

# Nuclear Fuel Performance

NE-533  
Spring 2025

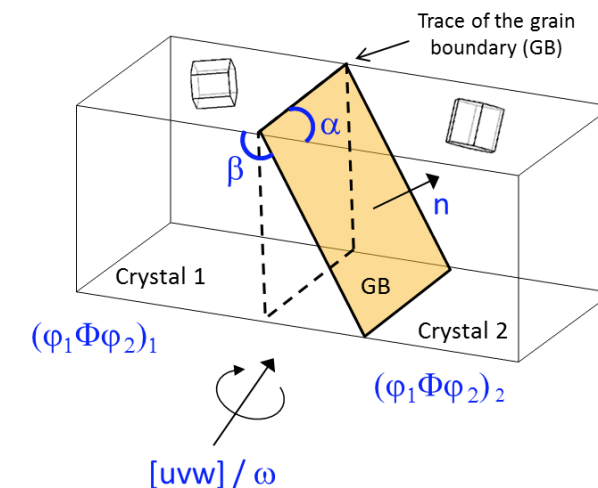
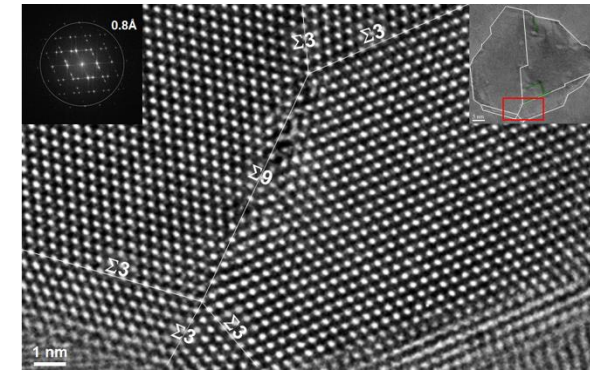
## Last Time

- Ended the last module going through some UO<sub>2</sub> radiation effects
- Will continue microstructural effects, burnup effects, different phenomena
- Start with the fuel, and work our way into cladding in this module
- MOOSE projects due tomorrow night
- Next week is paper presentation week, slides due Monday night
- Meet the submission deadlines on moodle, I do not have them set up to receive late submissions!
- Relevant seminar speaker today, NCSU alum

# GRAIN PROPERTIES/BEHAVIOR

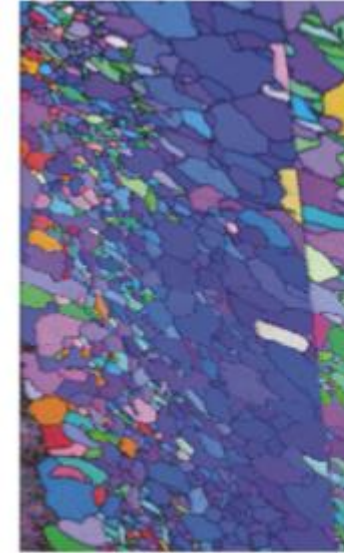
# Grain Boundaries

- 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)

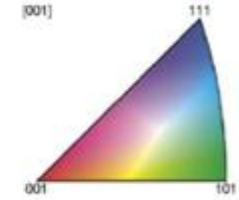


# Grain Texture

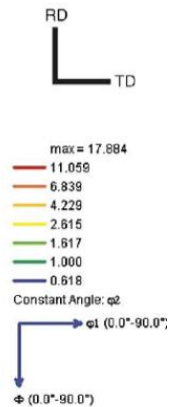
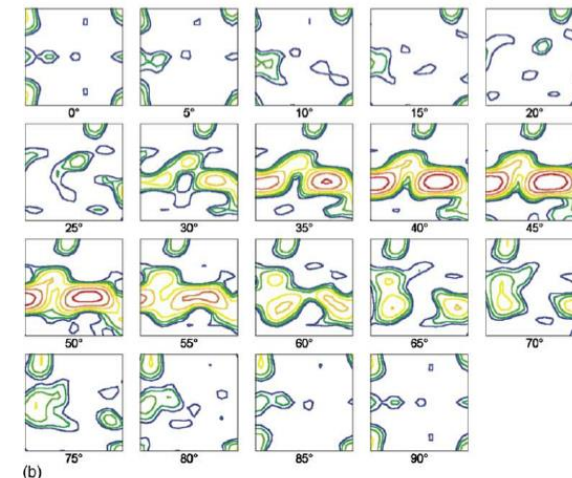
- The orientation of all the grains in a material is called the texture
- The degree of texture is dependent on the percentage of crystals having a preferred orientation
  - randomly oriented grains equals no texture
- Texture is seen in almost all engineered materials, and can have a great influence on materials properties



280.0  $\mu\text{m}$  = 35 steps



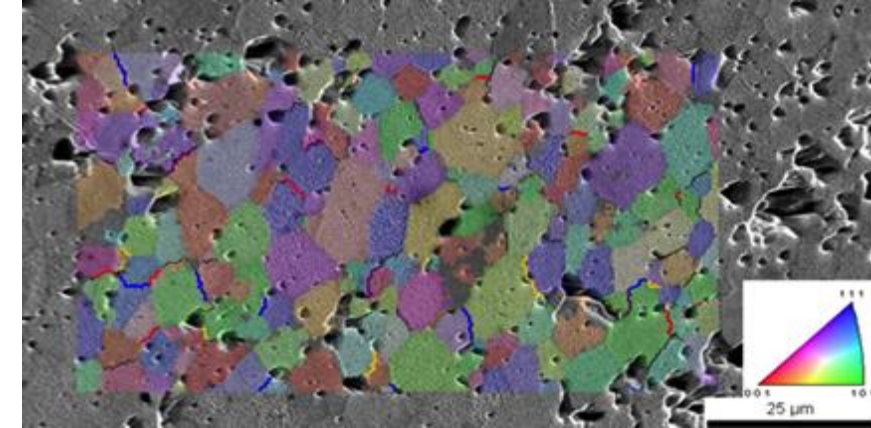
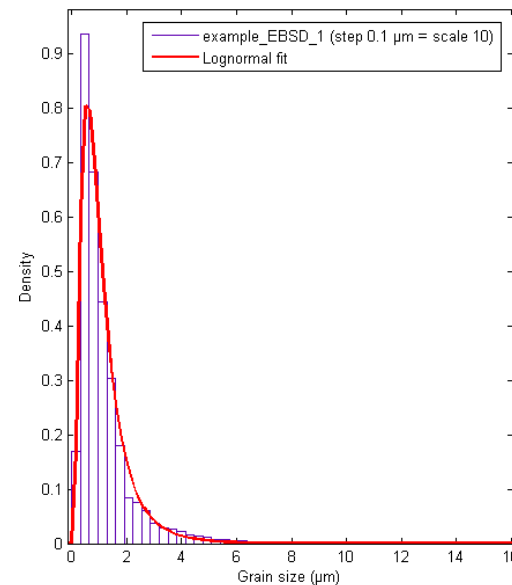
Electron back scatter diffraction map  
for cubic crystal structure



