NE 795-014: Advanced Reactor Materials
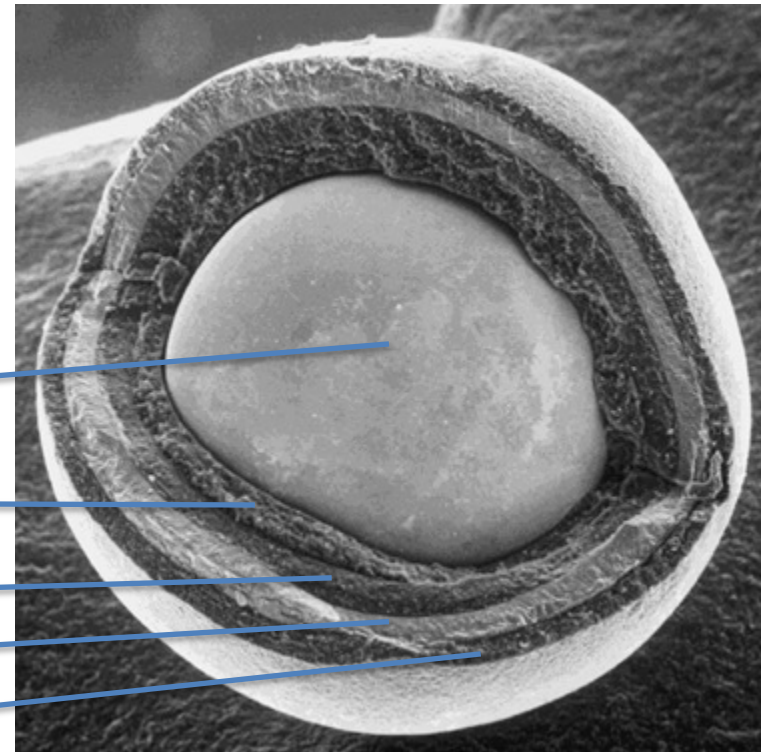
Fall 2023

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Last Time

- Intro to course
- Background and history of HTGRs/TRISO particles
- Difference from LWRs
  - helium cooled; much higher temperatures; thermal/fast options; extensive utilization of graphite; flexibility of fuel
- Pebble bed vs Prismatic Reactors

TRISO Particles

- TRISO: TRistructural ISOtropic particle fuel
- Layered fuel in mm-sized particles
- Layers:
  – Fuel Kernel
  – Buffer
  – Inner Pyrolitic Carbon (IPyC)
  – SiC
 – Outer Pyrolitic Carbon (OPyC)

Fuel Kernel + Buffer

- A variety of fissile and fertile kernels have been used in particles, including ThC2, ThO2, PuO2, (Th,U)O2, UC2, UO2, and UCO
- Nominal fuel kernel diameters range between 100 and 500 microns
- The fuel kernel is surrounded by a porous graphite buffer layer that absorbs fission recoils and allows space for swelling and fission gases produced during irradiation
- The buffer layer is generally about 100-micron thick
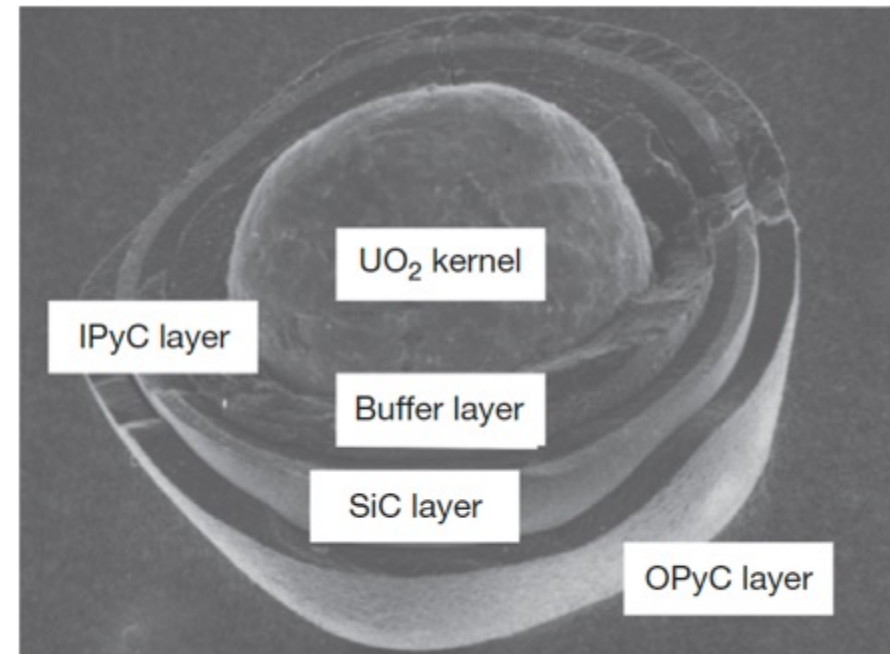
IPyC-SiC-OPyC

