

# Nuclear Fuel Performance

NE-533

Spring 2023

## Last Time

- Radiation effects in UO<sub>2</sub>
- Thermal conductivity degradation
- Formation of the HBS
- Started fuel chemistry

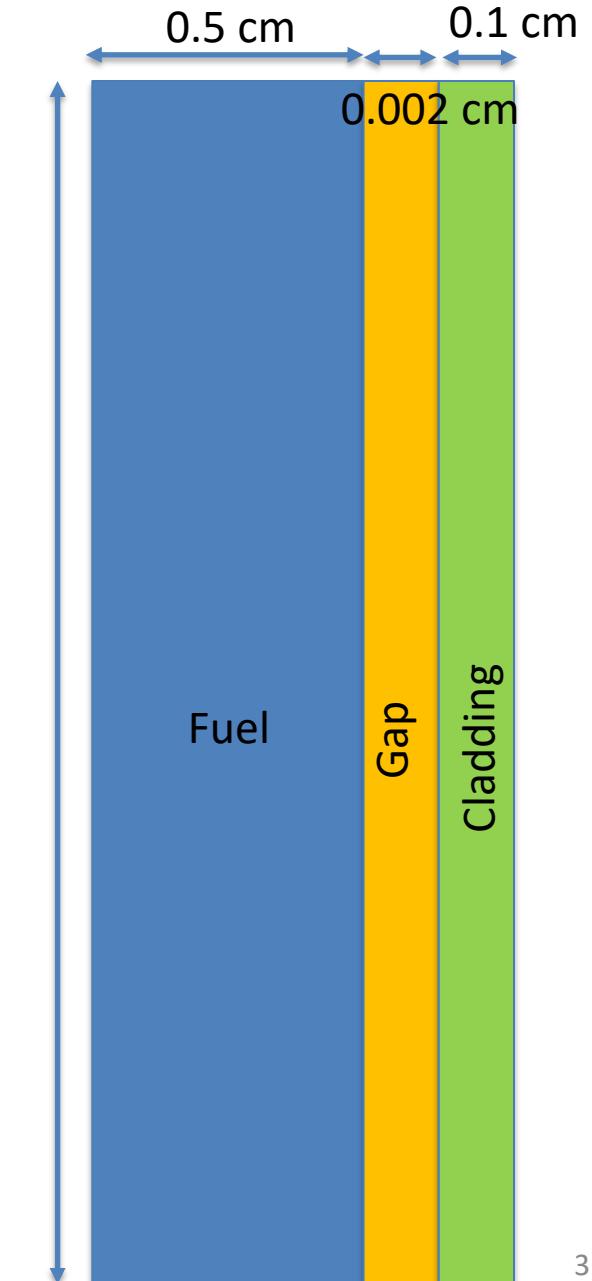
# MOOSE Project Part 2

- Fuel pin dimensions listed – 2D RZ
- Assume reasonable values for thermal conductivities, constant
- Utilize axial  $T_{cool}$ , with  $T_{cool}^{in}= 500$  K, reasonable flow rate, heat capacity, etc.
- Utilize axial LHR, with  $LHR^0=350$  W/cm

$$LHR\left(\frac{z}{Z_o}\right) = LHR^0 \cos\left[\frac{\pi}{2\gamma}\left(\frac{z}{Z_o}-1\right)\right] = LHR^0 F\left(\frac{z}{Z_o}\right)$$

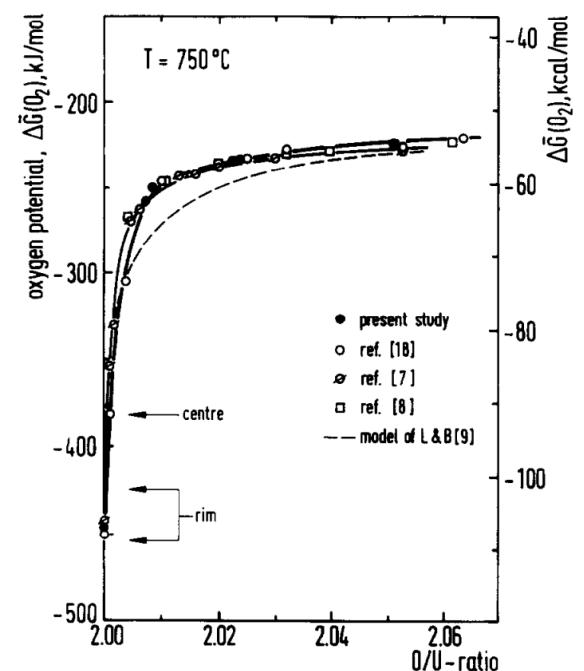
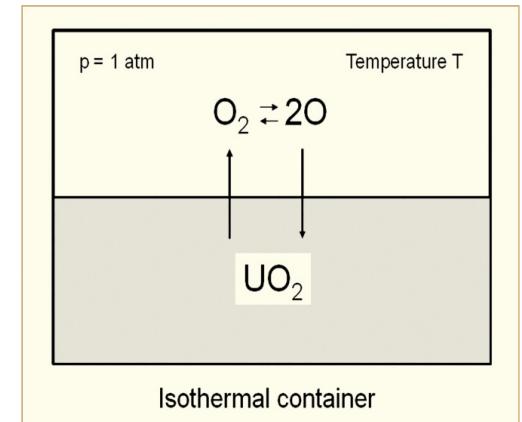
$$T_{cool} - T_{cool}^{in} = \frac{1}{1.2} \frac{Z_o \times LHR^0}{\dot{m} C_{PW}} \left\{ \sin(1.2) + \sin\left[1.2\left(\frac{z}{Z_o}-1\right)\right] \right\}$$

- Solve temperature profile for:
  - @  $z=0.25$ ,  $z=0.5$ ,  $z=1$
- Solve for centerline temperature vs time
  - Transient:  $LHR^0 = 500 * [(t/100)^{0.5}] * [(1-(t/100))^4] + 150$
  - @  $z=0.25$ ,  $z=0.5$ ,  $z=1$
- Find location of peak centerline temperature at steady-state and at  $t=100$  in transient
- Due March 31



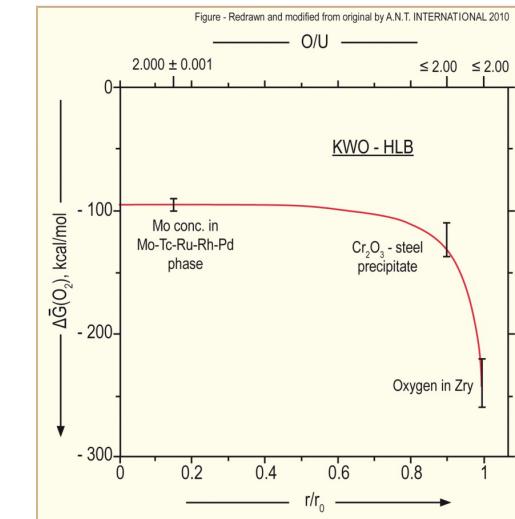
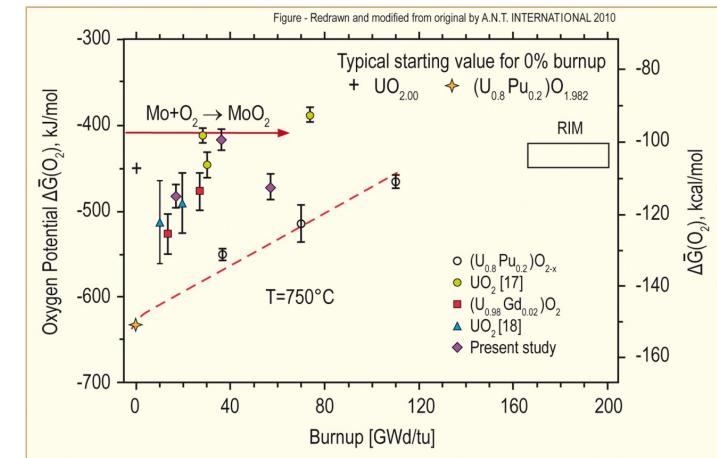
# Oxygen potential