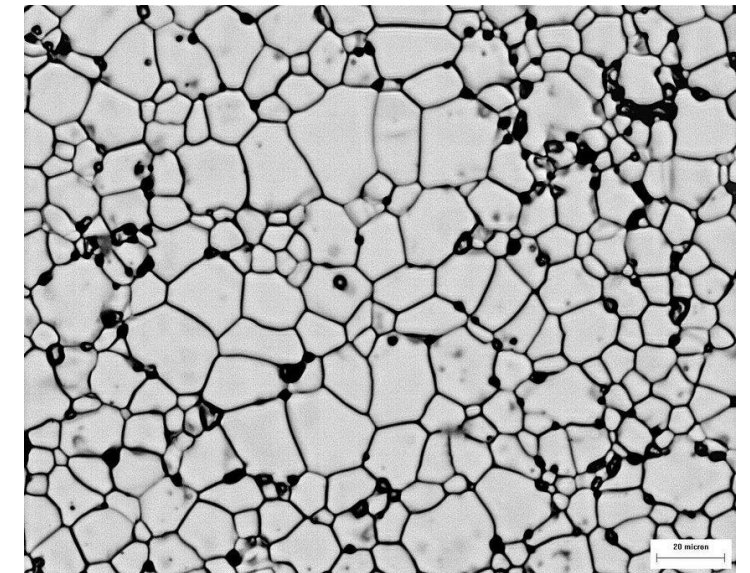
Orientation distribution function

# 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



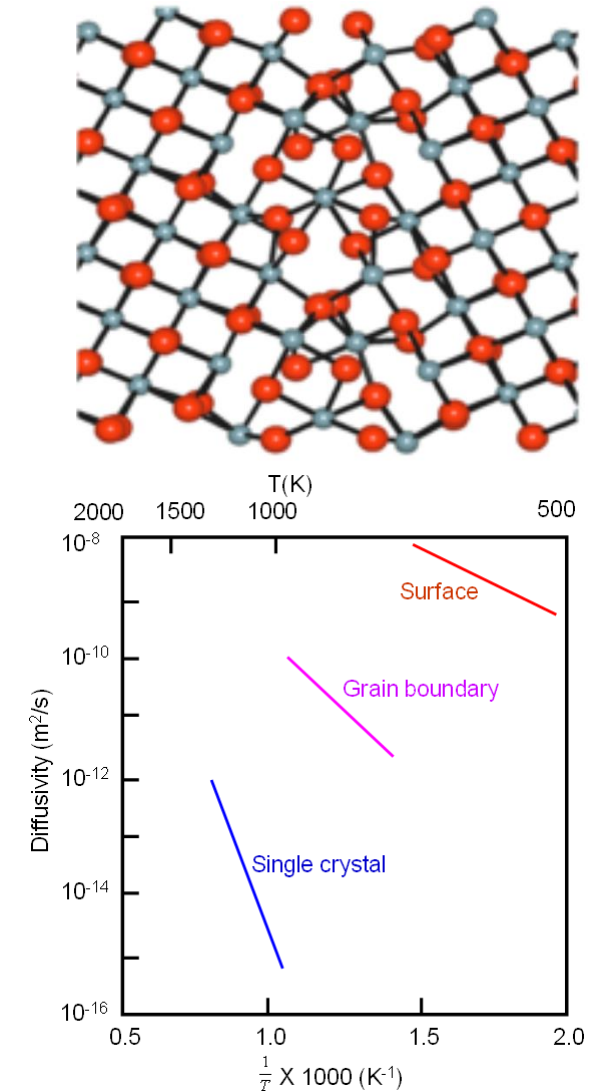
UO<sub>2</sub> grain structures





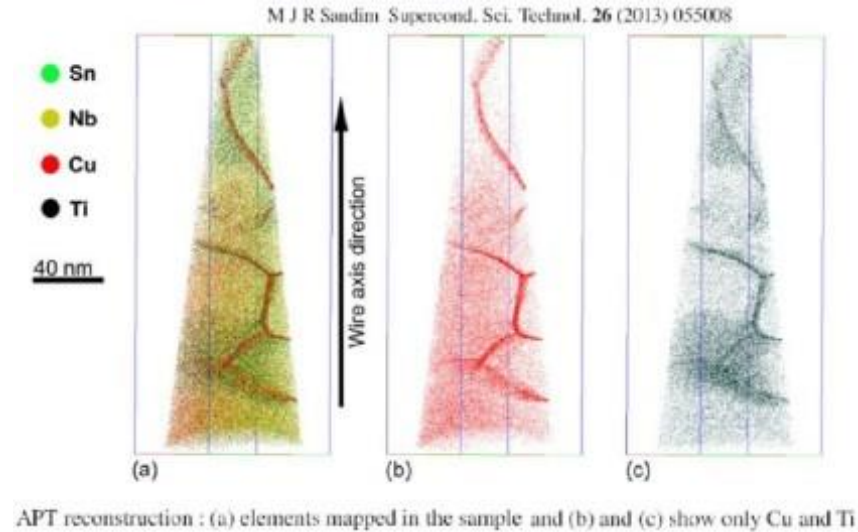
# Grain boundary diffusion

- 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
- This can become more pronounced as the temperature is reduced
- Grain boundary diffusion has a large impact on creep

