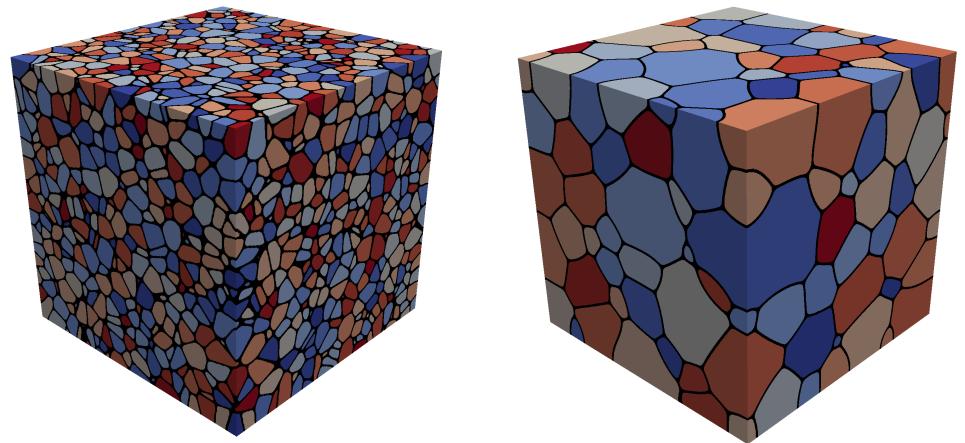
Grain size change

- A single crystal has a lower energy state than a polycrystal, due to the grain boundary energy
- So, grain boundaries migrate to reduce the energy
- $v_{GB} = M_{GB} (P_d - P_r)$
 - M_{GB} is the grain boundary mobility
 - P_d is the driving force (pressure) for grain growth
 - P_r is the pressure resisting grain growth



Grain growth

- Due to grain boundary migration, the average grain size goes up with time
- As grain boundaries migrate, some grains grow and some shrink
- Shrinking grains eventually disappear
- The average grain volume $\bar{V}_{gr} = V_{mat}/N_{grains}$
- Therefore, as N_{grains} decreases due to grain disappearance, the average grain volume goes up



Grain boundary mobility

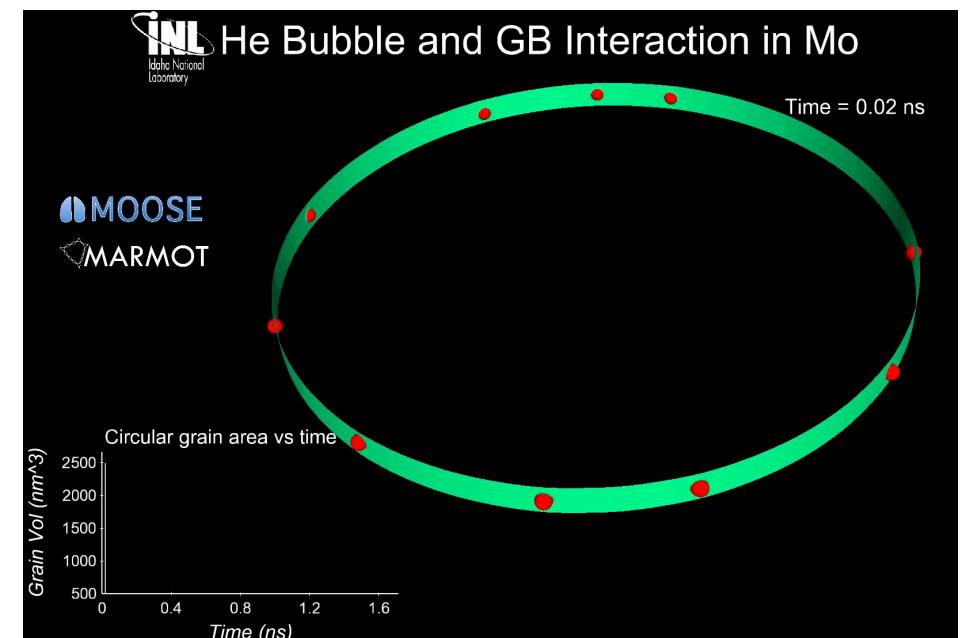
- The grain boundary mobility is a function of temperature and GrB type
- The grain boundary mobility is determined according to
 - $M_{GB} = M_0 e^{-\frac{Q}{k_b T}} \text{ m}^4/(\text{J s})$
 - $k_b = 8.6173e-5 \text{ eV/K}$ is the Boltzmann constant
- Both the pre-factor M_0 and the activation energy Q change as a function of the grain boundary misorientation
- We often use an average grain boundary for a material, taken from polycrystal measurements-> UO₂: $M_0 (\text{m}^4 / \text{J-s}) = 4.6e-09$, $Q (\text{eV}) = 2.77$
- What is the mobility of UO₂ at 1600 K?
 - $M_{GB} = 4.6e-9 * \exp(-2.77/(1600 * 8.6173303e-5)) = 8.7e-18 \text{ m}^4/\text{J-s}$