- 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



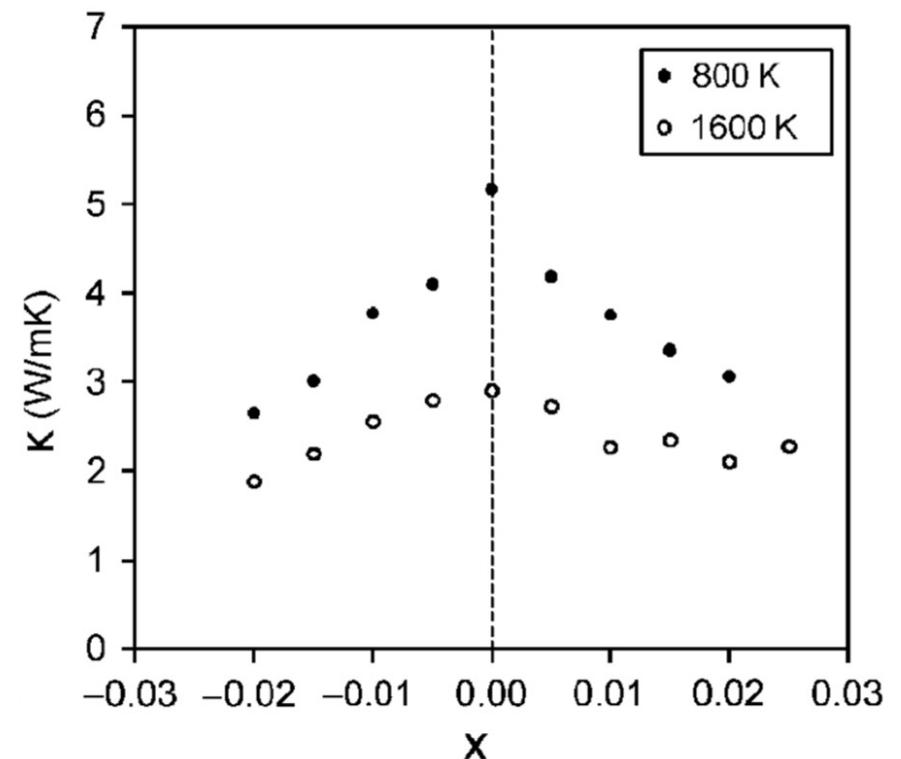
# Oxygen potential

- 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/MoO<sub>2</sub> reaction (from calculations)
- Mo serves as a buffer to the O potential, or a means of inferring what the oxygen potential may have been in the fuel from PIE
- Oxygen potential is low near the cladding, because the oxygen enters the cladding



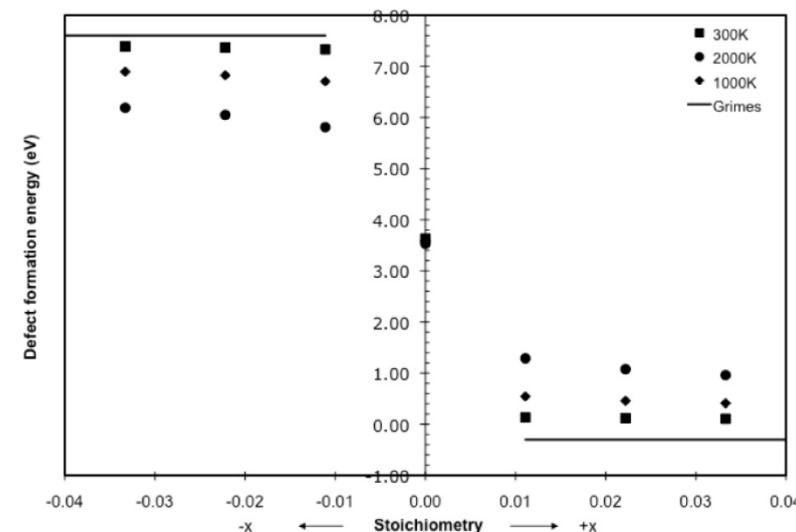
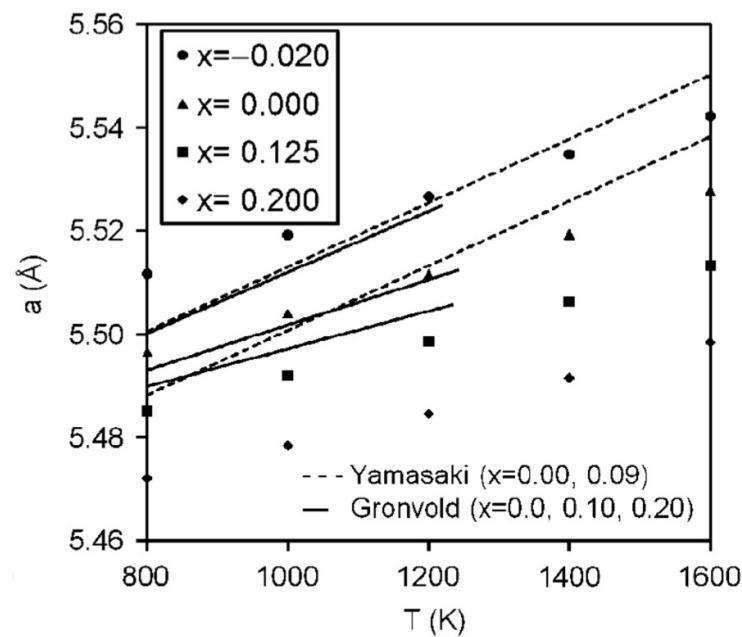
# Fuel Stoichiometry/Properties

- 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 UO<sub>2</sub>



# Fuel Stoichiometry/Properties

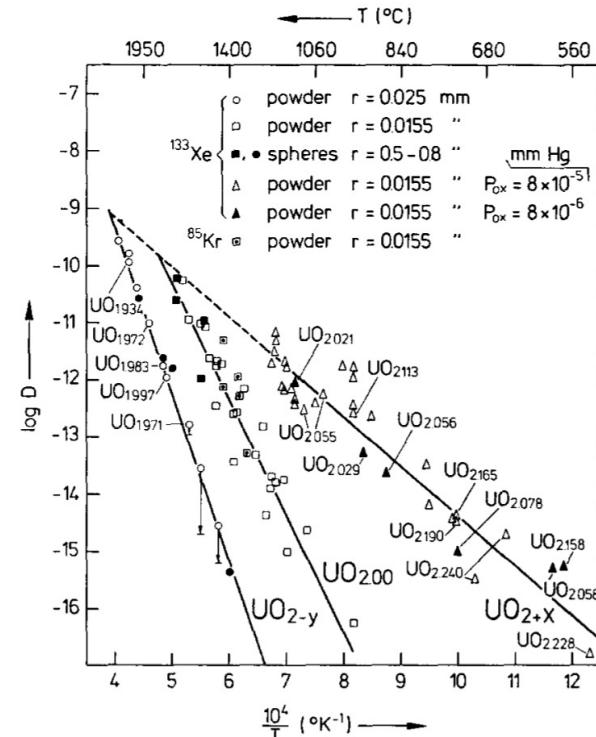
- The lattice constant of the material decreases with increasing stoichiometry
- The vacancy formation energy also changes with stoichiometry



# Fuel Stoichiometry/Properties

- The solution energy of Xe, Cs, and Sr in  $\text{UO}_2$  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	$\text{UO}_{1.97}$	$\text{UO}_2$	$\text{UO}_{2.03}$
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