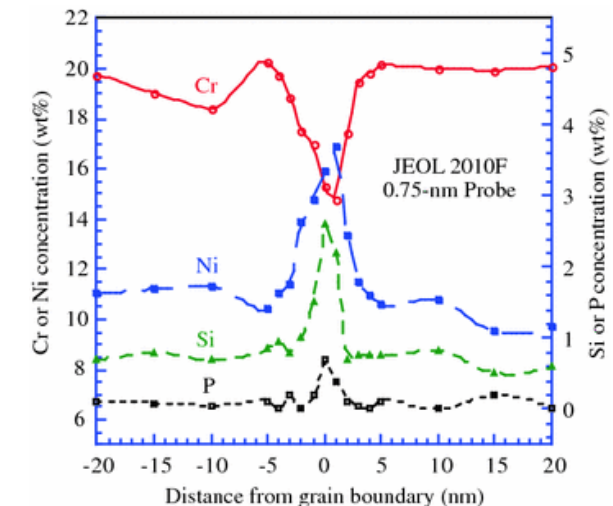


# Grain boundary segregation

- 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**
- Radiation induced segregation (RIS) is where radiation produces defects that drive towards the grain boundary and preferentially drag solute atoms



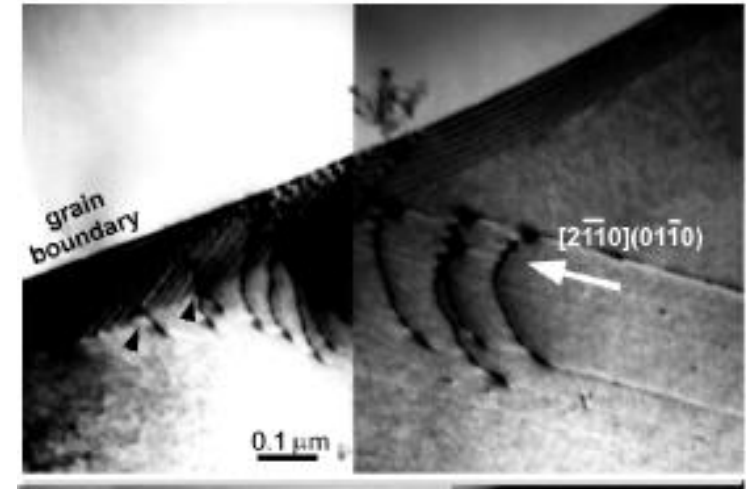
APT reconstruction : (a) elements mapped in the sample and (b) and (c) show only Cu and Ti



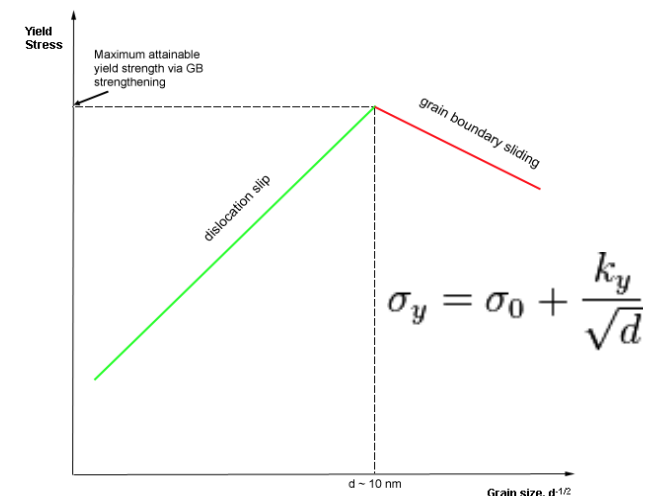


# Dislocation interaction with grain boundaries

- 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 changes barrier density, influencing dislocation movement and yield strength
- This is called the Hall-Petch effect
  - where  $\sigma_y$  is the yield stress,  $\sigma_0$  is a materials constant for the starting stress for dislocation movement (or the resistance of the lattice to dislocation motion),  $k_y$  is the strengthening coefficient (a constant specific to each material), and  $d$  is the average grain diameter

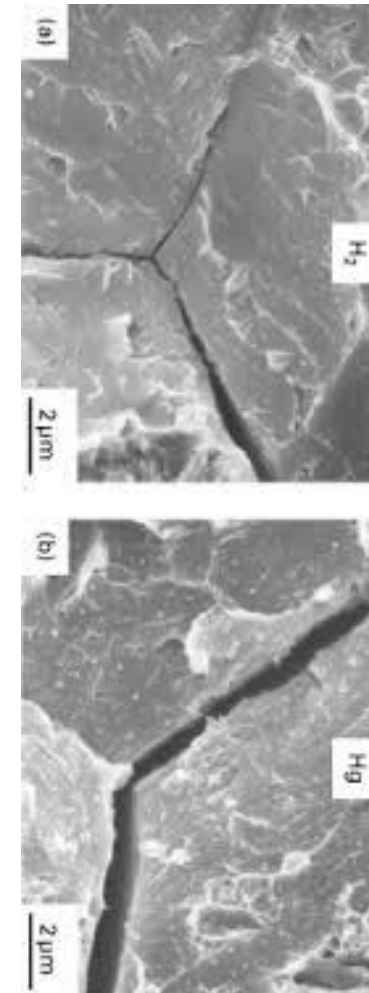
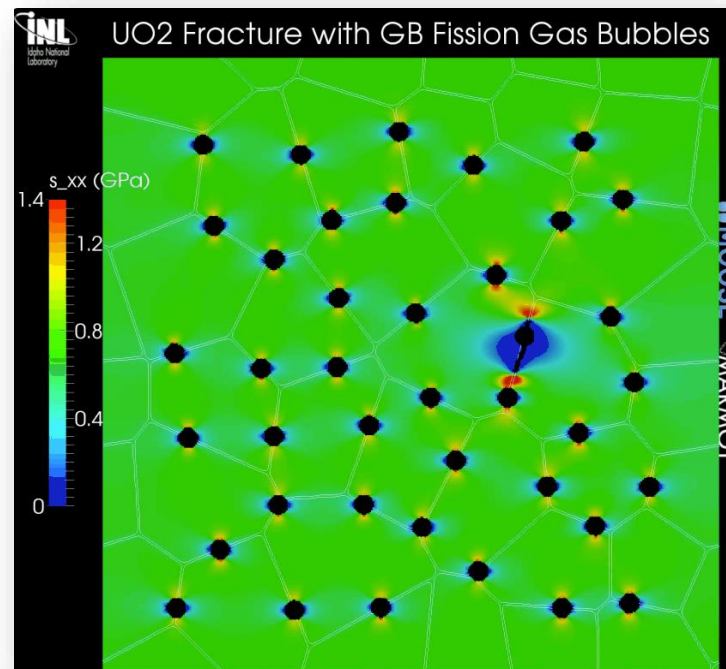