- Surrounding this inner buffer layer is a layer of dense pyrolytic carbon (IPyC), a silicon carbide (SiC) layer, and a dense outer pyrolytic carbon (OPyC) layer
- The pyrolytic carbon layers protect the SiC layer, which is the pressure boundary
- The pyrolytic carbon layers are approximately 40-micron thick; the SiC layer is usually about 35-micron thick
- Each microsphere acts as a mini pressure vessel, which is designed to impart robustness to the gas reactor fuel system
- TRISO diameter is typically ~750 microns
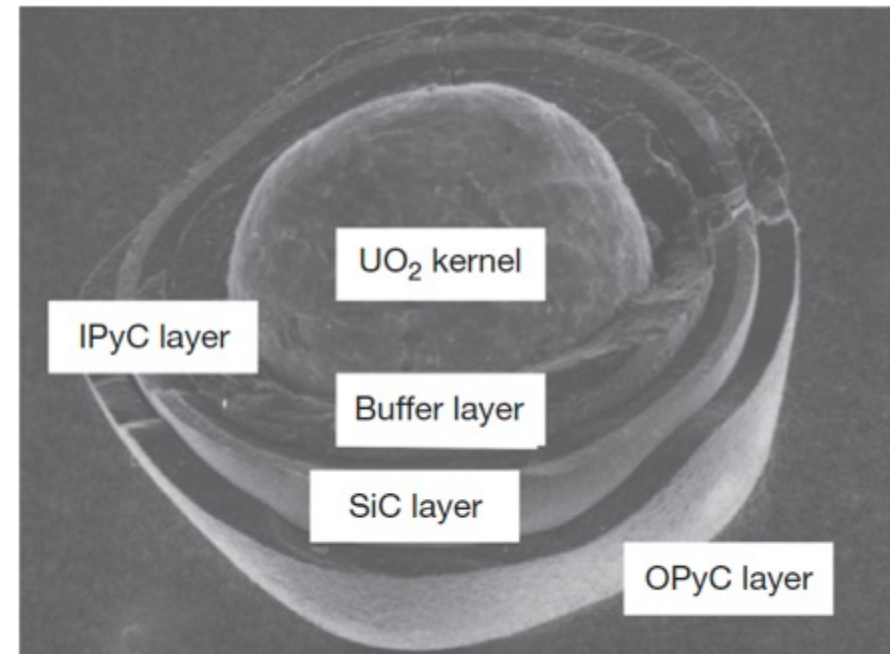
Early Concepts

- The concept of nuclear fuel microspheres with refractory coatings to contain fission products during operation in HTGRs can be traced to the Dragon Project in the 1950s

- The earliest versions involved fuel kernels coated with only a single pyrolytic carbon layer intended to protect the kernel during fabrication, this rapidly evolved in the following decade into more complex and more effective particle designs