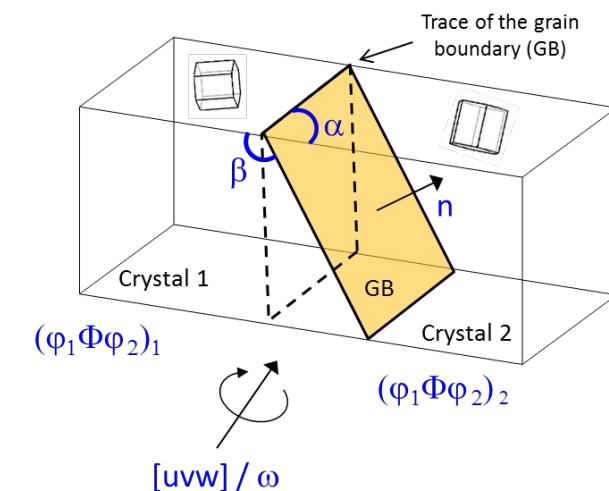
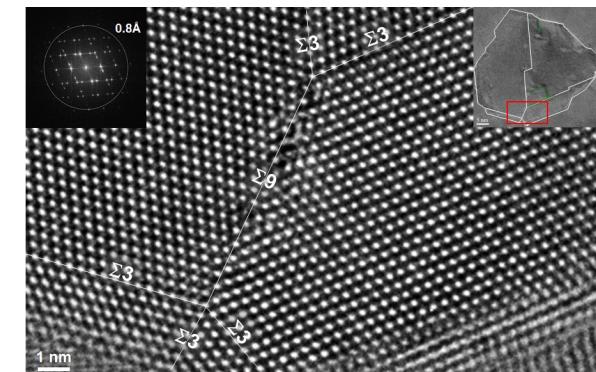
# Fuel Chemistry Summary

- $\text{UO}_2$  has a cubic fluorite structure that is very stable
- The charges are balanced with a  $\text{U}^{4+}$  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 PROPERTIES/BEHAVIOR

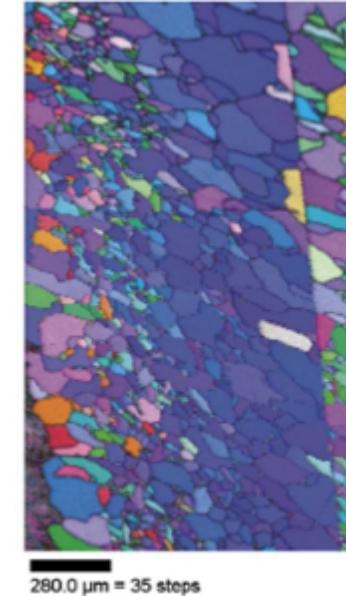
# Grain Boundaries

- 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)

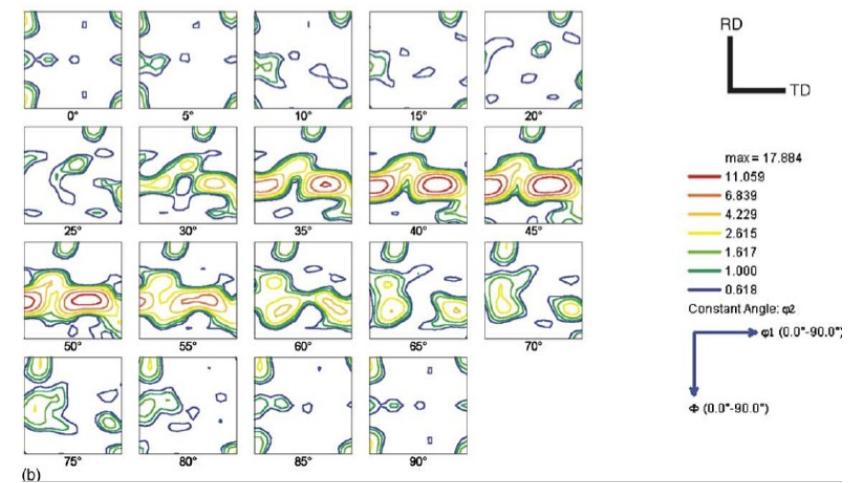


# Grain Texture

- 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



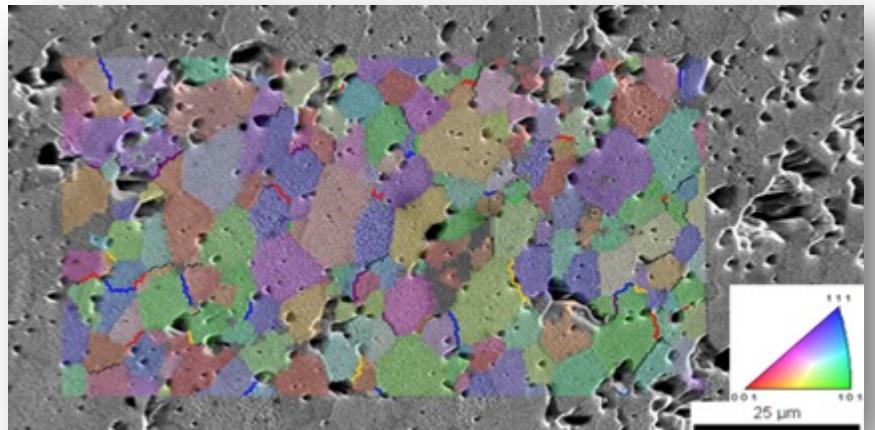
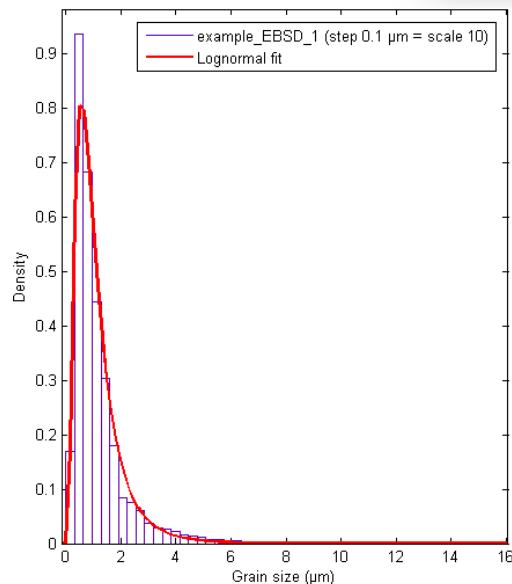
Electron back scatter diffraction map  
for cubic crystal structure