Hall-Petch Strengthening Limit



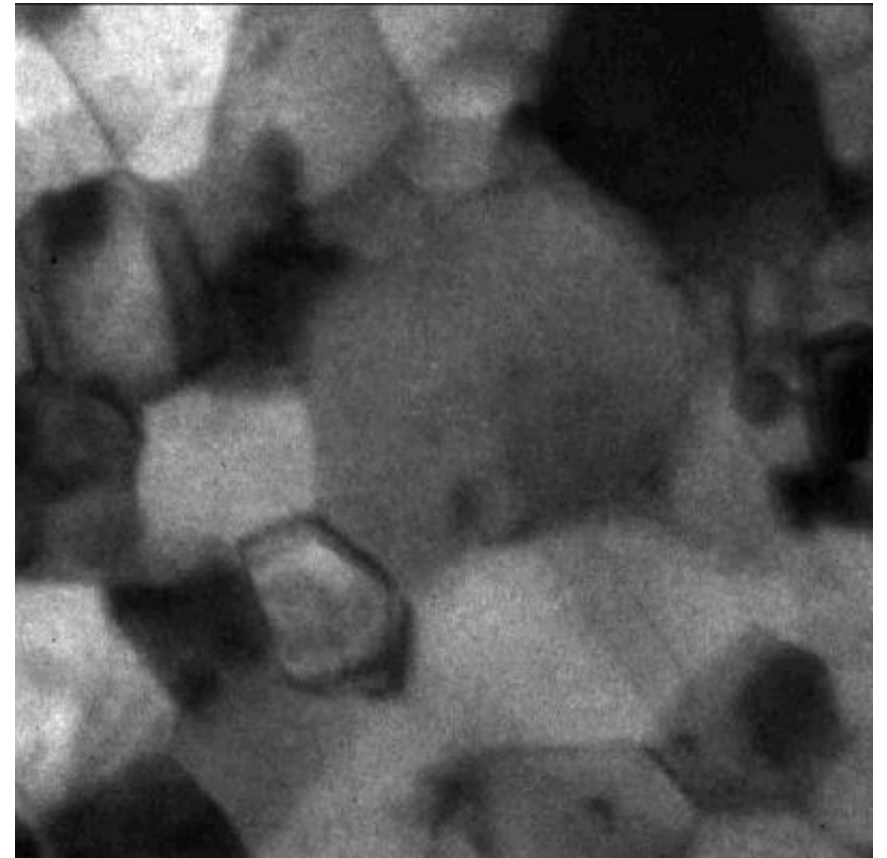
# Grain boundaries and cracks

- Materials often crack along grain boundaries
- Grain boundaries can be weaker than the perfect lattice
  - different bonding environment, increased extrinsic particles, etc.
- Thus, fracture will often occur along grain boundaries (intergranular fracture)



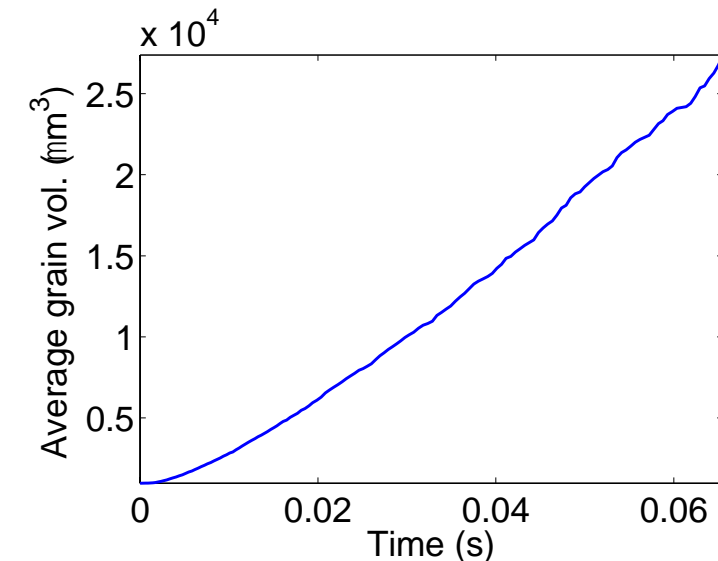
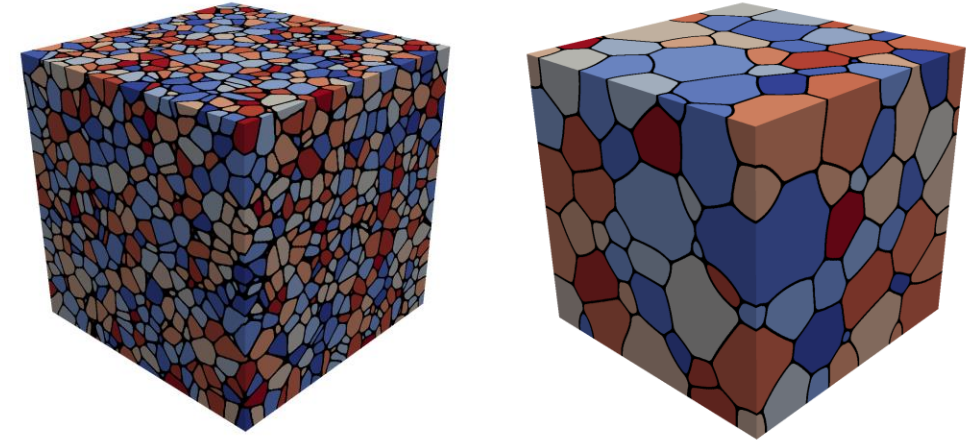
# Grain size change

