

Nuclear Fuel Performance

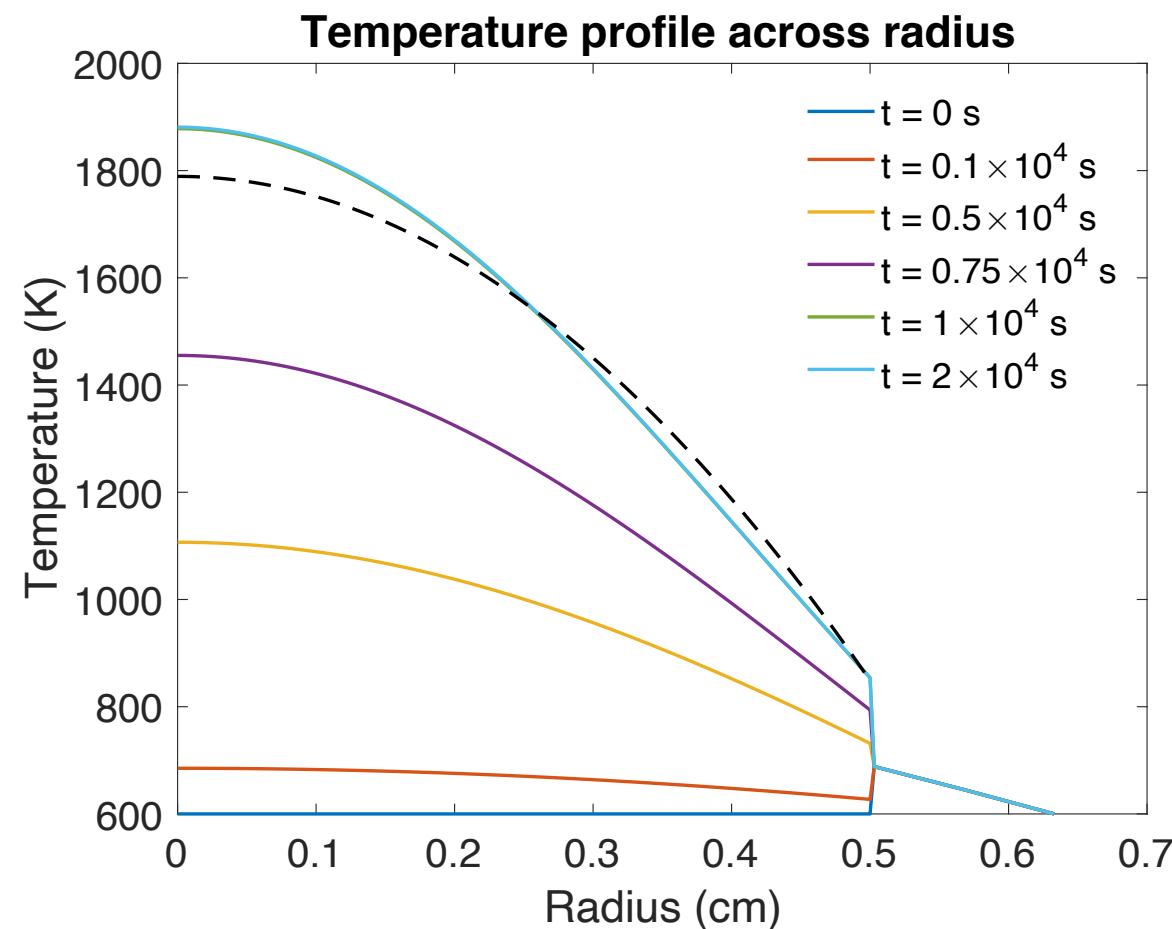
NE-591-010
Spring 2021

Last Time

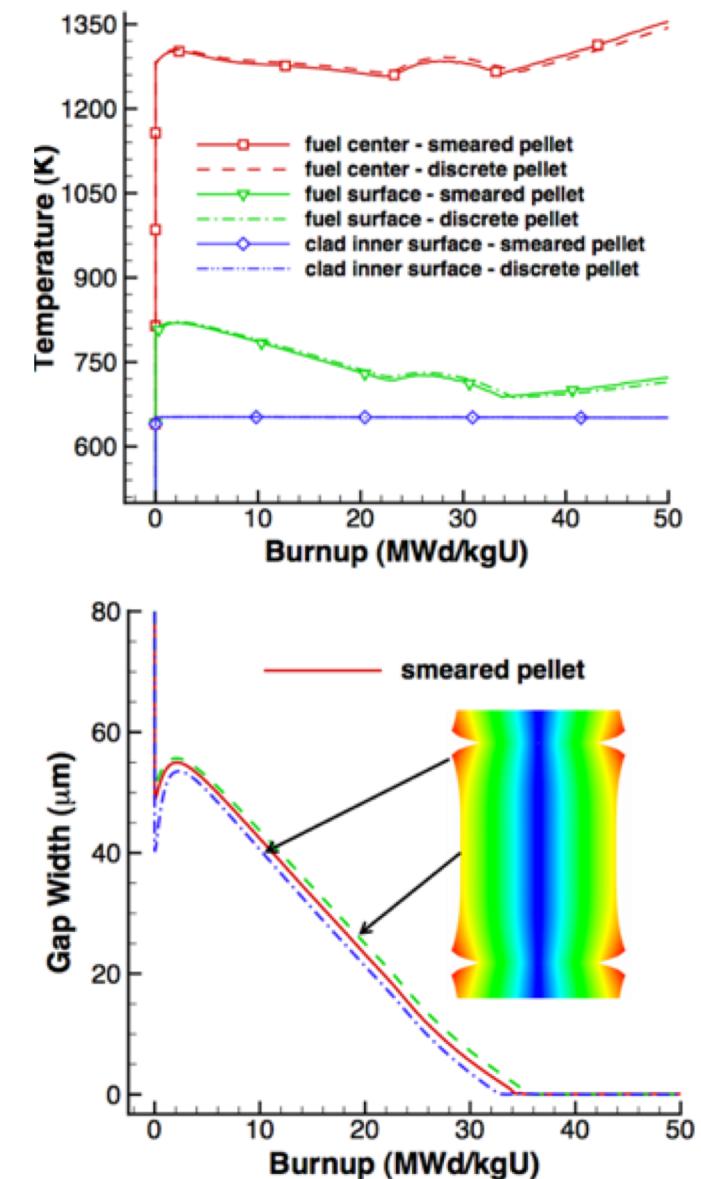
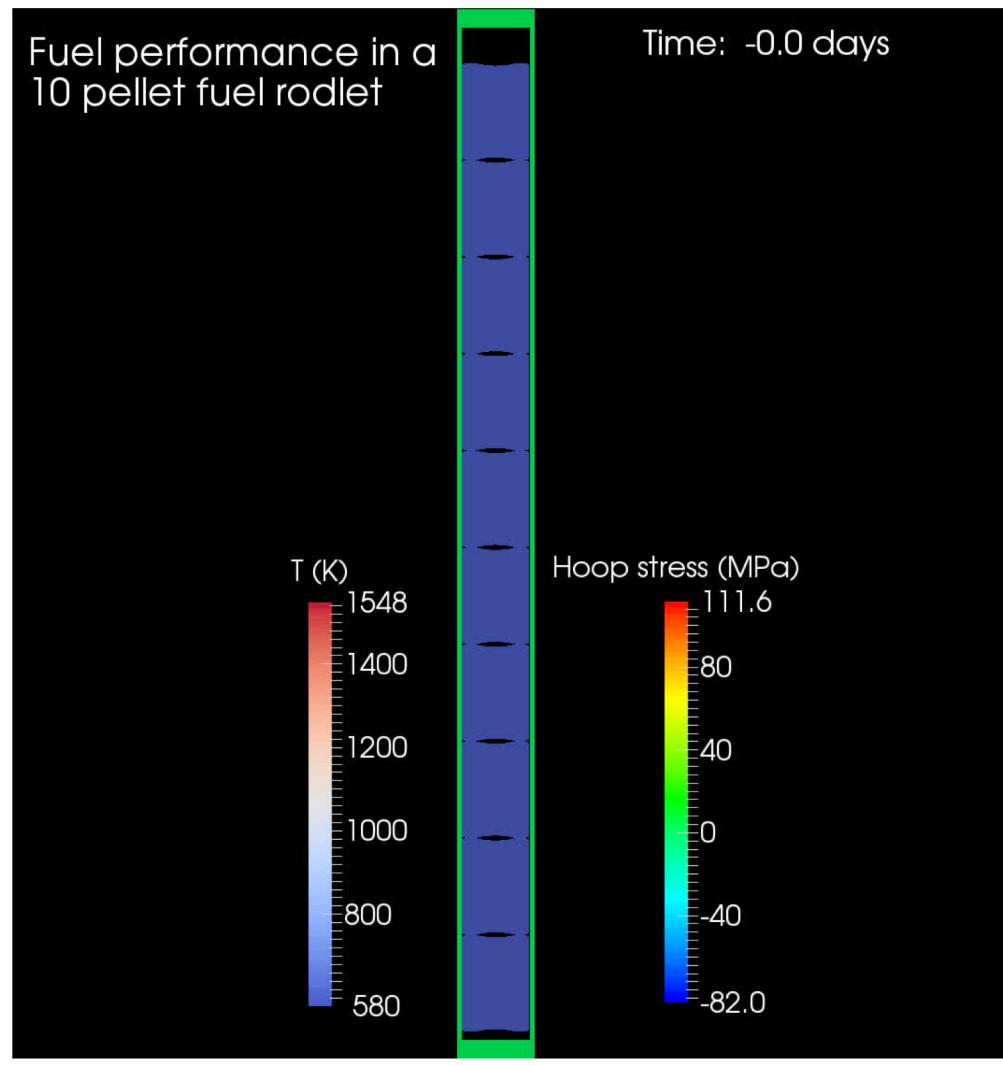
- Wrapped up thermomechanics
- Overviewed US fuel performance codes