Orientation distribution function

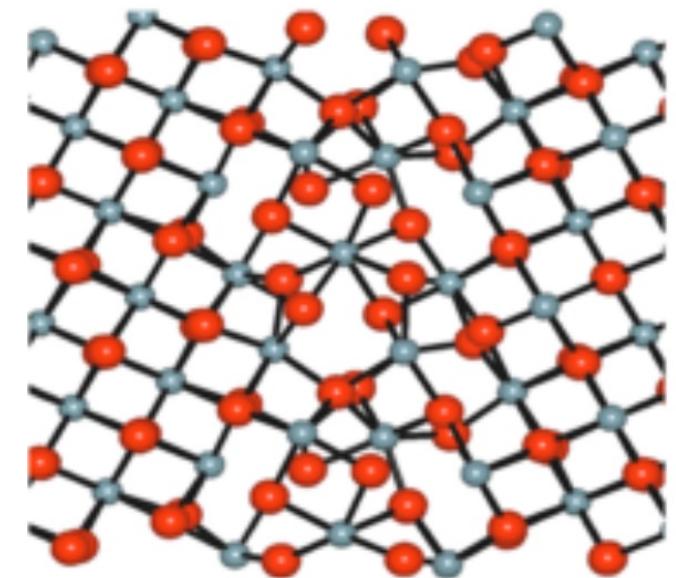
# Grain size

- 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



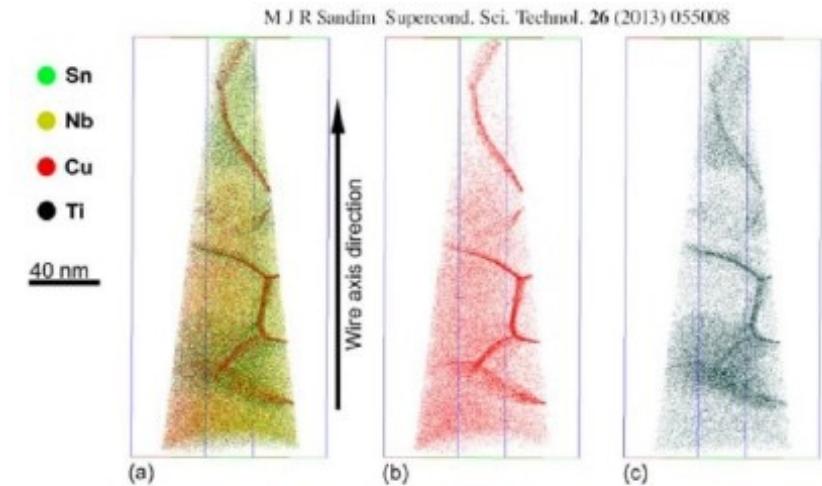
# Grain boundary diffusion

- 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

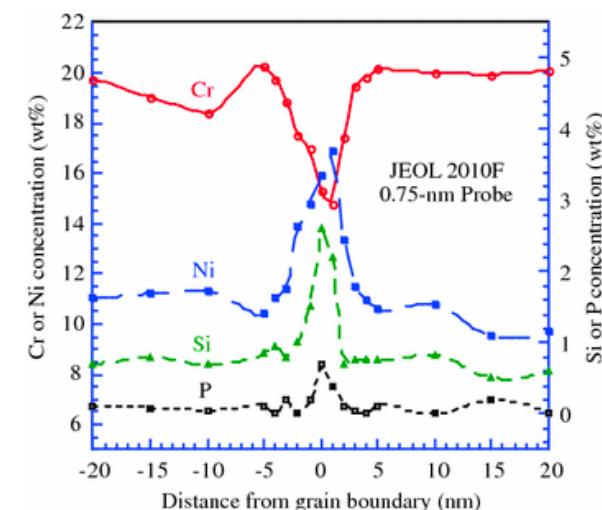


# Grain boundary segregation

- 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

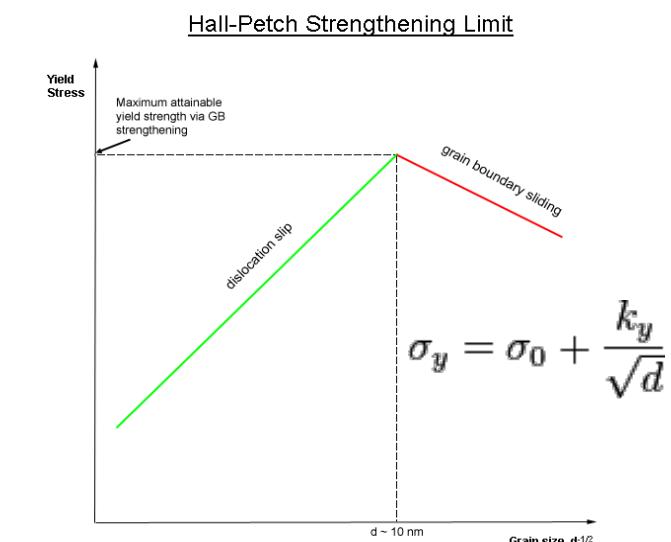
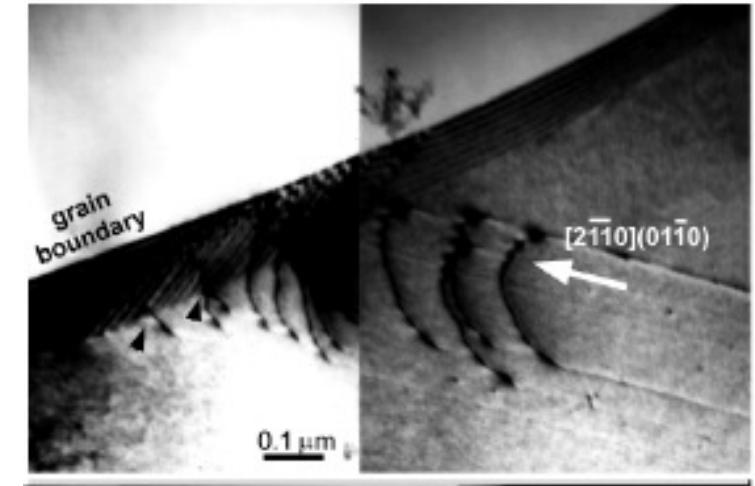


APT reconstruction : (a) elements mapped in the sample and (b) and (c) show only Cu and Ti



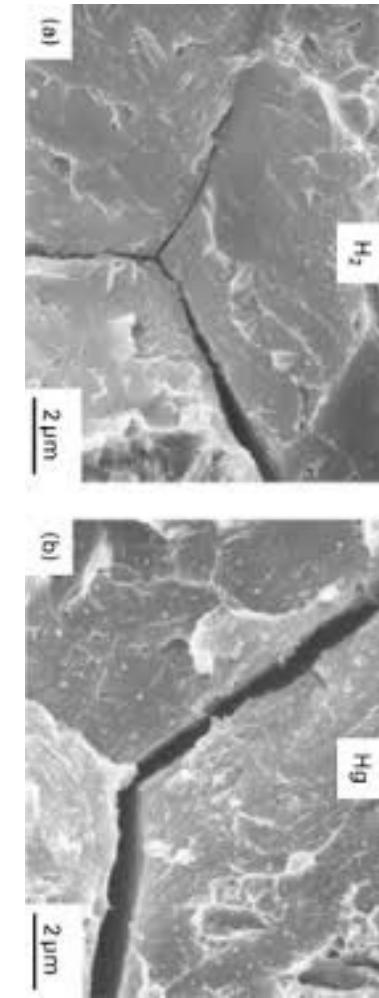
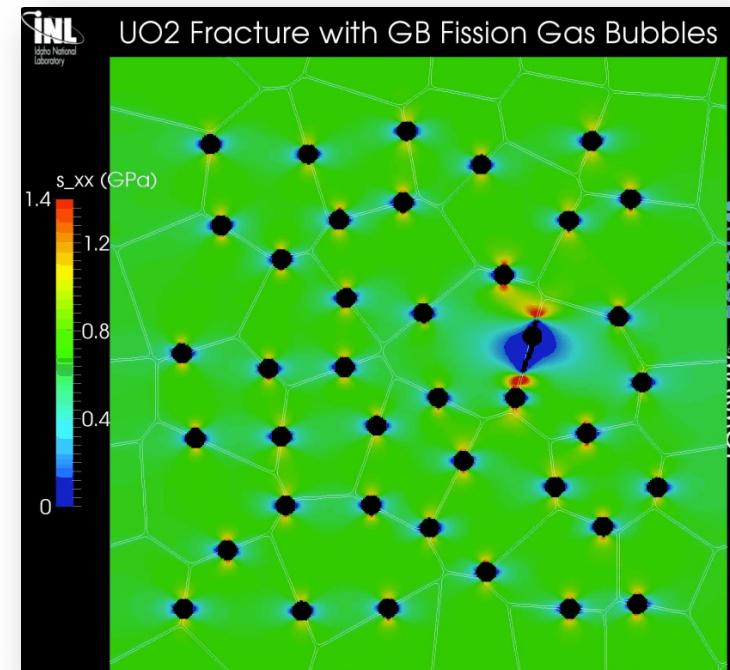
# Dislocation interaction with grain boundaries