Grain growth

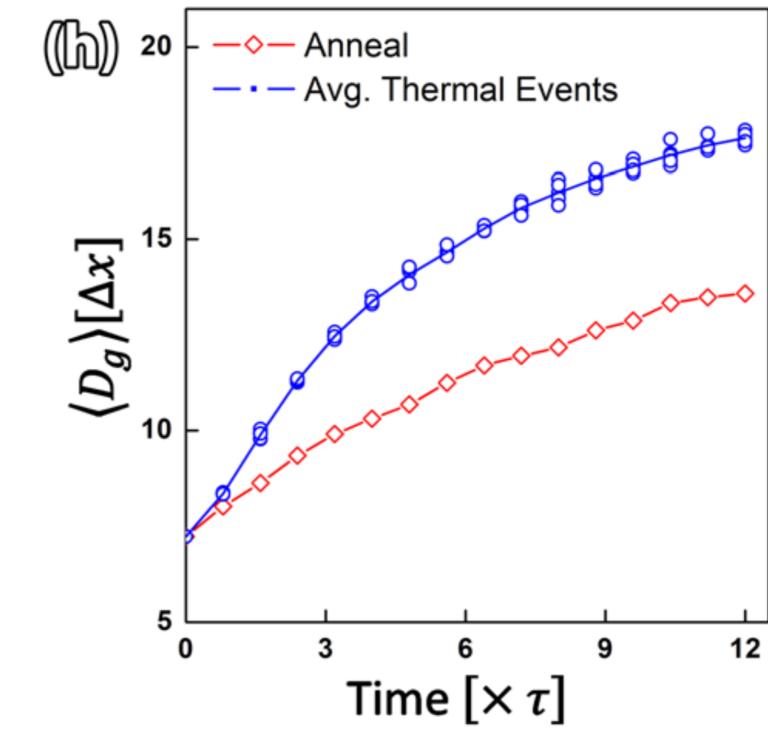
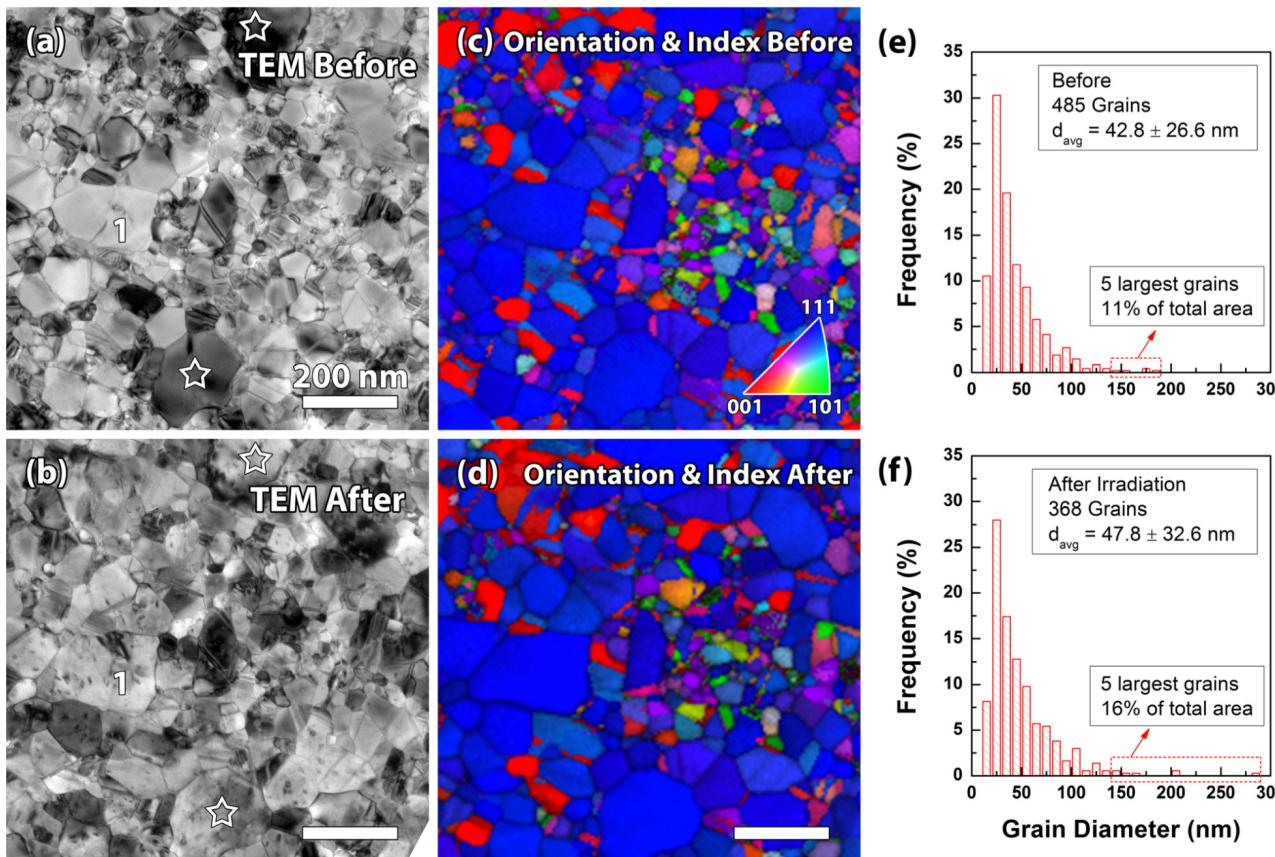
- There are various driving forces for grain growth
- The most common driving force is the reduction of grain boundary energy
 - $P_d = \frac{2\gamma_{GB}}{R}$, where γ_{GB} is the GB energy and R is the radius of curvature
 - It is often called the curvature driving force, because it drives grain boundaries to be straight
 - It also causes larger grains to grow at the expense of smaller ones
- Other driving forces include
 - Temperature gradients
 - Elastic energy gradients
 - Dislocation energy gradients
- Velocity of a spherical grain: $v = M \frac{2\gamma_{GB}}{R}$