MATERIAL PROPERTY EVOLUTION

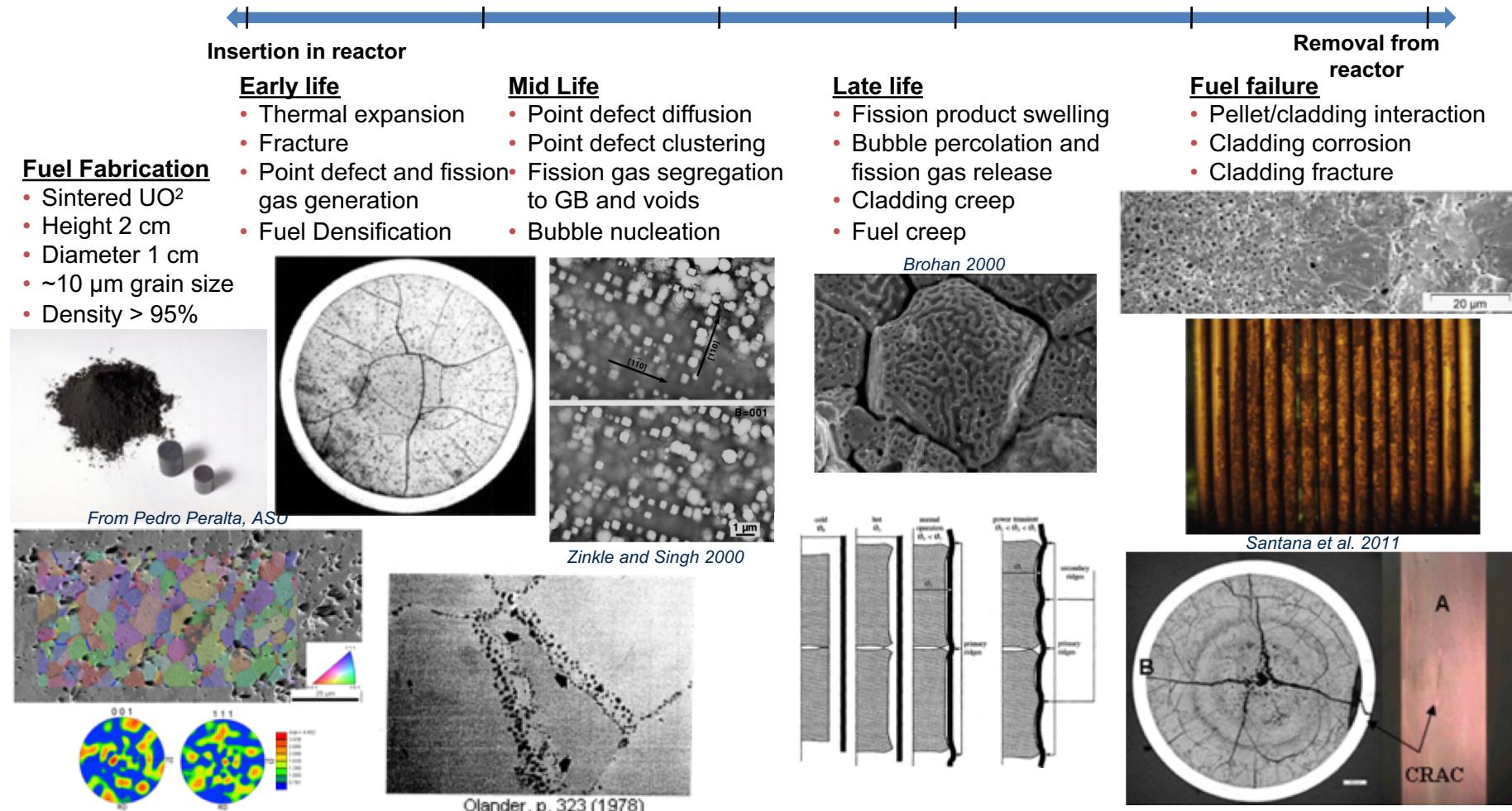
Pretty much everything we have learned so far, nothing changes once the fuel and cladding reach steady state



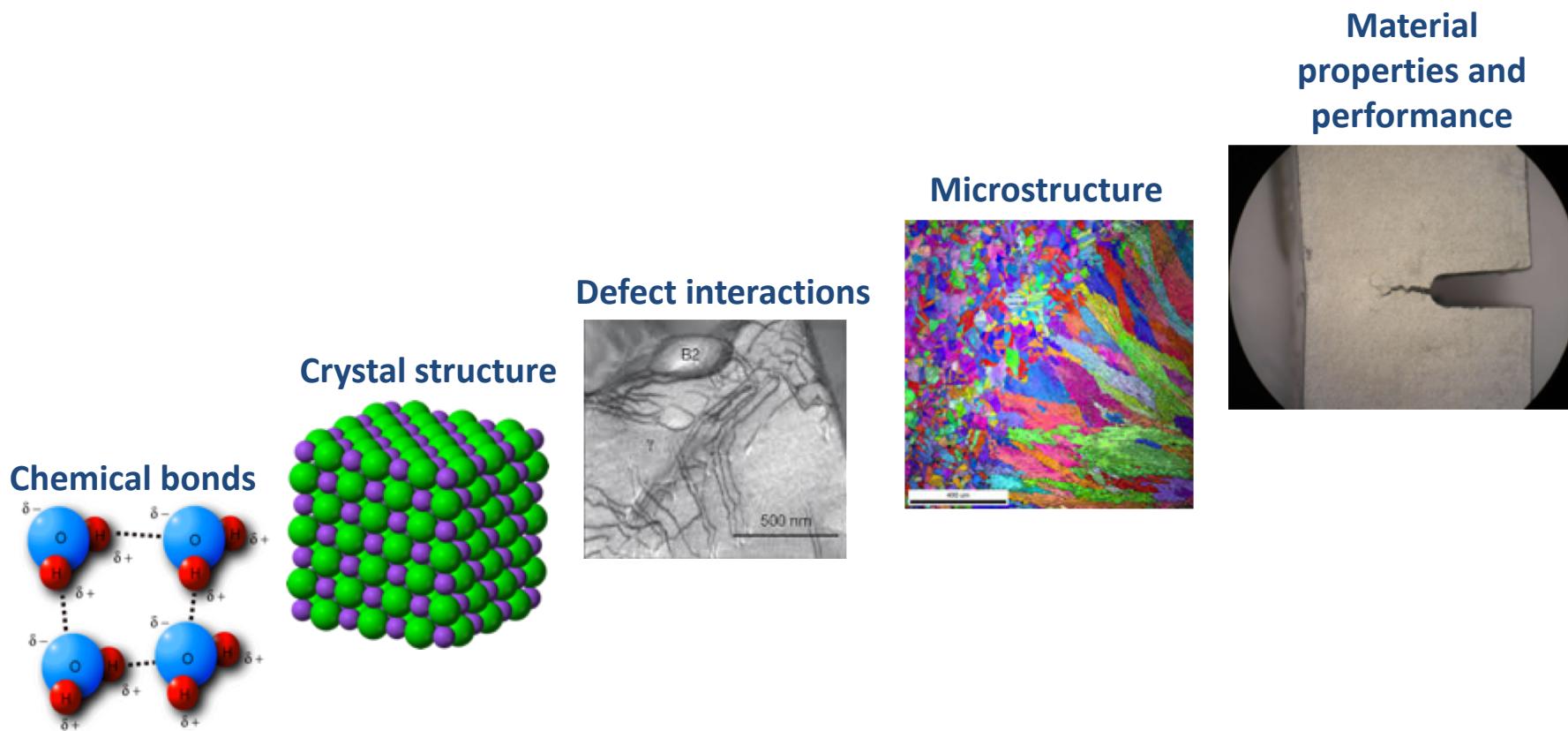
Fuel is dynamic!