- 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



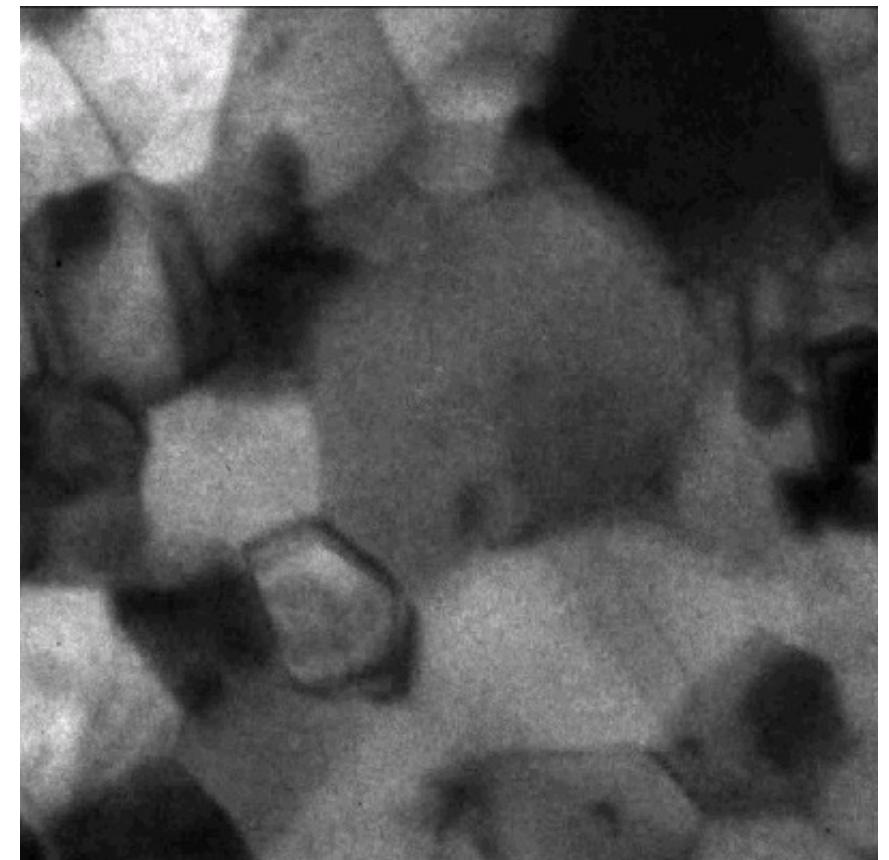
# Grain boundaries and cracks

- 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)



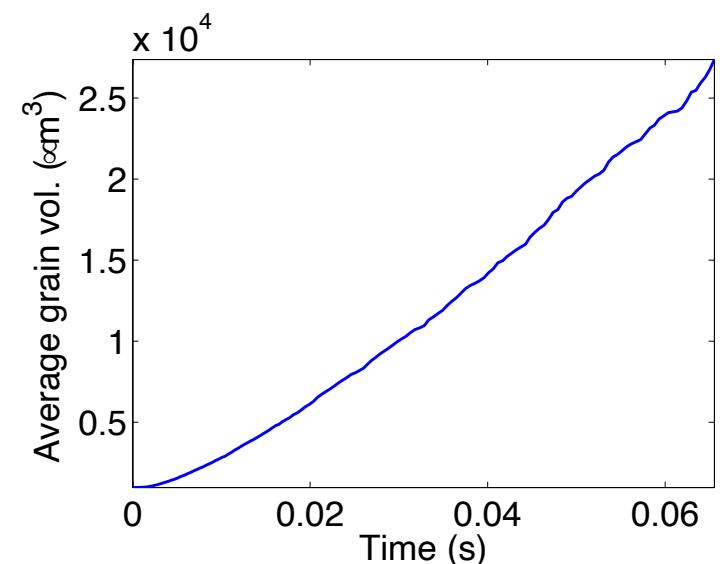
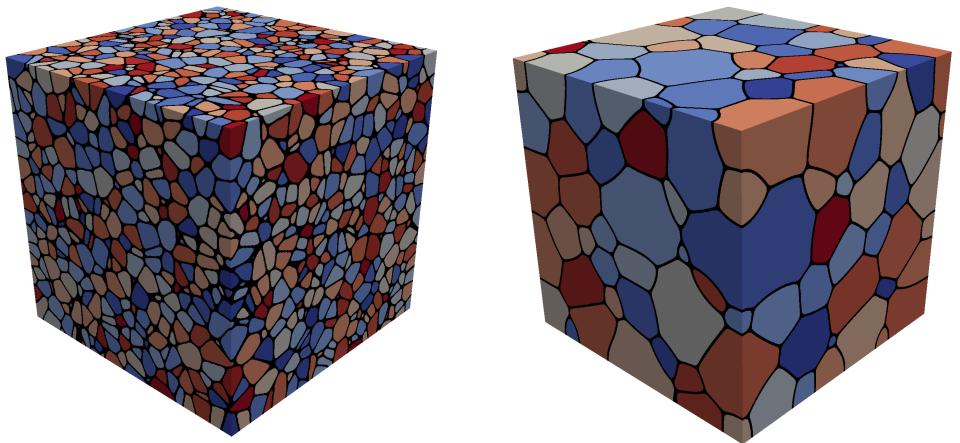
# Grain size change

- 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

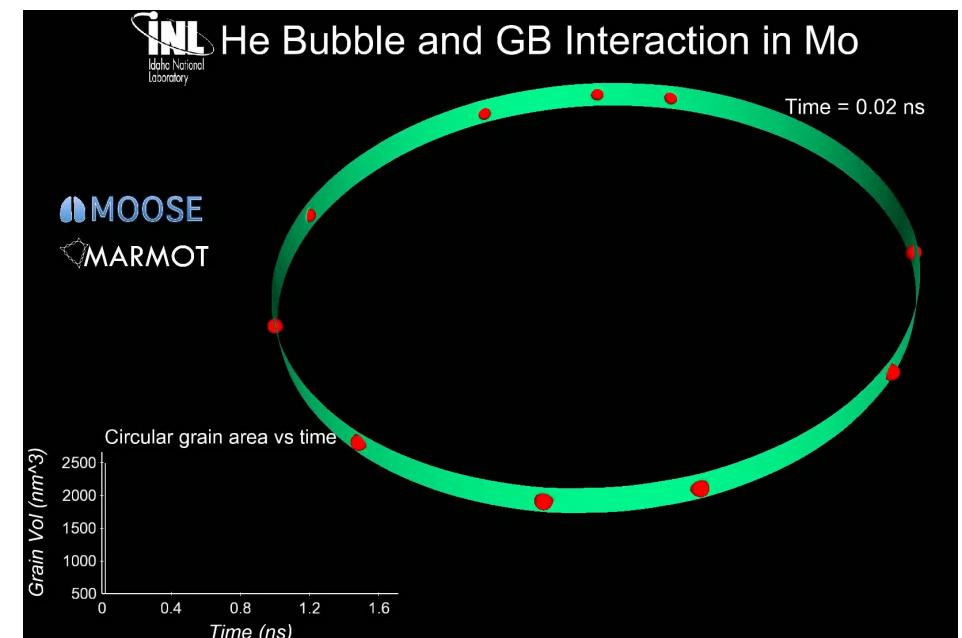
- The grain boundary mobility is a function of temperature and GrB type
- The grain boundary mobility is determined according to
  - $M_{GB} = M_0 e^{-\frac{Q}{k_b T}} \text{ m}^4/(\text{J s})$
  - $k_b = 8.6173e-5 \text{ eV/K}$  is the Boltzmann constant
- Both the pre-factor  $M_0$  and the activation 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-> UO<sub>2</sub>:  $M_0 (\text{m}^4 / \text{J-s}) = 4.6e-09$ ,  $Q (\text{eV}) = 2.77$
- What is the mobility of UO<sub>2</sub> 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