- 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 during annealing/heat treating
- 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
  - $M_{GB} = M_0 e^{-\frac{Q}{k_b T}} \text{ m}^4/(\text{J s})$
  - $k_b = 8.6173\text{e-}5 \text{ eV/K}$  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->  $\text{UO}_2$ :  $M_0 \text{ (m}^4 \text{ /J-s)} = 4.6\text{e-}09$ ,  $Q \text{ (eV)} = 2.77$
- What is the mobility of  $\text{UO}_2$  at 1600 K?
  - $M_{GB} = 4.6\text{e-}9 * \exp(-2.77/(1600 * 8.6173303\text{e-}5)) = 8.7\text{e-}18 \text{ m}^4/\text{J-s}$

# 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  $\gamma_{GB}$  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:  $v = M \frac{2\gamma_{GB}}{R}$
- Simplified size (diameter) of a spherical grain vs time:  $D(t)^2 - D_0^2 = 2M\gamma_{GB}t$



# 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

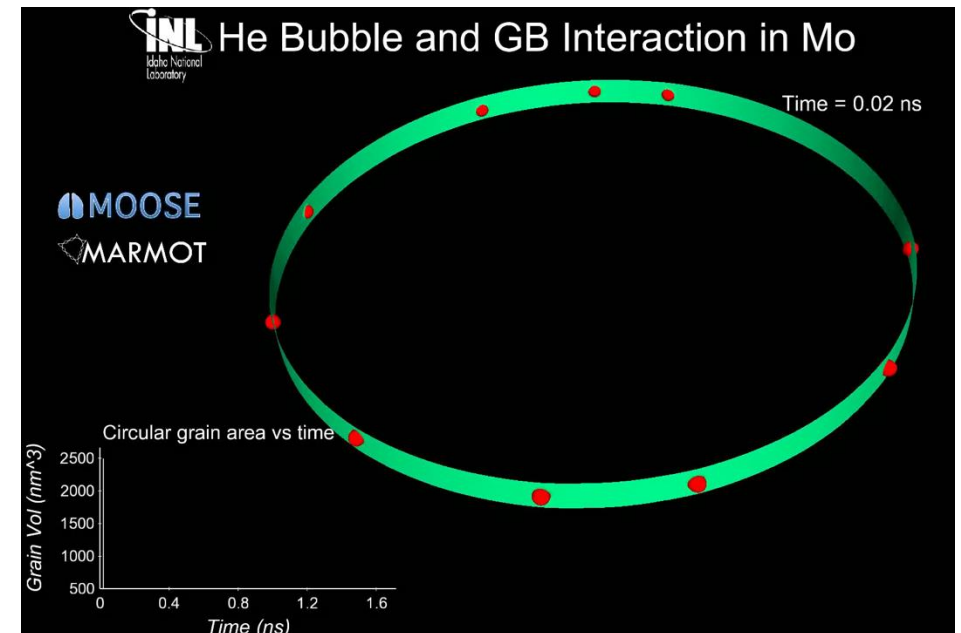
- For UO<sub>2</sub>:

Material	$M_0$ (m <sup>4</sup> J/s)	$Q$ (eV)	$\gamma_{GB}$ (J/m <sup>2</sup> )
UO <sub>2</sub>	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