Property changes due to microstructure evolution during reactor operation must be considered

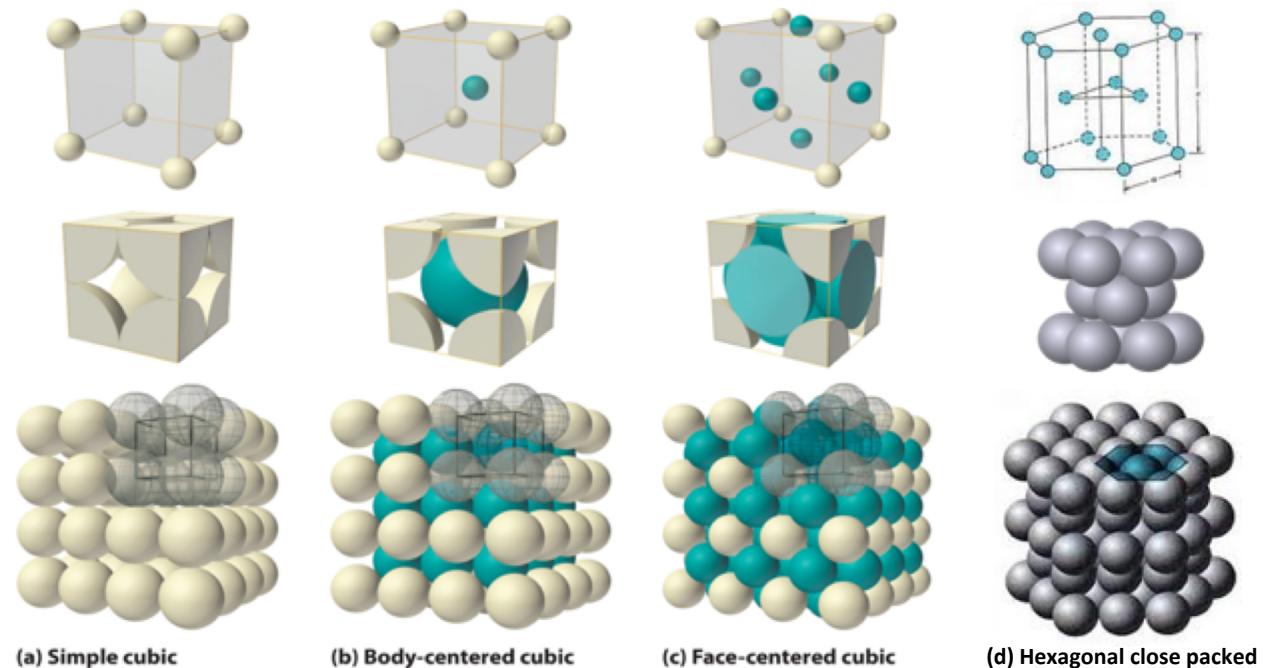


The properties and performance of a material are a result of factors across various length scales



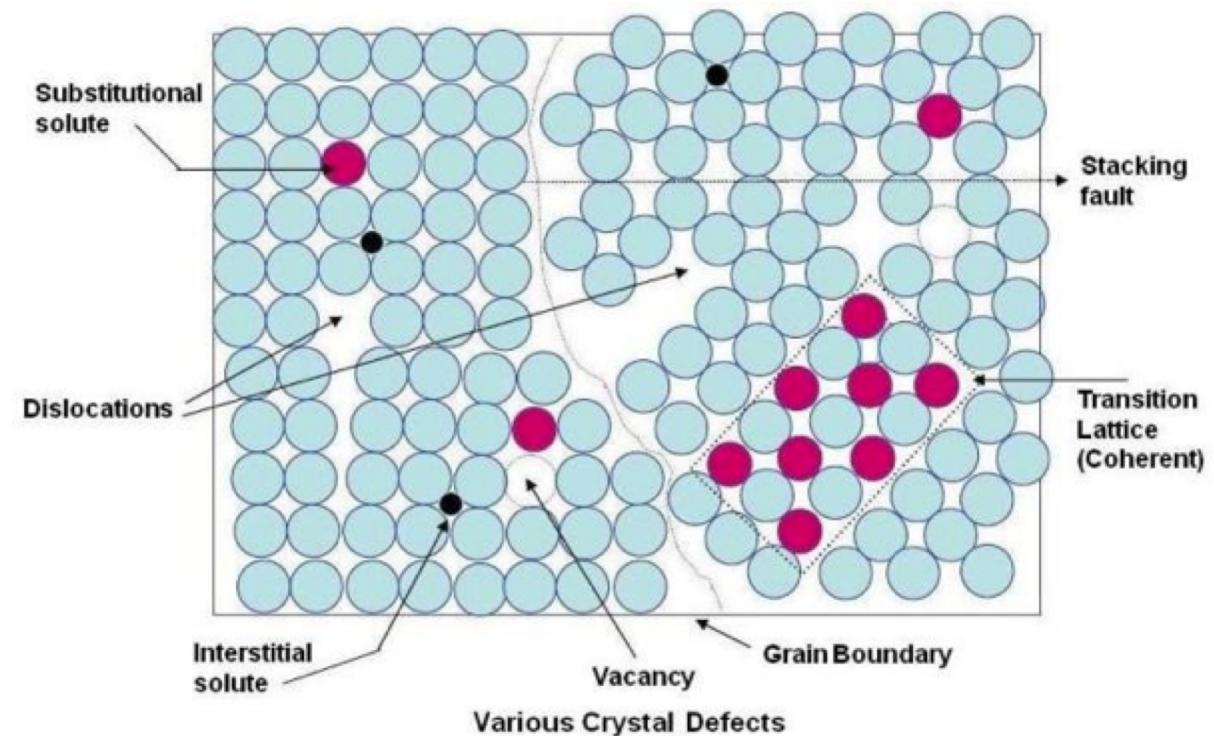
The crystal structure of a material is the shape of the ordered structure of the atoms

- The atoms of many materials form an organized lattice, these are called **crystalline materials**. All reactor materials are crystalline.
- The configuration of the atoms in the lattice impacts the properties of the material (density, thermal expansion coefficient, elastic modulus, etc.)
- All major light water nuclear materials are either cubic or hexagonal



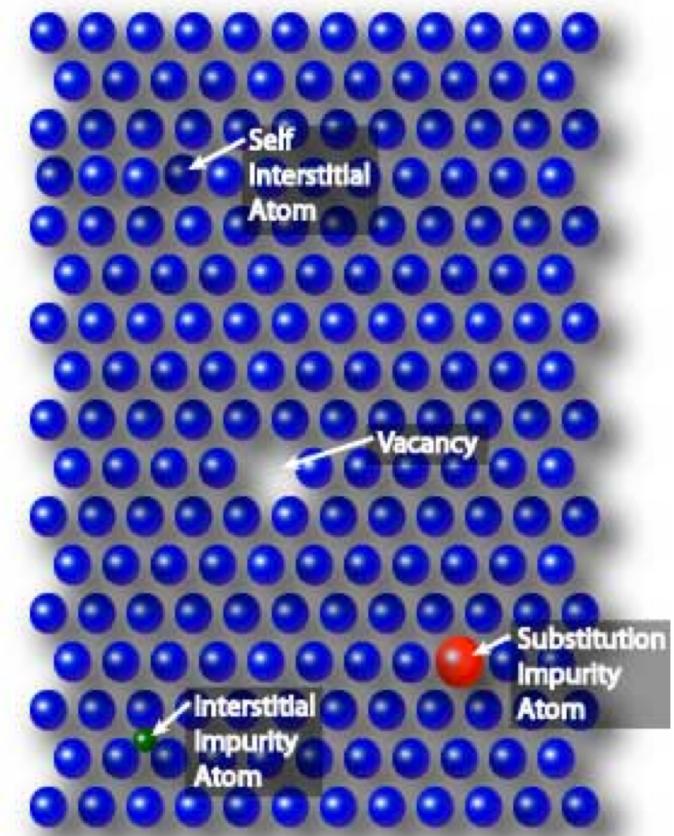
Crystalline materials

- In crystalline materials, the lattices are not perfect, they have defects
- Defects can be 0D, 1D, 2D, 3D
- The interactions between defects seriously impact material properties and how they perform



Point defects

- Point defects (zero-dimensional defects) are lattice imperfections related to one or two lattice sites
- There are several types of point defects
 - **Vacancies**
 - **Self interstitial atoms (SIA)**
 - **Interstitial impurity atoms**
 - **Substitutional impurity atoms**
- Point defects control the mobility of atoms and, therefore influence all processes that depend on diffusion