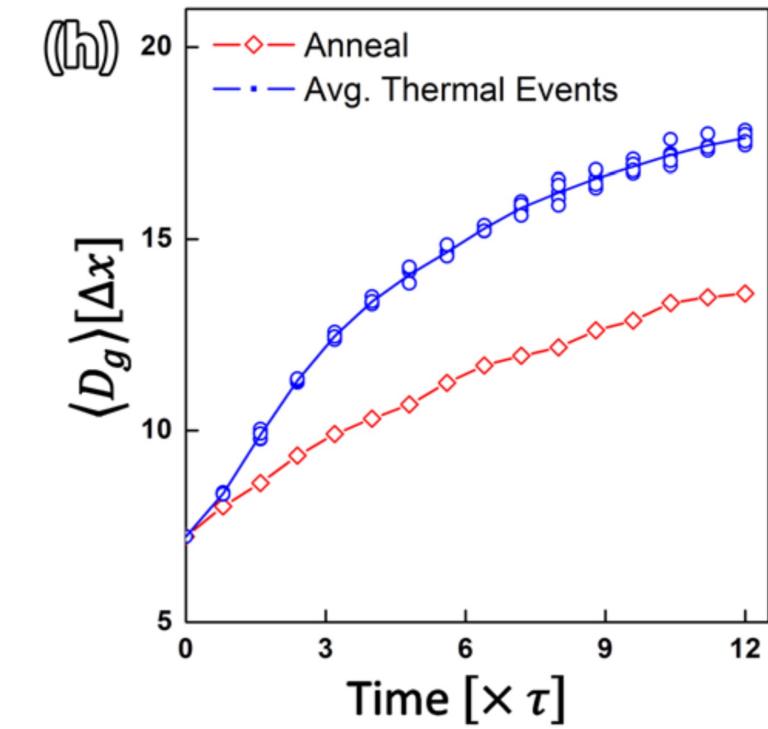
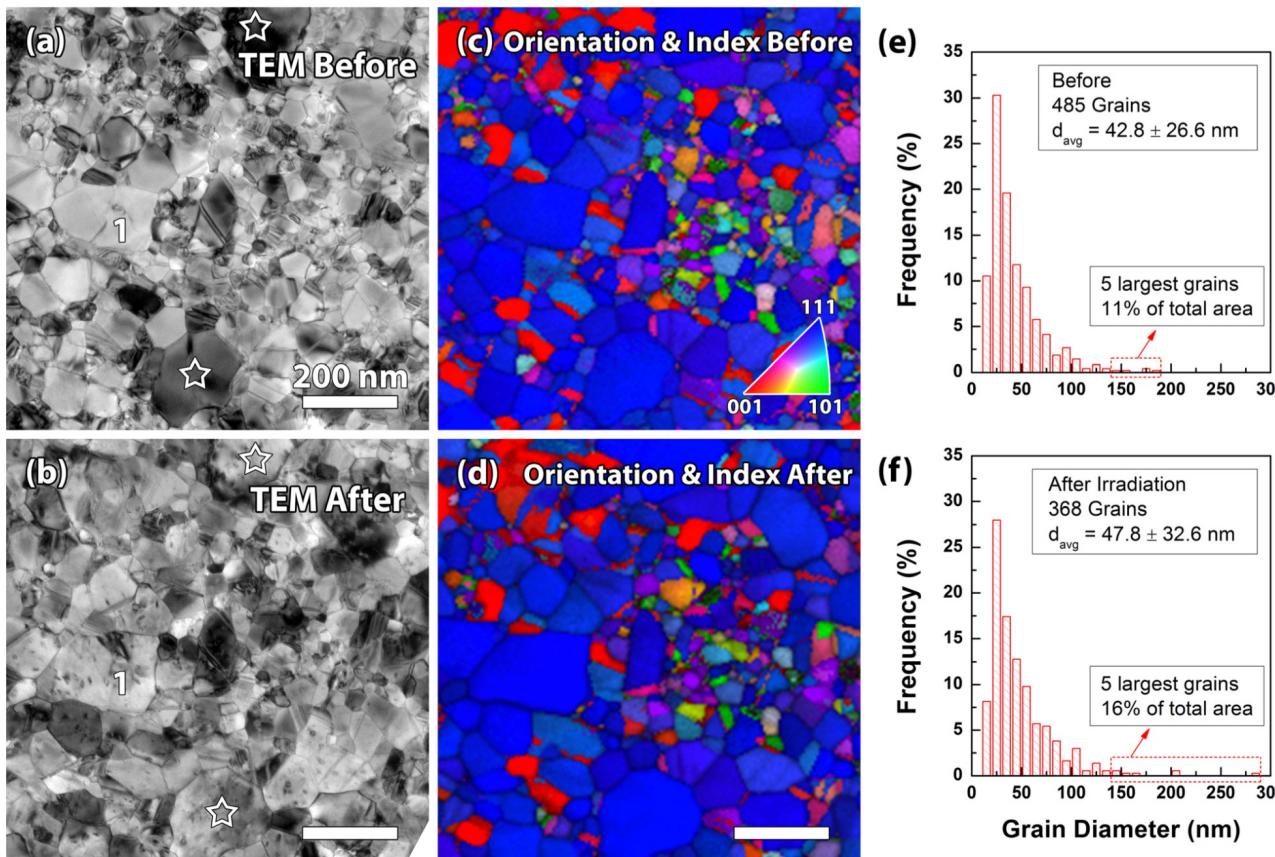
- There are various driving forces for grain growth
- The most common driving force is the reduction of grain boundary energy
  - $P_d = \frac{2\gamma_{GB}}{R}$ , where  $\gamma_{GB}$  is the GB energy and R is the radius of curvature
  - It is often called the curvature driving force, because it drives 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:  $v = M \frac{2\gamma_{GB}}{R}$

# 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

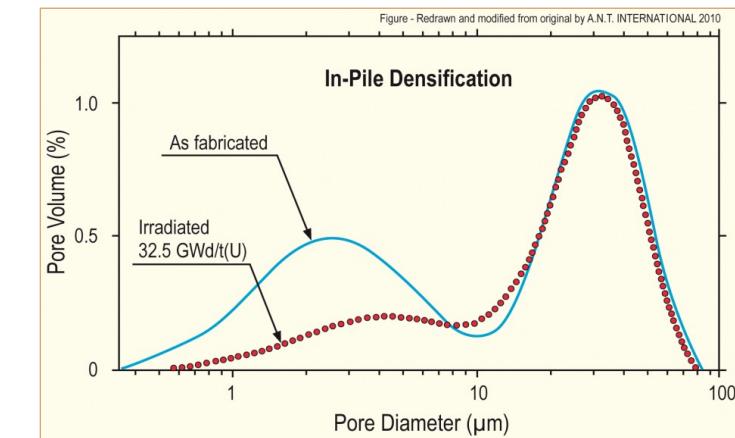
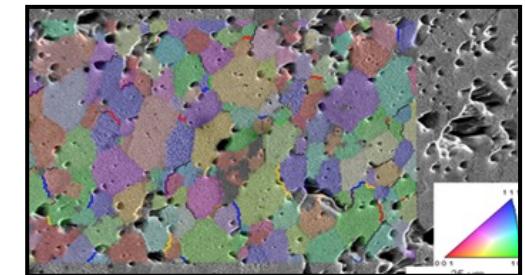
$$\frac{dD}{dt} = k \left( \frac{1}{D} - \frac{1}{D_m} \right)$$

- $k = 2 M_{GB} \gamma_{GB}$  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 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

# Fuel Densification

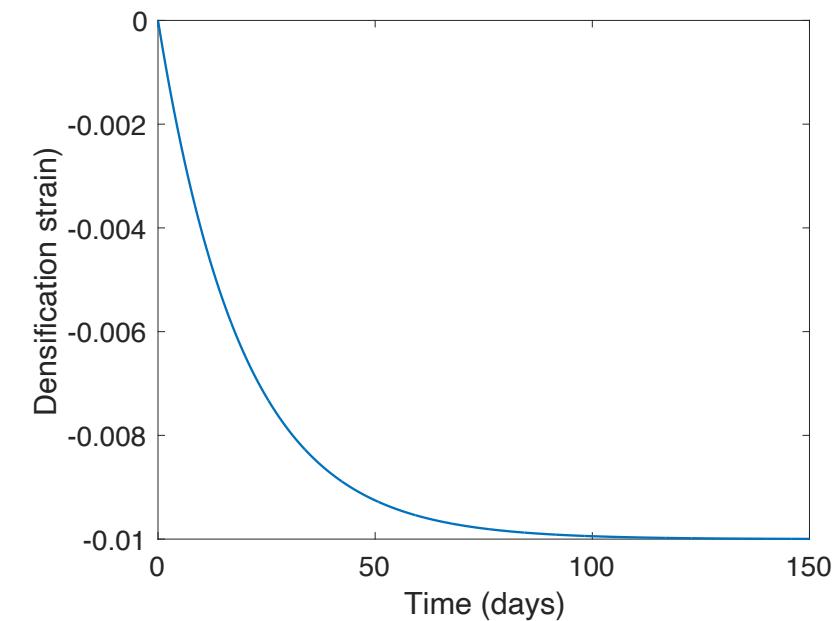
- Remember that fresh fuel pellets are not fabricated to be 100% dense, more like 95-99% dense
- Early in life, fuel pellets shrink and the initial porosity is largely eliminated
- In some ways, densification is a continuation of the sintering process
- However, irradiation accelerates the process
- 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  $T < 750C$  and  $C_D = 1$  for  $T \geq 750C$