Grain growth

- Grain boundary motion is inhibited by pores, precipitates, solute atoms, etc.
- Solute atoms (whether in interstitial sites or vacancies) can decrease the grain boundary mobility.
 - This is called **Solute Drag**
 - Even a small concentration of impurities can decrease the mobility by 3 to 4 orders of magnitude
- Particles and pores resist grain boundary motion



Irradiation can accelerate grain growth, but it is only significant with small grains and low temperature



Maximum grain size

- Consider a material with an average grain size D
- The change in D can be written as

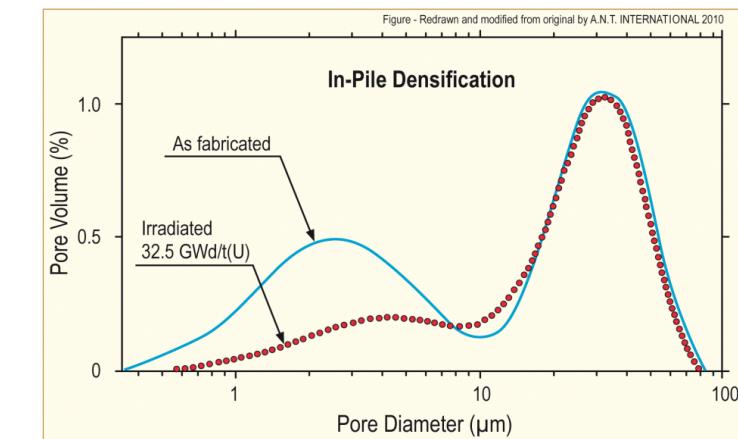
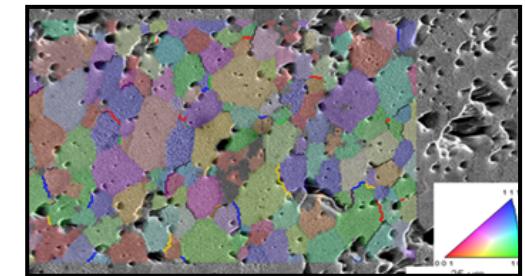
$$\frac{dD}{dt} = k \left(\frac{1}{D} - \frac{1}{D_m} \right)$$

- $k = 2 M_{GB} \gamma_{GB}$ is a rate constant that can be determined from experiments
- D_m is the grain size at which the driving force equals the resistive pressure
- For UO₂:

Material	M_0 (m ⁴ J/s)	Q (eV)	γ_{GB} (J/m ²)
UO ₂	4.6e-09	2.77	1.58
- D_m is a function of temperature $D_m = 2.23 \cdot 10^3 \exp(-7620/T)$ microns