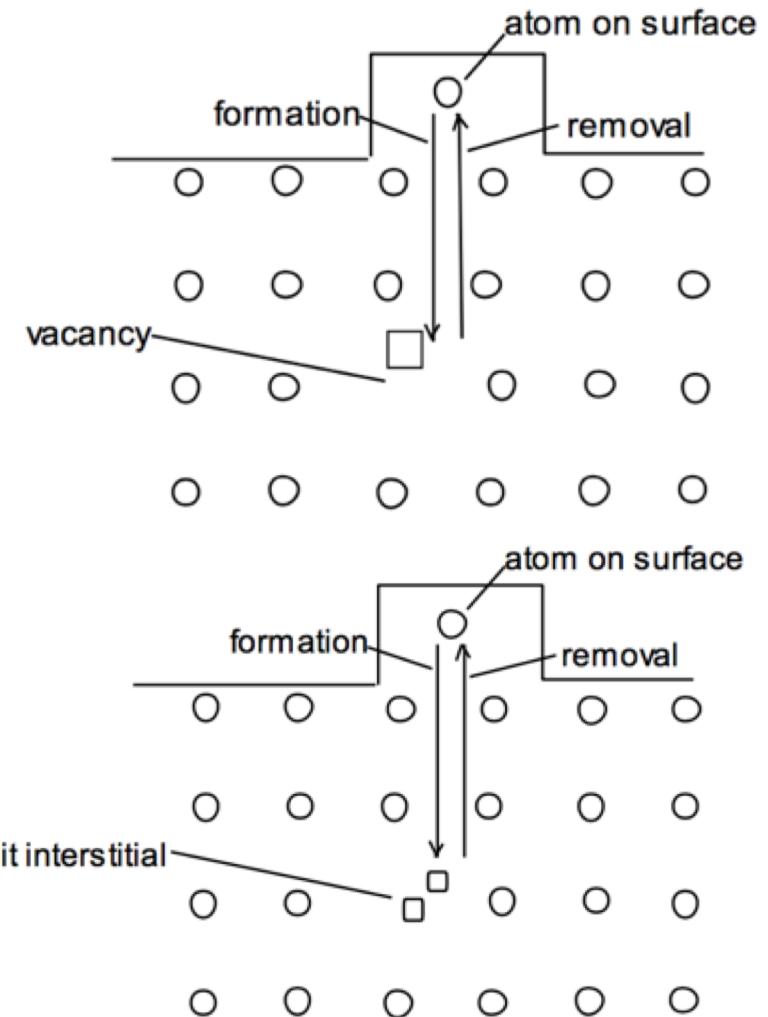
Point defects

- Vacancies and interstitials form naturally in materials
- Extra atoms can sit on a surface, creating a vacancy, or a surface can have a missing atom, creating a self interstitial atom (SIA)
- We define the number of vacancies or interstitials in terms of a concentration

$$C_v = \frac{N_v}{N_s} = \frac{\text{number of empty sites}}{\text{total number of sites}}$$

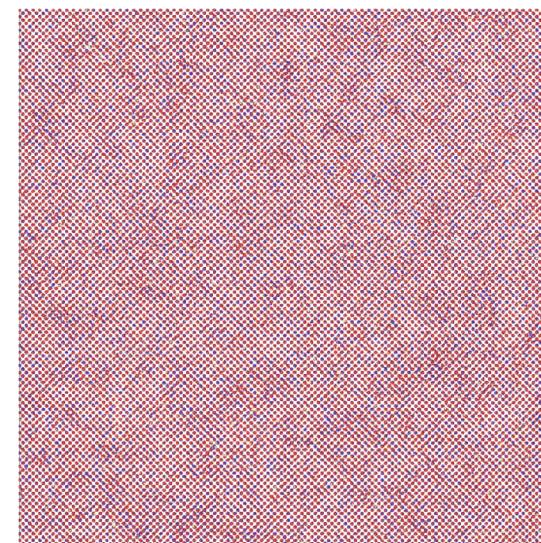
- There exists an equilibrium concentration of point defects

$$C_v = \exp\left(\frac{S_f^v}{k}\right) \exp\left(\frac{-E_f^v}{kT}\right)$$



Radiation damage

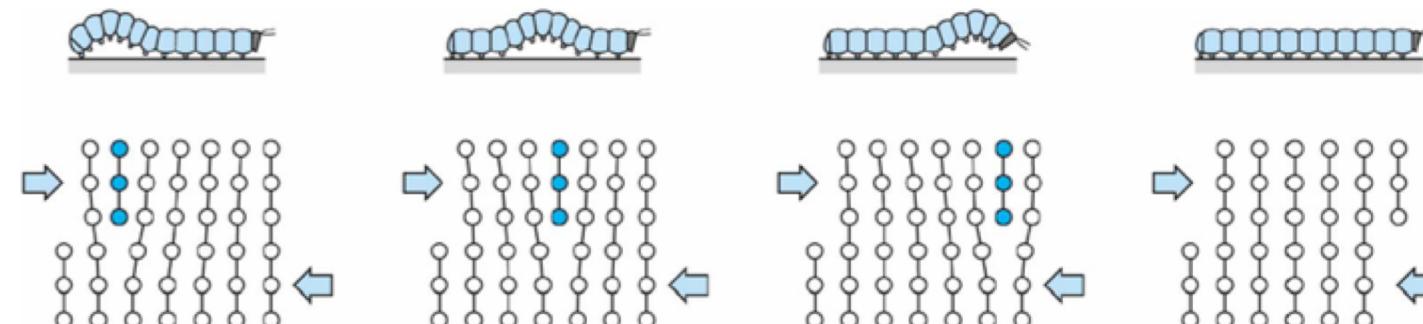
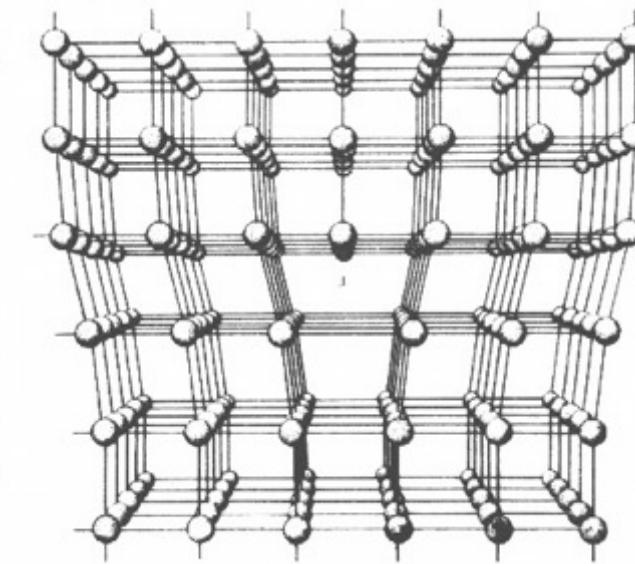
- Ionizing radiation can introduce defects into the crystal lattice, called radiation damage
- PKA collisions create a collision cascade, which results in the generation of defects (point and clusters)



Duration (ps)	Event	Result	Parameters
10^{-6}	Transfer of energy from energetic particle	Creation of PKA	$\Sigma_n(E_n, E)$
10^{-6} to 0.2	Slowing down of PKA, generation of displacement cascade	Recoil atoms Vacancies Subcascades	E_d = energy V_{NRT} = # atoms T = energy transferred
0.2 – 0.3	Thermal spike cool down	Stable interstitials, clusters, atomic mixing	$V(T)$ = # stable defects F = clustering fraction
3 – 10	Cascade cooling to bulk solid temperature	SIA depleted zone in cascade core	Loop collapse probability
> 10	Diffusion of defects and interaction with sinks	Microstructure evolution	Many

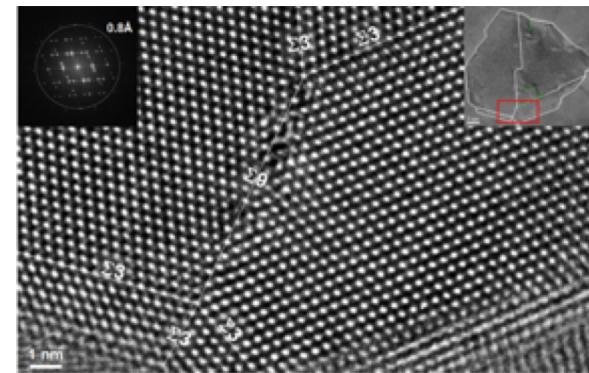
Dislocations are imperfections associated with a line of lattice sites (1D defect)

- In a dislocation, an extra half plane of atoms is inserted into the lattice
- When it moves, only a small number of bonds are broken at a time
- Dislocation motion controls the plastic (permanent) deformation of crystalline materials

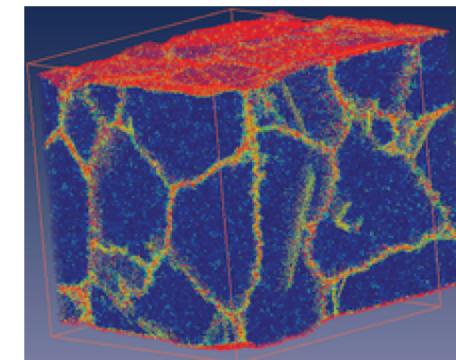


Grain boundaries

- Materials are typically composed of various regions where the crystal lattice is oriented differently. These regions are called **grains**
- When two grains meet, there is a plane of atoms that do not follow the crystal lattice called a **grain boundary**
- Most crystalline materials are polycrystalline, not single crystal