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

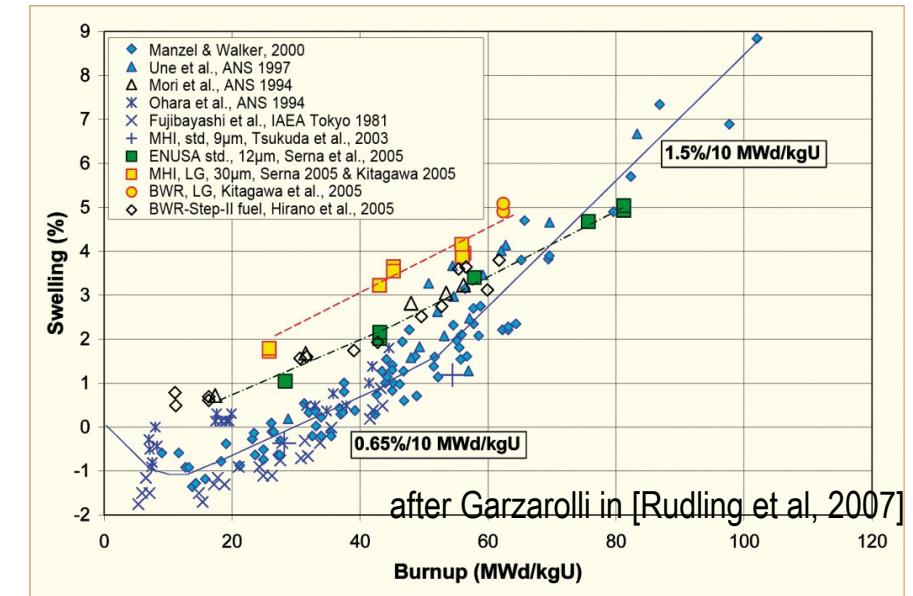


# Empirical models

- 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



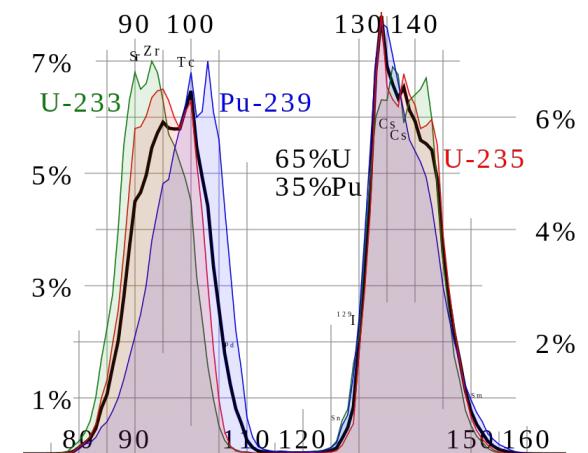
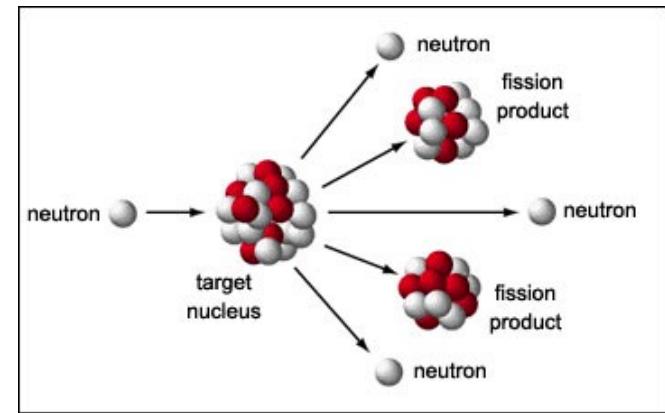
# Summary

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

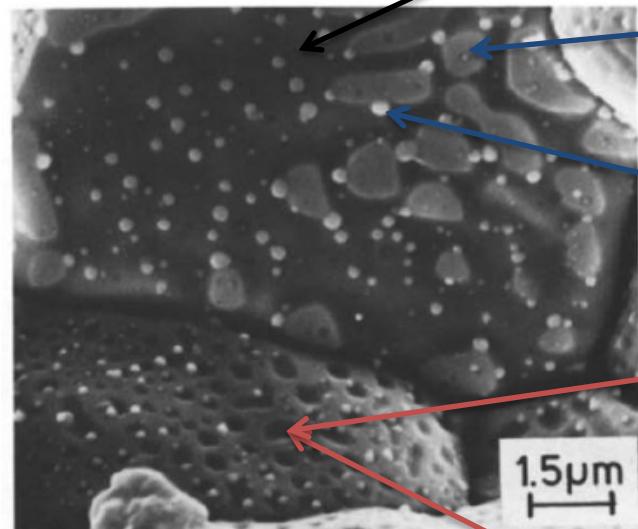
# FISSION PRODUCTS

# Fission Product Generation

- Fission releases around 200 MeV
  - The fission fragments have 169 MeV of kinetic energy
  - 2 to 3 neutrons with an average energy of 2 MeV
  - 7 MeV of prompt gamma ray photons
  - The remaining energy is released by beta decay
- Every fission product that is produced is now in the crystal lattice of the fuel, changing the microstructure



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



## Soluble oxides (Y, La and the rare earths)

- Dissolved in the cation sublattice

## Insoluble oxides (Zr, Ba and Sr)

- Form insoluble oxides in the fluorite lattice

## Metals (Mo, Ru, Pd, and Tc)

- Form metallic precipitates

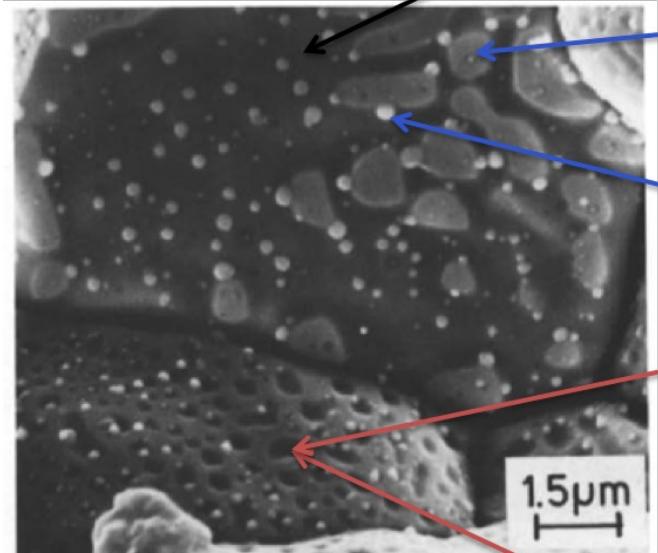
## Volatiles (Br, Rb, Te, I and Cs)

- Exist as gases at high temperatures of the pellet interior
- Also exist as solids at the cooler pellet exterior

## Noble gases (Xe, Kr)

- Essentially insoluble in the fuel matrix
- Form either intragranular (within grain) voids or bubbles or intergranular (grain boundary) bubbles

# All of the fission products impact the behavior of the fuel



## Soluble oxides (Y, La and the rare earths)

- Cause swelling, decrease thermal conductivity

## Insoluble oxides (Zr, Ba and Sr)

- Can cause swelling

## Metals (Mo, Ru, Pd, and Tc)

- Slightly raise thermal conductivity,

## Volatiles (Br, Rb, Te, I and Cs)

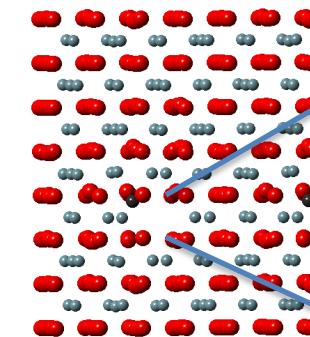
- Cause swelling, decrease thermal conductivity
- Escape from fuel, corrode the cladding