Fuel Densification

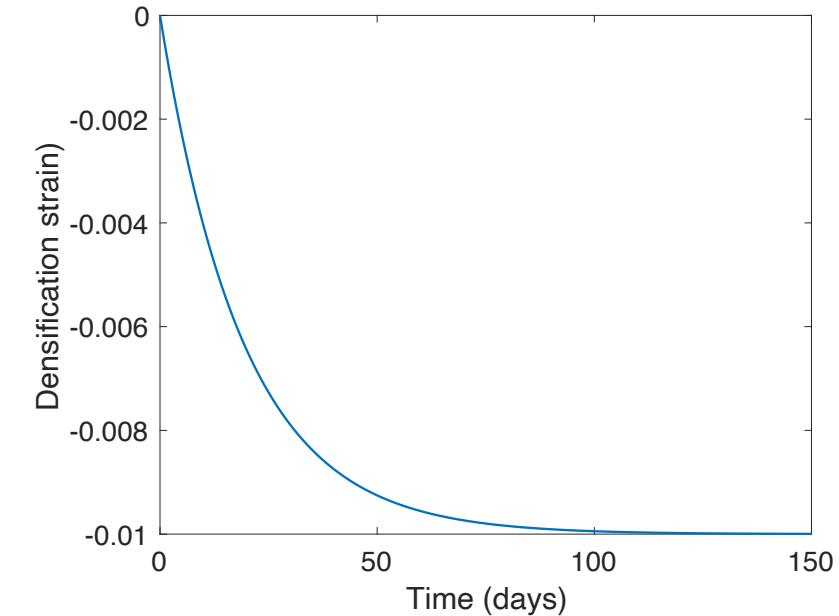
- Remember that fresh fuel pellets are not fabricated to be 100% dense, more like 95-99% dense
- Early in life, fuel pellets shrink and the initial porosity is largely eliminated
- In some ways, densification is a continuation of the sintering process
- However, irradiation accelerates the process
- Small pores close due to effects of fission spikes and vacancy diffusion
- Large pores stable (in absence of large hydrostatic stress)
- Pellets with higher initial density, densify less



Densification

- The driving force for densification is the change in free energy from the decrease in surface area of pores and lowering of the surface free energy
- An empirical relation to describe densification has been built as a function of
 - β - Burnup (in FIMA)
 - $\Delta\rho_0$ – Total densification that can occur ~ 0.01
 - β_D – Burnup at which densification stops ~5 MWD/kgU, ~0.005 FIMA
 - $C_D = 7.235 - 0.0086(T - 25)$ for $T < 750C$ and $C_D = 1$ for $T \geq 750C$

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

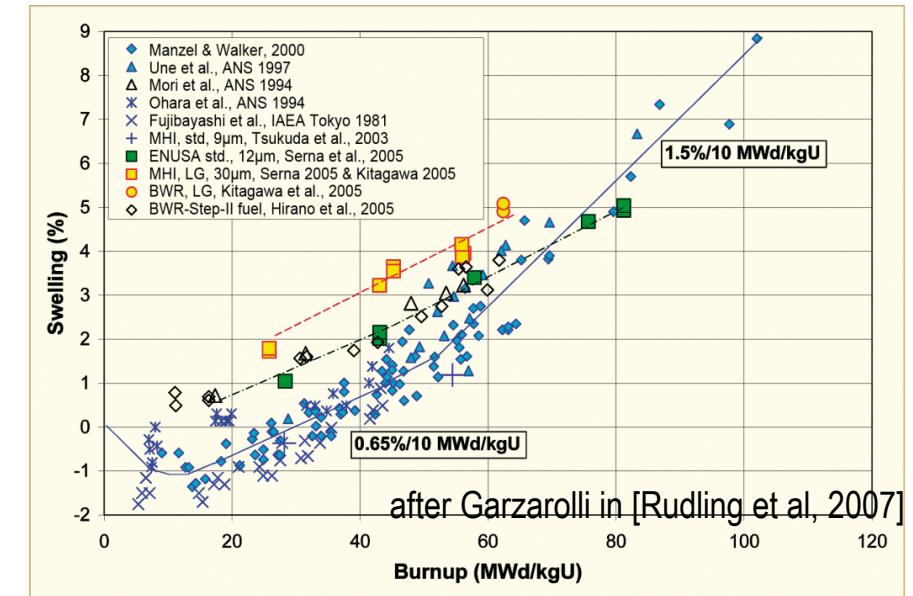


Empirical models

- Many models of reactor fuel behavior are fits to experimental data
- They are typically correlated to burnup
- Burnup is a measure of how much fissioning has taken place. Typical units are:
 - MWD/kgU
 - FIMA
- It can be calculated from the volumetric fission rate

$$\beta = \frac{\dot{F}t}{N_U}$$

- Units of this equation are FIMA
- To convert from FIMA to MWD/kgU, multiply by 950



Summary

- The average grain size in UO_2 impacts fuel behavior and performance:
 - Fission gas release
 - Swelling
 - Thermal conductivity
 - Creep
- The material wants to reduce its energy by having large grains grow at the expense of small grains
- Grain growth is reduced due to other defects reducing the grain boundary migration
- Fuel densification is driven by reduction in surface area of pores – continuation of sintering process
- Empirical models describe densification as a function of burnup

Notes

- No class Tuesday
- Presentations on Thursday
- Problem Session 3/3
- Exam 3/5