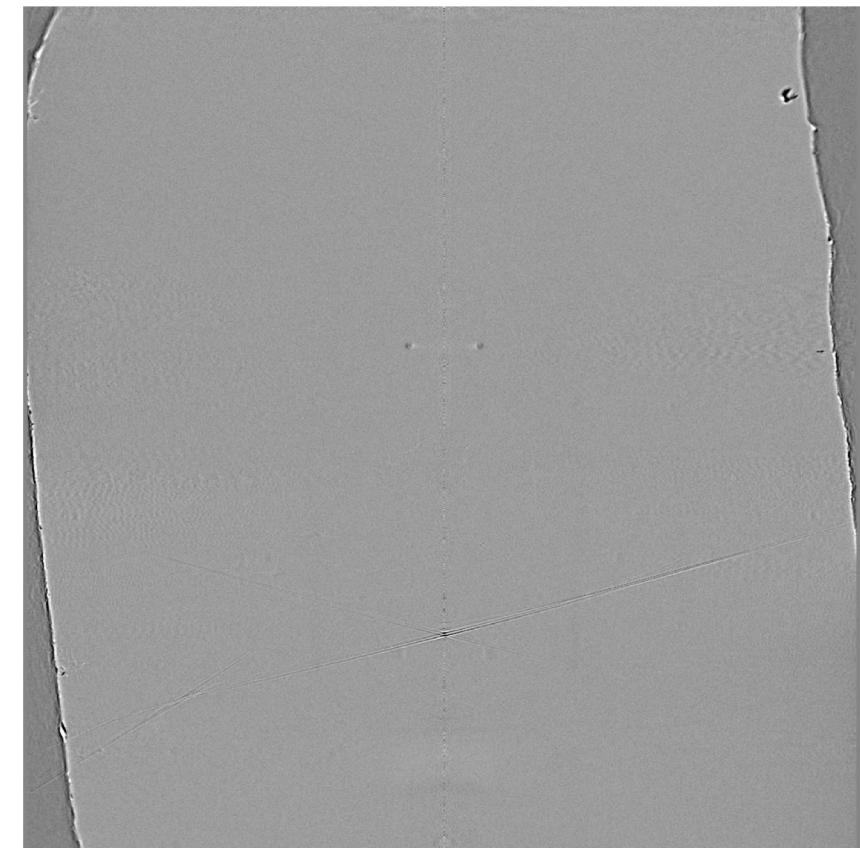


High-res
transmission
electron
microscopy can also
show individual
atoms (palladium)
[www.knmf.kit.edu/T
EM.php](http://www.knmf.kit.edu/TEM.php)



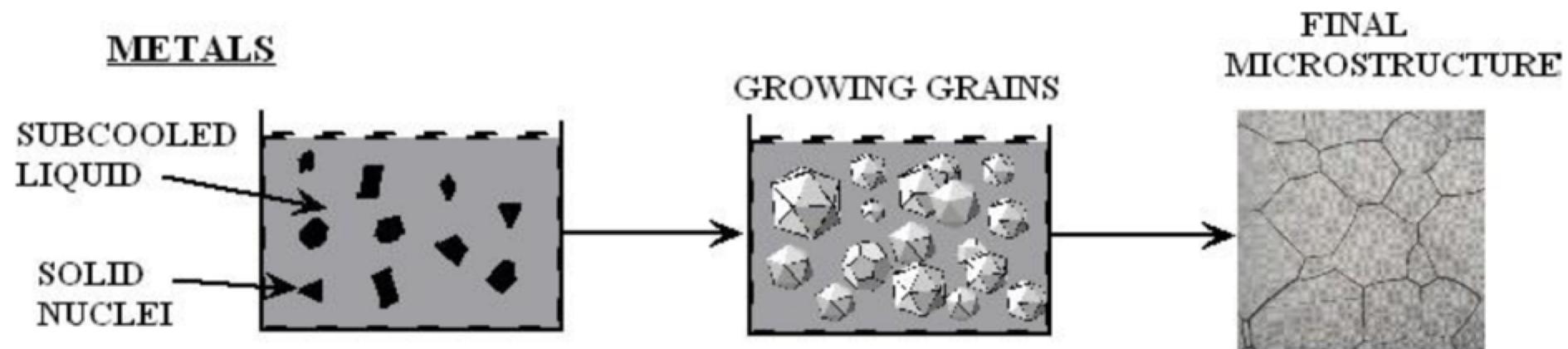
Atomistic simulation of grain boundaries in 3D

Metals are often cast, and polycrystals naturally form during casting



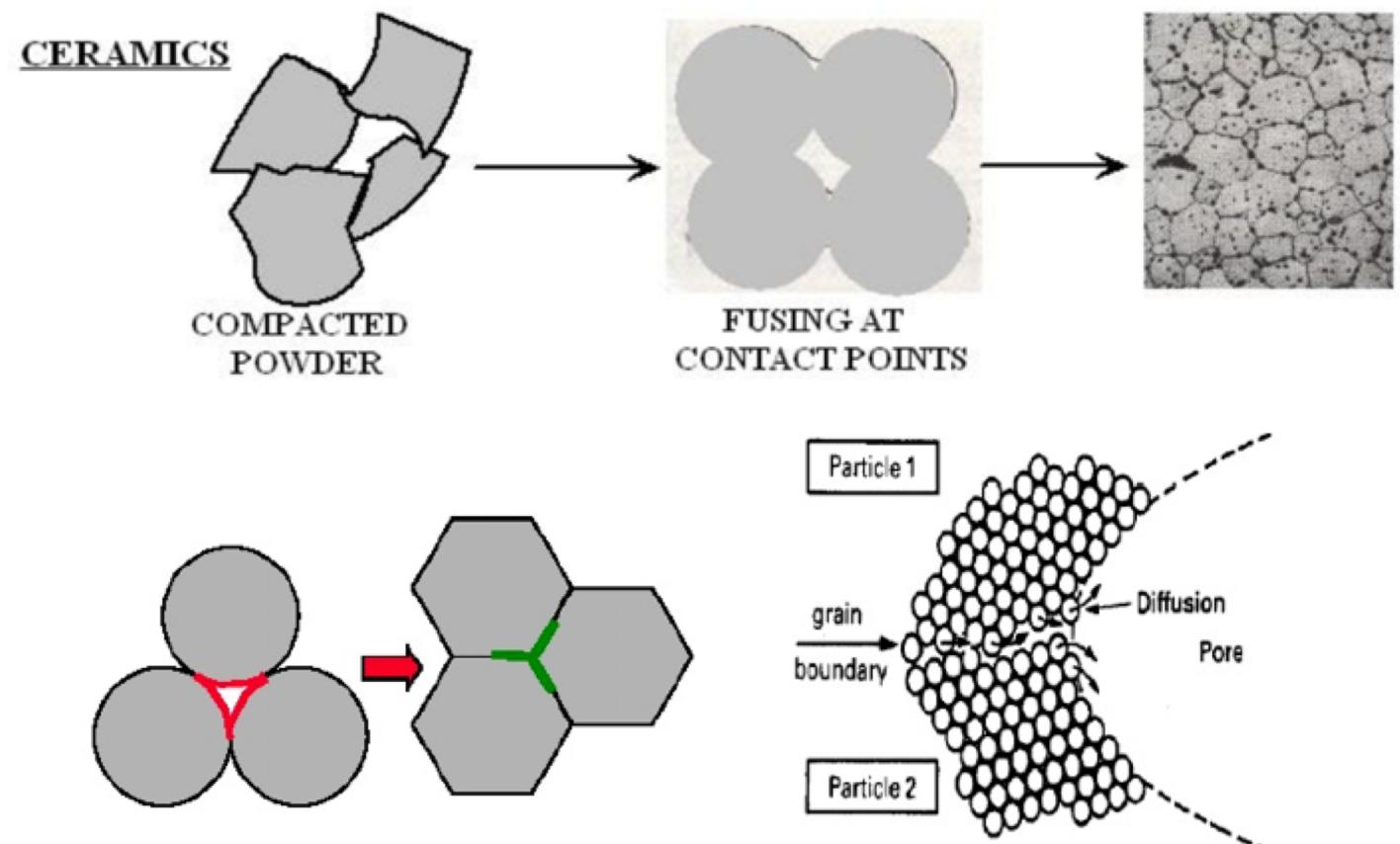
Polycrystals naturally form during casting

- Solidification begins in different regions of the melt, each with a different orientation
- Once the different regions meet, grain boundaries form between them



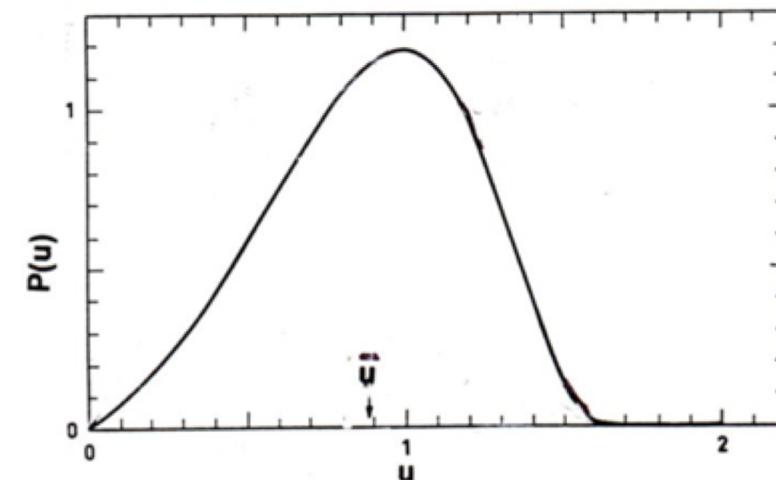
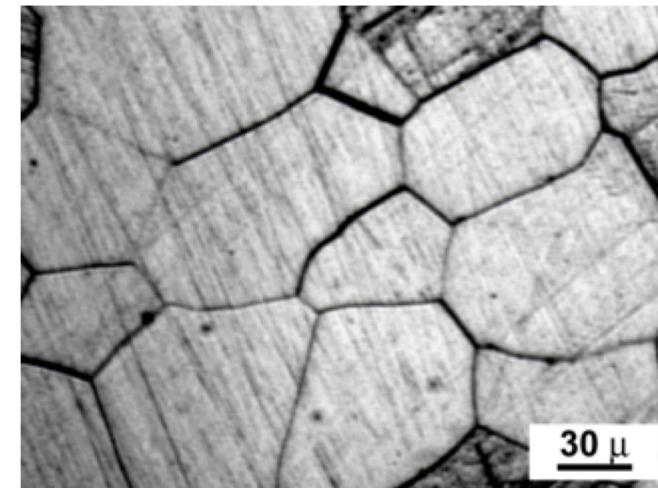
Ceramic sintering