## Noble gases (Xe, Kr)

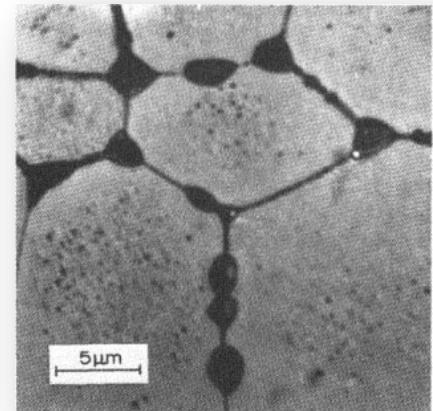
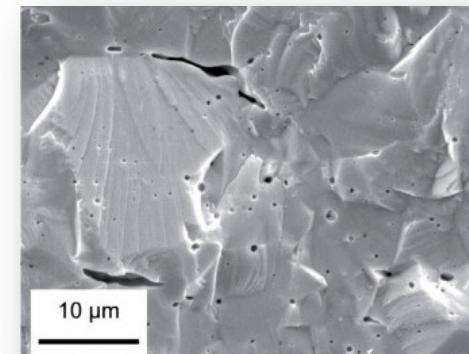
- Cause swelling
- Decrease thermal conductivity
- After release, raise gap pressure and lower thermal conductivity

# Fission Gas Release

- Fission gases (Xe, Kr) are released in a process composed of three stages in UO<sub>2</sub>
- Stage 1: Gas atoms are produced throughout the fuel due to fission and diffuse towards grain boundaries
- Small intragranular bubbles form within the grains, but never get larger than a few nm radius due to resolution from energized particles
- Gas atoms that don't get trapped within the intragranular bubbles migrate to grain boundaries

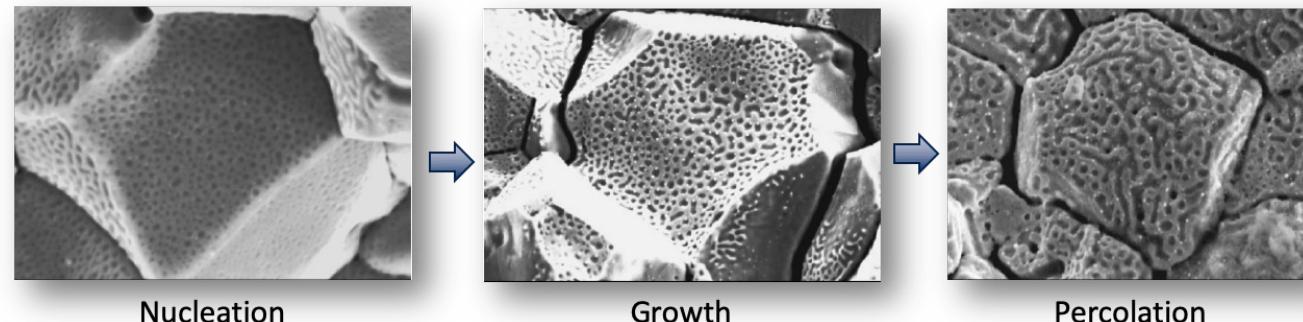


Atoms forming a  
vacancy cluster

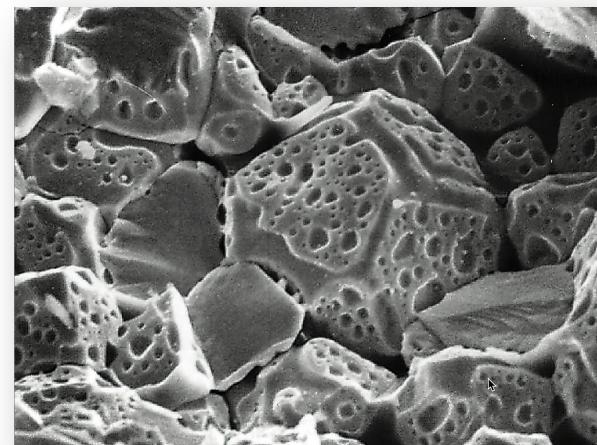


# Fission Gas Release

- Stage 2: Gas bubbles nucleate on grain boundaries, growing and interconnecting

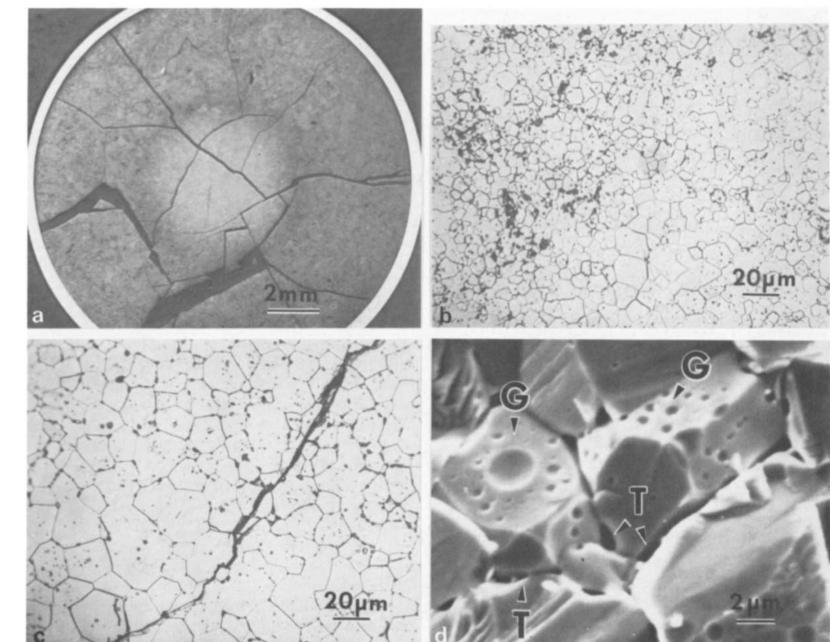
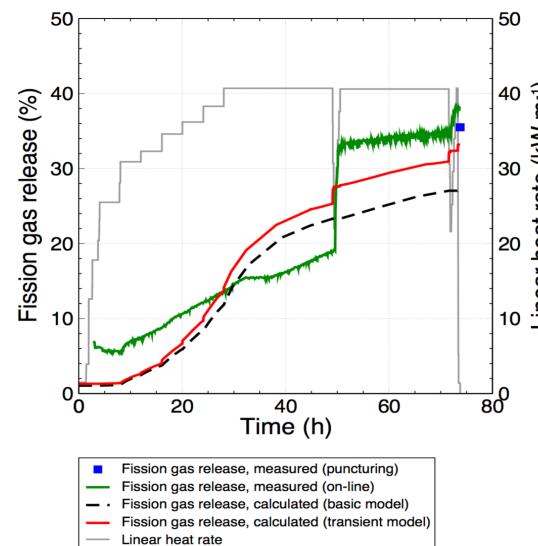


- Stage 3: Gas travels through interconnected bubbles to a free surface



# Fission Gas Release

- Fission gas release also occurs due to mechanisms that don't depend on diffusion
- Release can occur to particle recoil and knockout at low temperature
- It can occur due to fracture during rapid transients



# Fission Gas Release

- Released fission gas enters the gap and plenum, causing various problems
- Xe and Kr have very low thermal conductivities, reducing the gap conductance
- The plenum pressure increases
- The volatile fission gases corrode the cladding
- They are also radioactive and hazardous, causing problems when the cladding is breached
- Fission gas release experiments:
  - Post irradiation annealing
    - Fuel is irradiated at low temperature
    - Fuel is then placed into a furnace and heated
    - Gas atom release is then measured
  - In-pile release
    - Gas release is measured during reactor operation
    - It is much more difficult than post-irradiation annealing
    - Total amount released is measured by puncturing cladding after irradiation
    - Release with time can be estimated using a pressure transducer inside an instrumented fuel rod

# 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

# Summary

- Five families of fission products
- Fission products 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