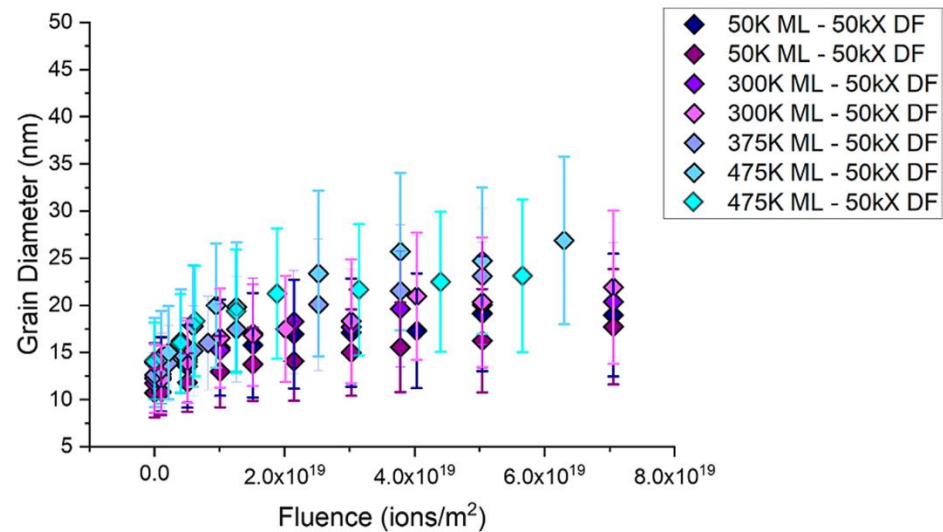
# Grain growth

- 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

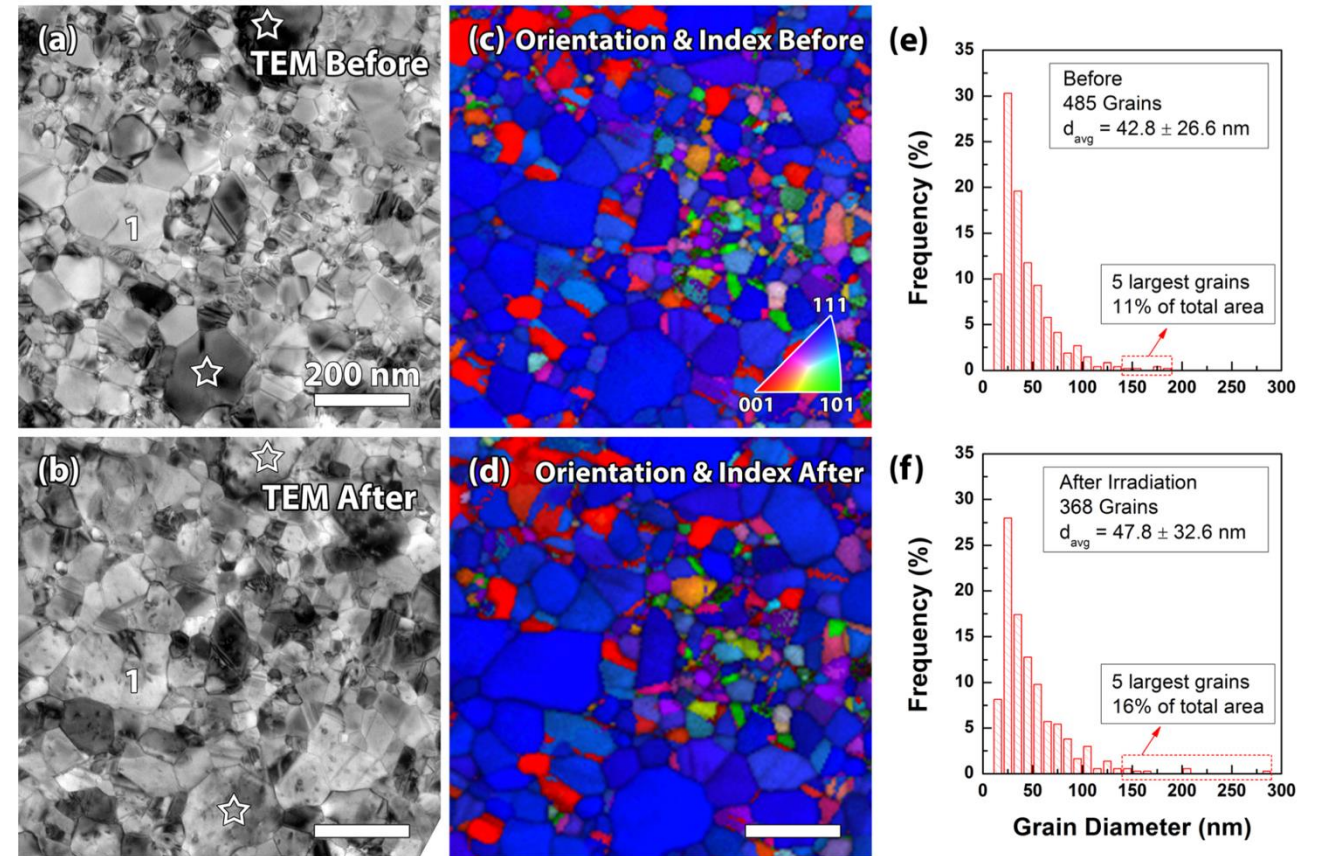


# Irradiation effects on grain growth

- Irradiation can accelerate grain growth
- Can be significant with small grains and at low temperatures



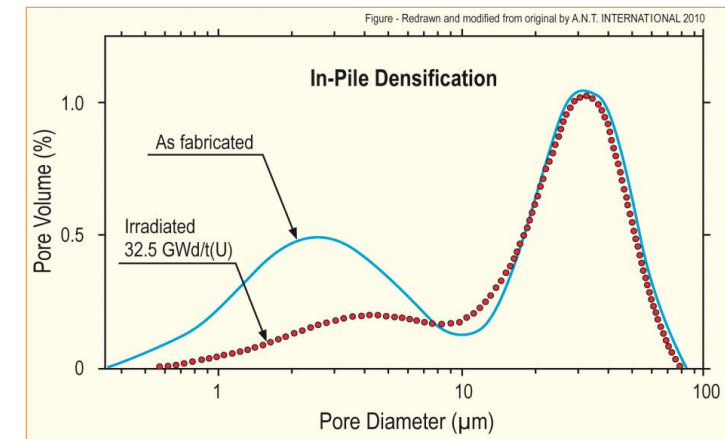
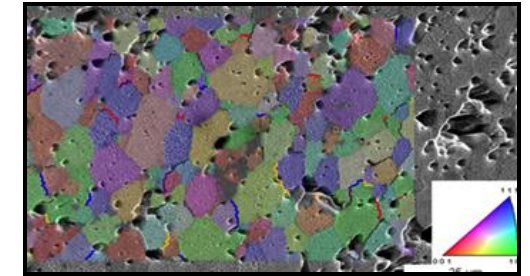
<https://doi.org/10.1016/j.actamat.2022.117856>



<https://doi.org/10.1063/1.4935238>

# Fuel Densification

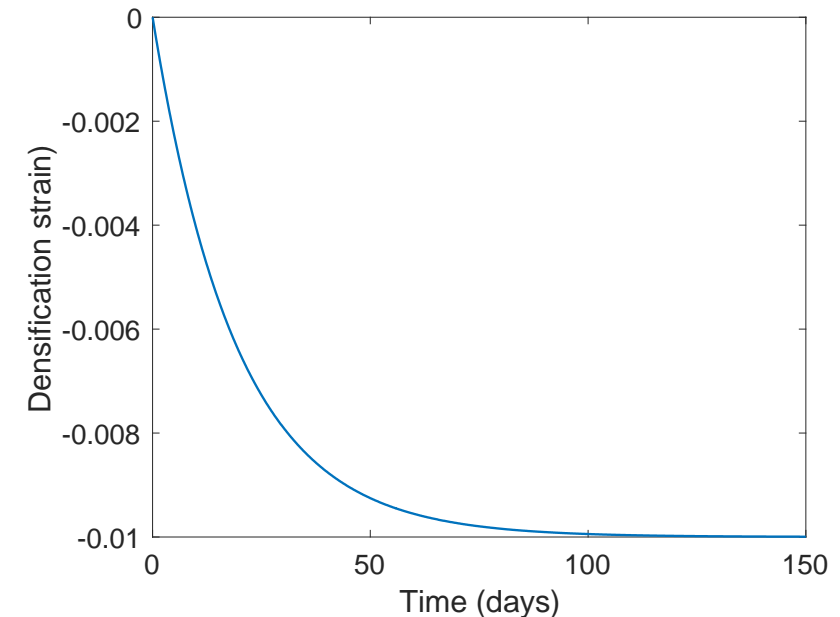
- Remember that fresh fuel pellets are not fabricated to be 100% dense, more like 95-99% dense
- Early in life, fuel pellets shrink, and the initial porosity is largely eliminated
- In some ways, densification is a continuation of the sintering process
- However, irradiation accelerates the process
- 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
  - $\beta$  - Burnup (in FIMA)
  - $\Delta\rho_0$  – Total densification that can occur  $\sim 0.01$
  - $\beta_D$  – Burnup at which densification stops  $\sim 5$  MWD/kgU,  $\sim 0.005$  FIMA
  - $C_D = 7.235 - 0.0086 (T - 25)$  for  $T < 750^\circ\text{C}$  and  $C_D = 1$  for  $T \geq 750^\circ\text{C}$