- Ceramics are typically sintered, and polycrystals also naturally form from sintering
- In sintering, powders are compacted at high temperature
- The particles are each oriented differently, and as they fuse, grain boundaries form
- The differences between the grain orientations result in the grain boundary



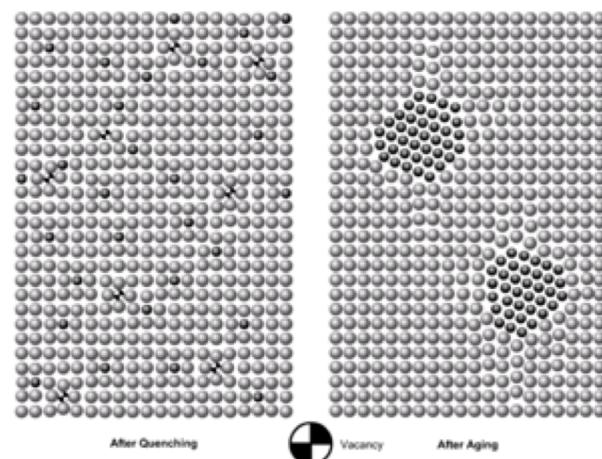
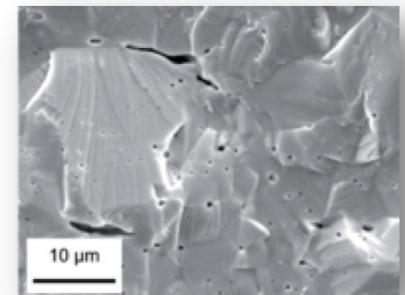
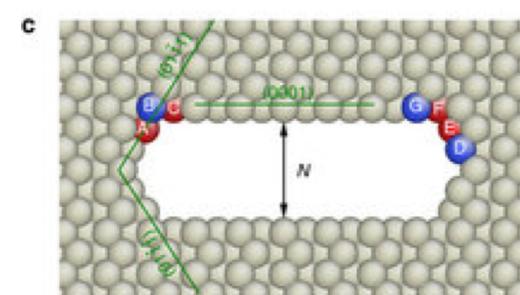
Distribution of grain sizes

- In a polycrystal, there is also a distribution of grain sizes
- Therefore, we commonly refer to the grain size distribution and the **average grain size**
- The Hillert distribution is an analytical distribution for grain size
- Real materials often vary from this behavior



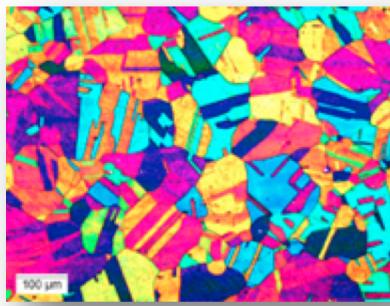
3D Defects

- When point defects cluster, they form three dimensional defects
- The energy of a point defects is reduced when several point defects cluster together
- Larger clusters of vacancies are called **voids**
- Clusters of impurity atoms are called **precipitates**

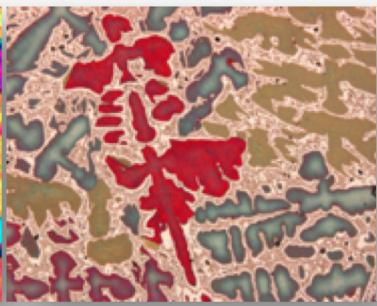


Microstructure

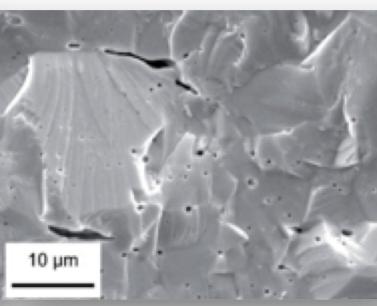
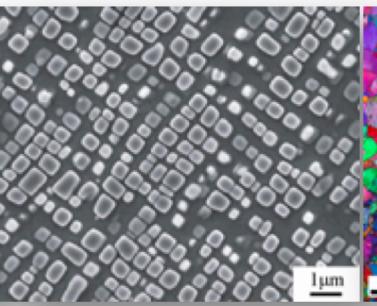
- Material microstructure is the structure observable with 25x magnification
- The microstructure includes grain structure, secondary phases, porosity, and more
- The microstructure can strongly influence physical properties such as strength, toughness, ductility, hardness, corrosion resistance, high/low temperature behavior or wear resistance.
- These properties in turn govern the application of these materials in industrial practice



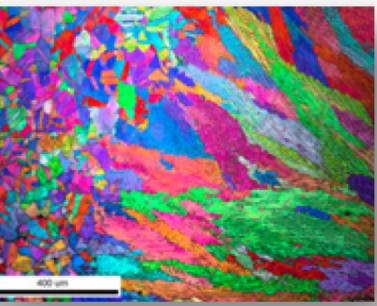
Annealed Stainless Steel



Cast Bronze

Sintered UO₂

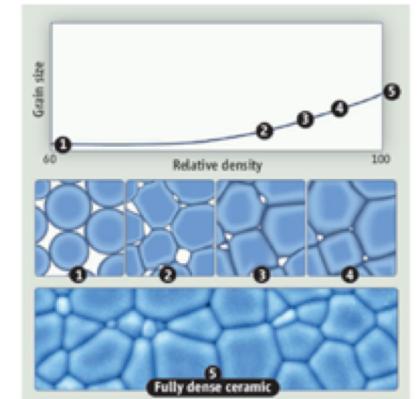
Co-Al-W Superalloy



Friction stir welded stainless steel

Material processing

- The process we use to make a material has a huge impact on its microstructure and properties
- **Casting** – manufacturing process in which a liquid material is poured into a mold and then allowed to solidify
 - Can be used to make complex shapes
 - The solidified microstructure typically has properties that are far from ideal
- **Sintering** – Forming a solid from a powder using heat and/or pressure without melting the material
 - Applicable to metals and ceramics
 - Difficult to obtain a material that is fully dense
 - Used to make fuel pellets
- **Heat treatment** – heating or cooling a material to extreme temperatures to get desired microstructure and properties
 - Used to control the rate of microstructure change, including diffusion, grain growth, or phase change
 - Use on many types of materials (metals, ceramics, glasses)



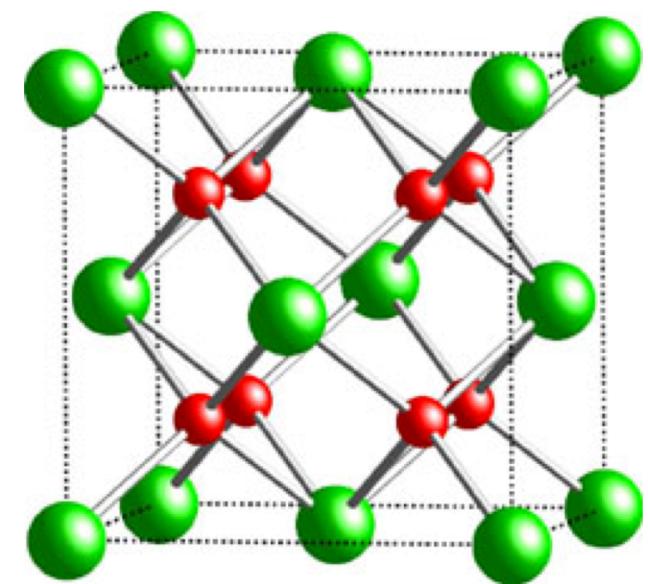
Summary

- Even during steady state operation, fuel and pellet conditions change with time due to microstructure evolution
- Atoms in the fuel and cladding materials are arranged in a crystal lattice
- The crystal lattice is never perfect; it has defects
 - Point defects include vacancies, interstitials, and impurity atoms
 - Dislocations are line defects
 - Grain boundaries are planar defects
 - Voids and precipitates are volume defects
- All materials have defects
- Radiation damage causes many more defects

FUEL CHEMISTRY

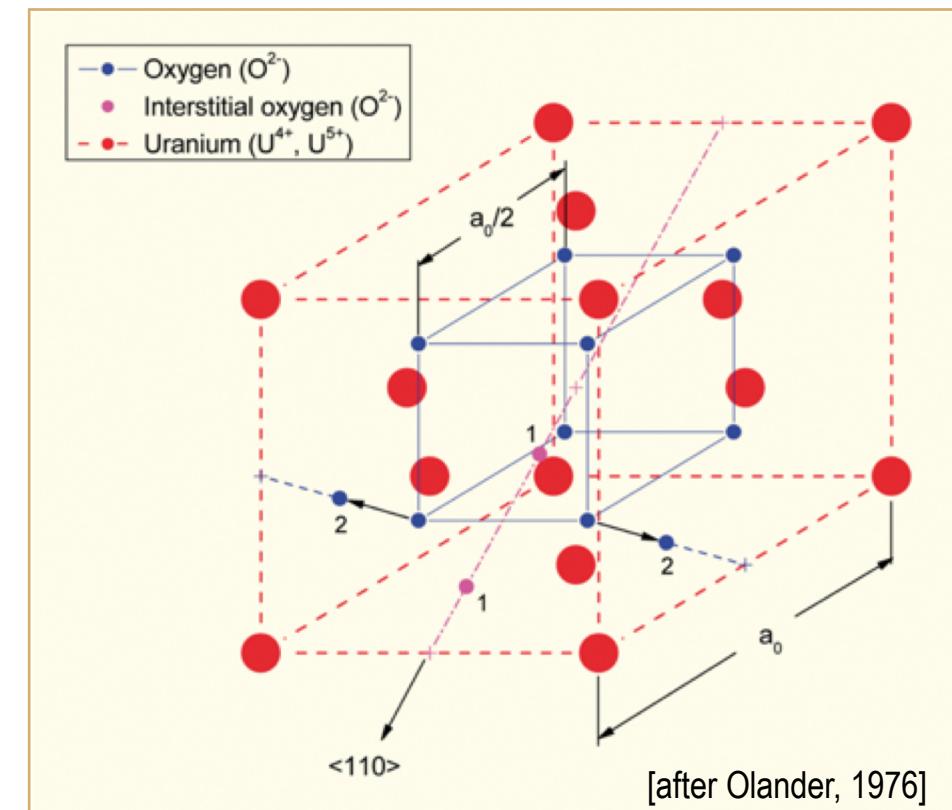
Fuel Chemistry

- UO_2 is an ionic compound that must have balanced charges
- What is the charge of a typical oxygen ion?
 - O^{2-}
- Uranium valence states
 - Possible: U^{3+} , U^{4+} , U^{5+} , U^{6+}
 - Most stable: U^{4+} , U^{5+} , U^{6+}
- The 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



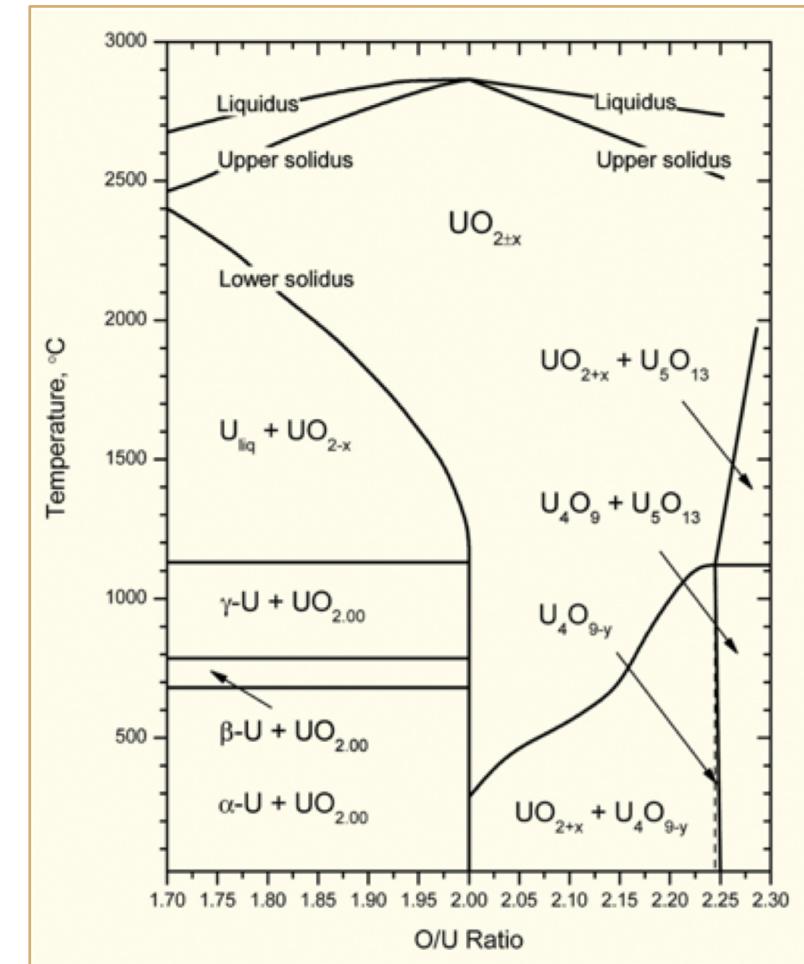
Excess O

- The crystal structure of UO_2 can also accommodate extra oxygen
- Excess oxygen resides at interstitial locations
- Oxygen in neighboring sites is displaced
- Cation valence increases to maintain electrical neutrality



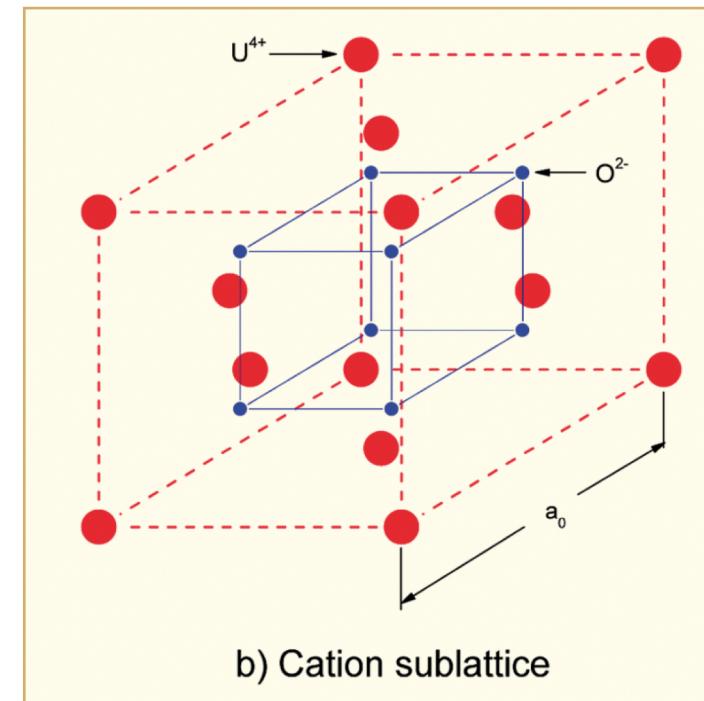
O/M ratio

- The ratio of oxygen to uranium metal (O/M ratio) can vary
- This is the stoichiometry
- 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
- 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



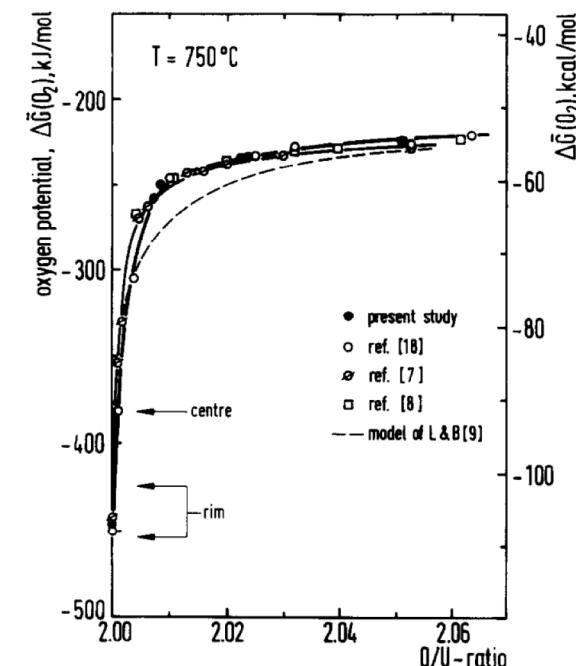
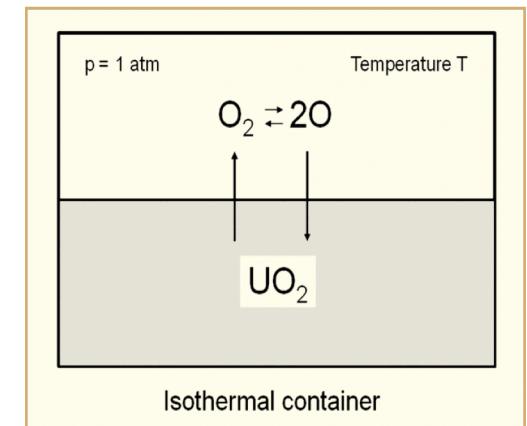
Incorporation of Fission Products