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



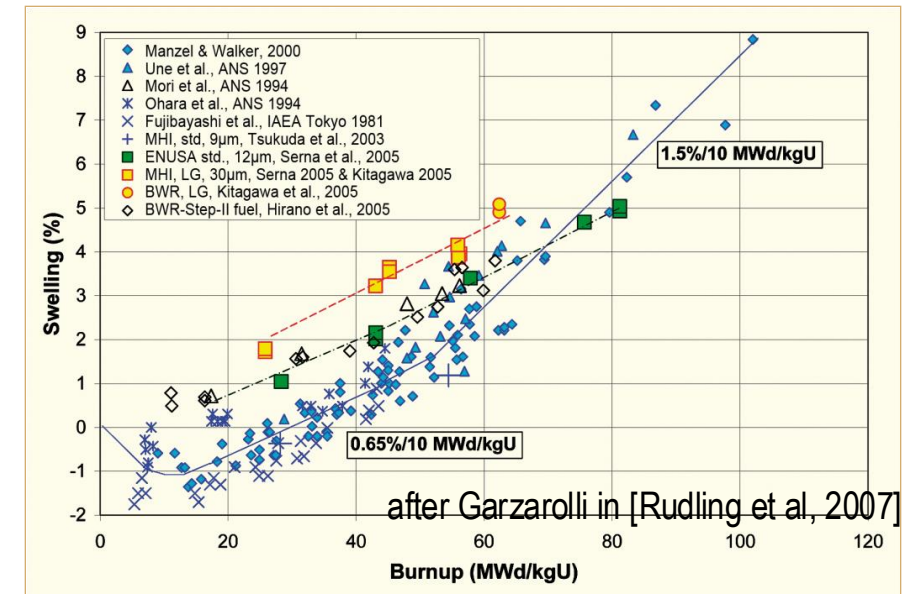


# Empirical models

- 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





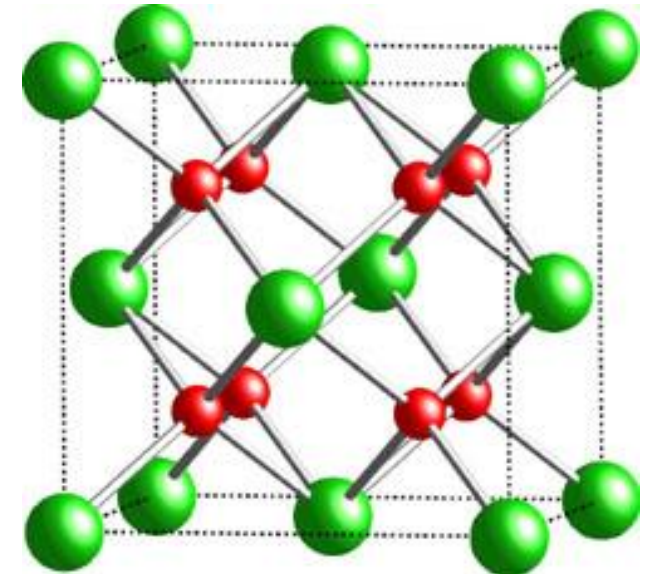
# Summary

- The average grain size in  $\text{UO}_2$  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

# FUEL CHEMISTRY

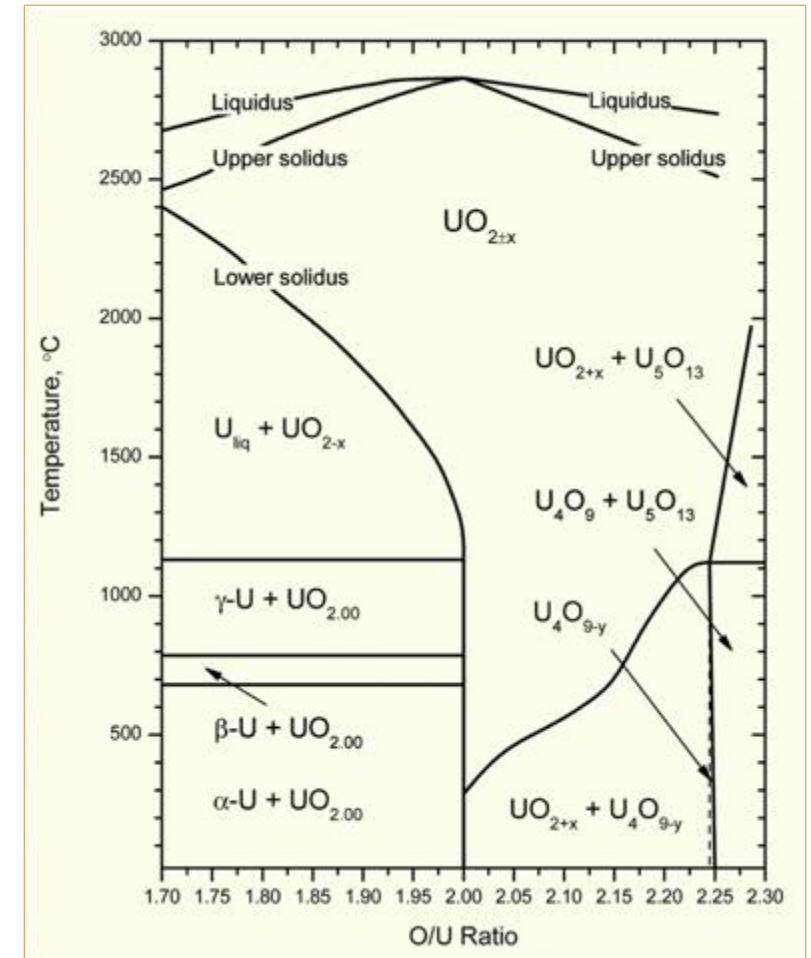
# Fuel Chemistry

- $\text{UO}_2$  is an ionic compound that must have balanced charges
- What is the charge of a typical oxygen ion?
  - $\text{O}^{2-}$
- Uranium valence states
  - Possible:  $\text{U}^{3+}$ ,  $\text{U}^{4+}$ ,  $\text{U}^{5+}$ ,  $\text{U}^{6+}$
  - Most stable:  $\text{U}^{4+}$ ,  $\text{U}^{5+}$ ,  $\text{U}^{6+}$
  - Beyond  $\text{UO}_2$ , can have  $\text{U}_4\text{O}_9$ ,  $\text{U}_3\text{O}_8$ ,  $\text{UO}_3$
- The  $\text{UO}_2$  structure is very stable all the way up to the melting temperature and down to extremely low temperatures, even with irradiation damage
- There is space in the uranium lattice that can accommodate fission products