- 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



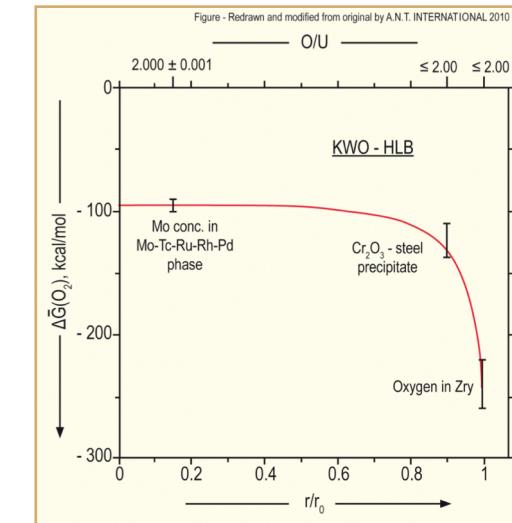
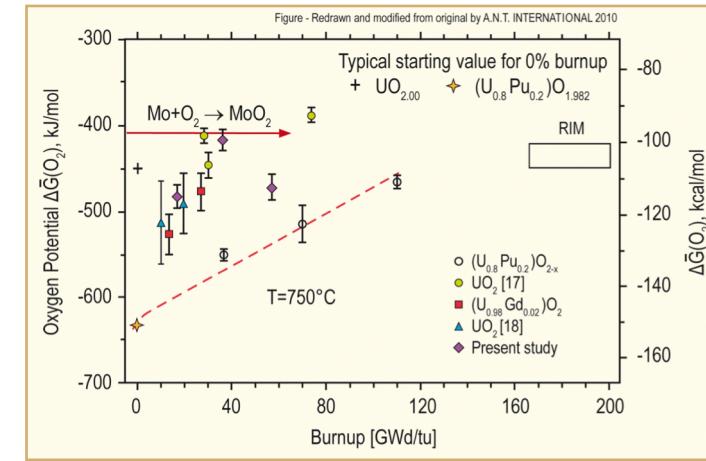
Oxygen potential

- 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



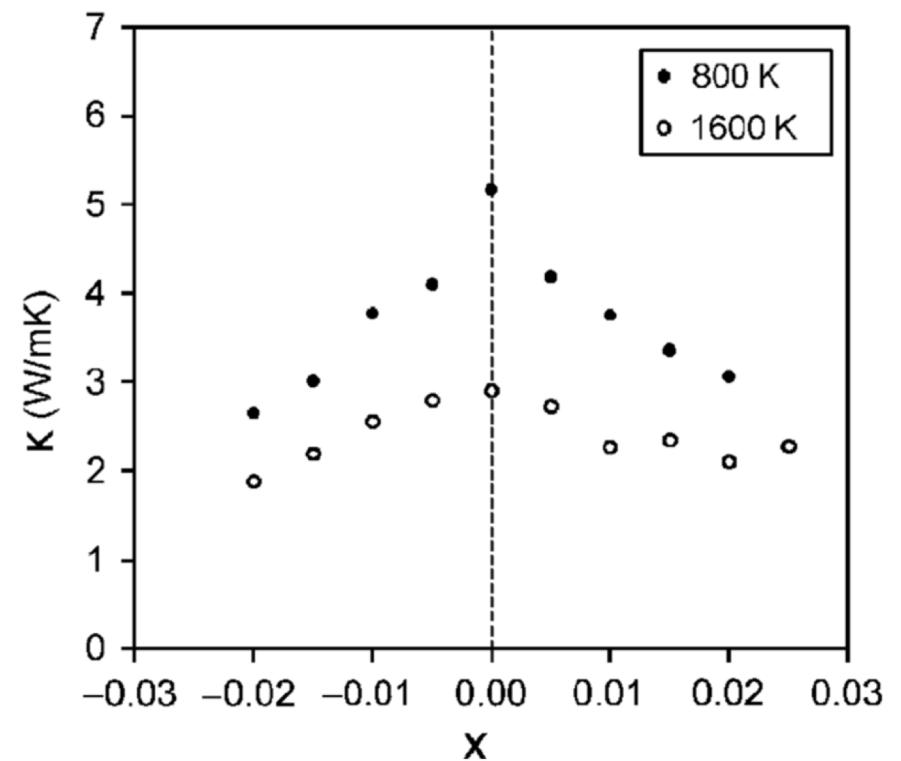
Oxygen potential

- 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



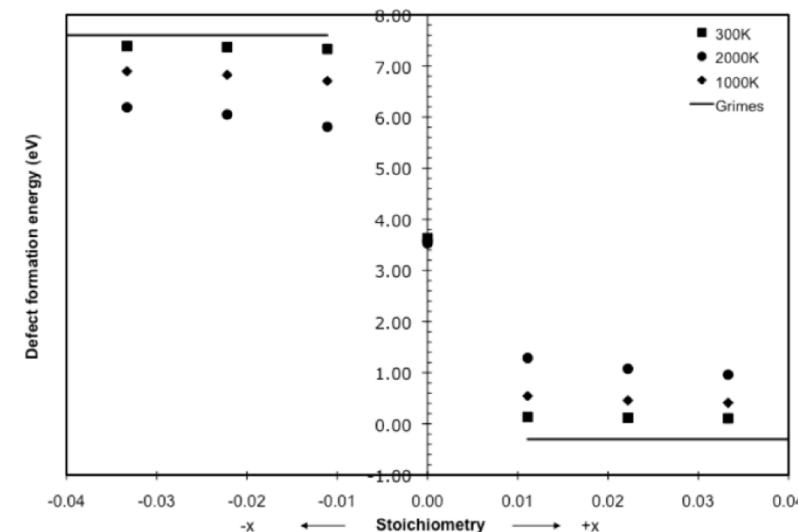
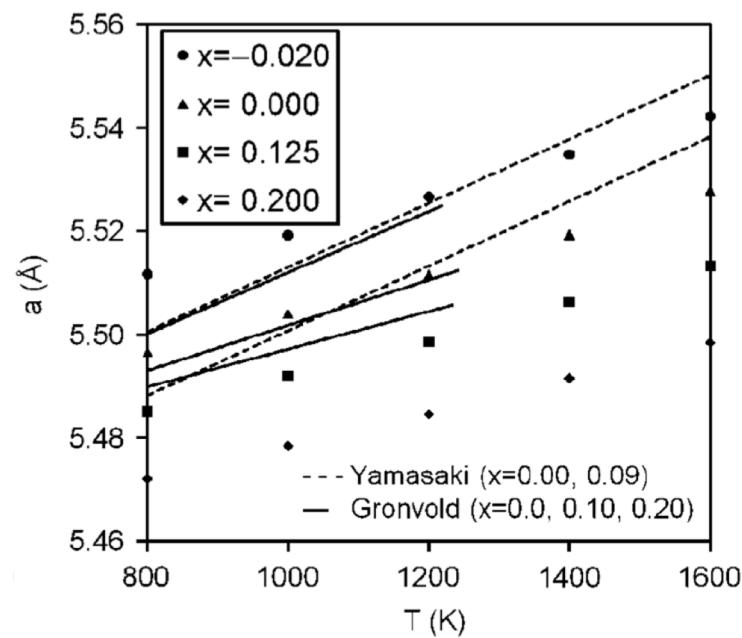
Fuel Stoichiometry/Properties

- 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

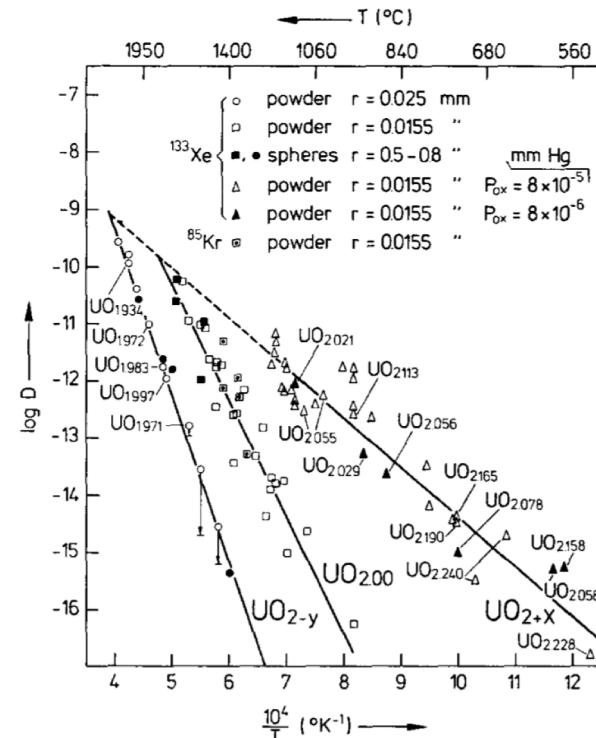
- The lattice constant of the material decreases with increasing stoichiometry
- The vacancy formation energy also changes with stoichiometry



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