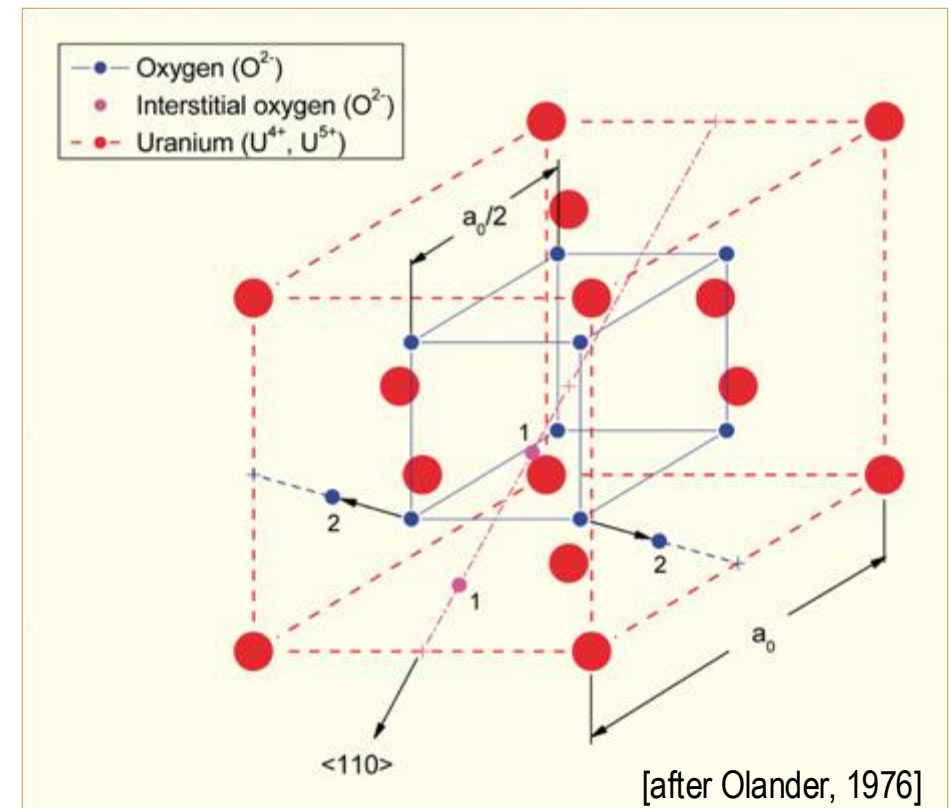
# O/M ratio

- The ratio of oxygen to uranium metal (O/M ratio) can vary
- This is the stoichiometry
- The homogeneity range of uranium dioxide extends to both hypo-( $\text{UO}_{2-x}$ ) and hyper( $\text{UO}_{2+x}$ )-stoichiometric compositions in oxygen
- The minimum and maximum oxygen contents in the dioxide correspond to the compounds with the formula of respectively  $\text{UO}_{1.67}$  at 2720 K and  $\text{UO}_{2.25}$  at approximately 2030 K
- Will the O/M ratio go up or down during reactor operation?
  - It is complicated, because of the formation of fission products that also react with the oxygen, and O interaction with Zr cladding



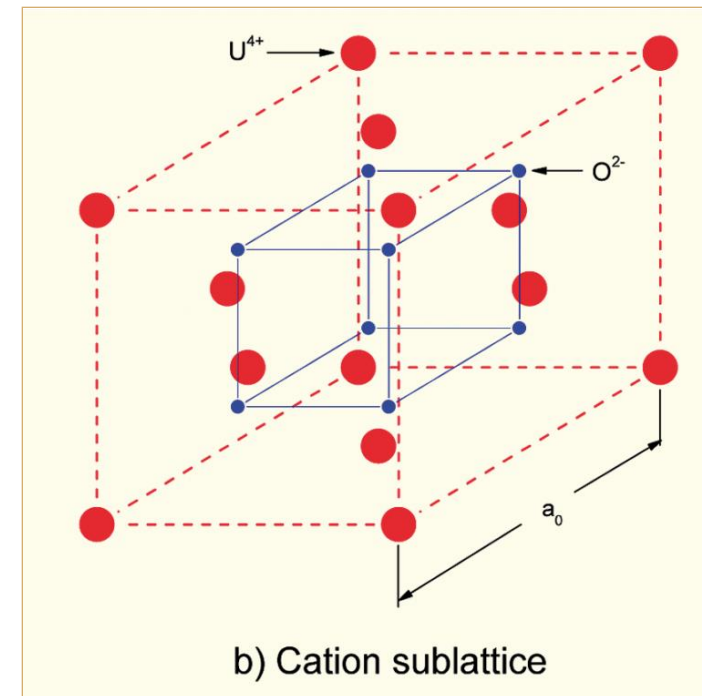
# Excess O

- The crystal structure of  $\text{UO}_2$  can accommodate extra oxygen
- Excess oxygen resides at interstitial locations
- Oxygen in neighboring sites is displaced
- Cation valence increases to maintain electrical neutrality
- Fuel fabricated to be nearly stoichiometric; i.e.,  $\text{UO}_{2.00 \pm}$  because:
  - It is the most stable
  - It has the highest melting temperature



# 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: 
$$D\bar{G}_{O_2} \circ RT \ln(p_{O_2})$$
- 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