- It was recognized almost from the beginning that the coating layers could provide some degree of advantageous fission product retention when properly designed
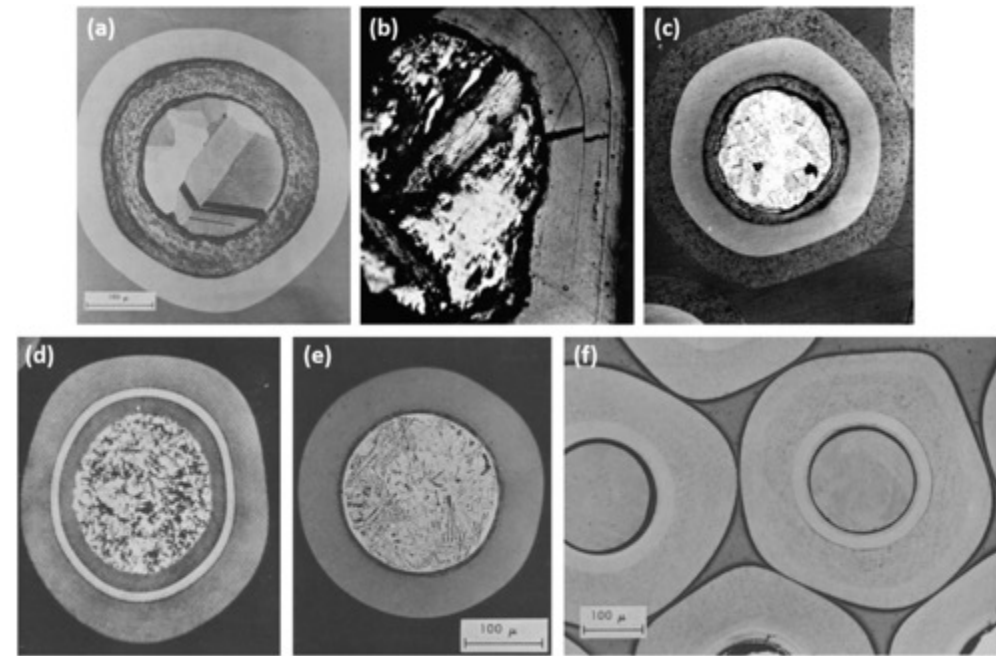
(a) BISO particle, (b) Particles with "laminated" pyrocarbon layer structure, (c) Particle with "Triplex" structure, (d) Fertile (Th,U)C2 with of PyC-SiC-PyC structure, (e) Carbide particle with single PyC coating, (f) "Duplex" (Th,U)C2 particle

Early Failure

- Fracturing of the pyrocarbon layer in these particles during irradiation was found to be a concern

- Causes included kernel swelling, radiation-induced pyrocarbon dimensional change, damage from fission recoils, fission gas pressure, and chemical reaction of fission products with the coating

- A design modification was the introduction of a sacrificial layer of pyrocarbon between the kernel and the dense, outer pyrocarbon layer

- This two-layered particle design was termed "BISO" for Buffer-isotropic
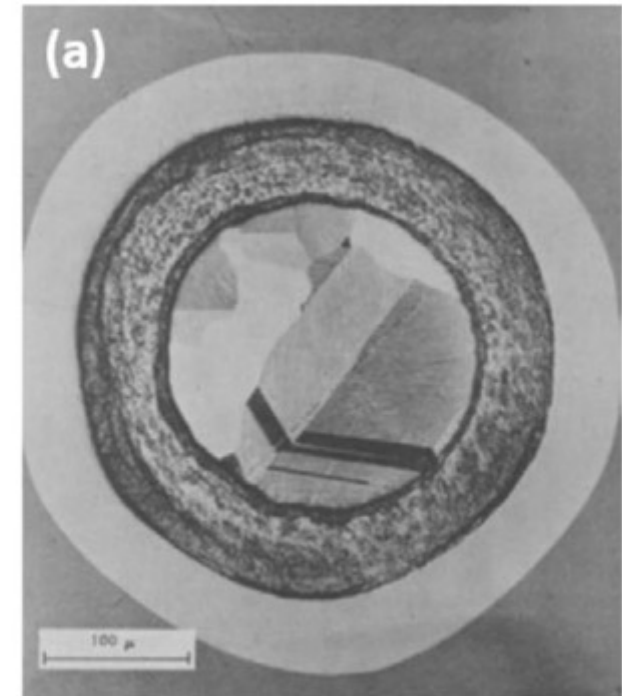
Transition to TRISO

- The notion that refractory ceramics could provide significantly improved particle strength and retention of fission products compared to pyrocarbon alone was suggested near the very beginning of coated particle development

- This led to the addition of a silicon carbide layer placed between two layers of dense pyrocarbon

- This SiC layer, along with the porous buffer layer of BISO particles, formed the basis for the modern TRISO coating design
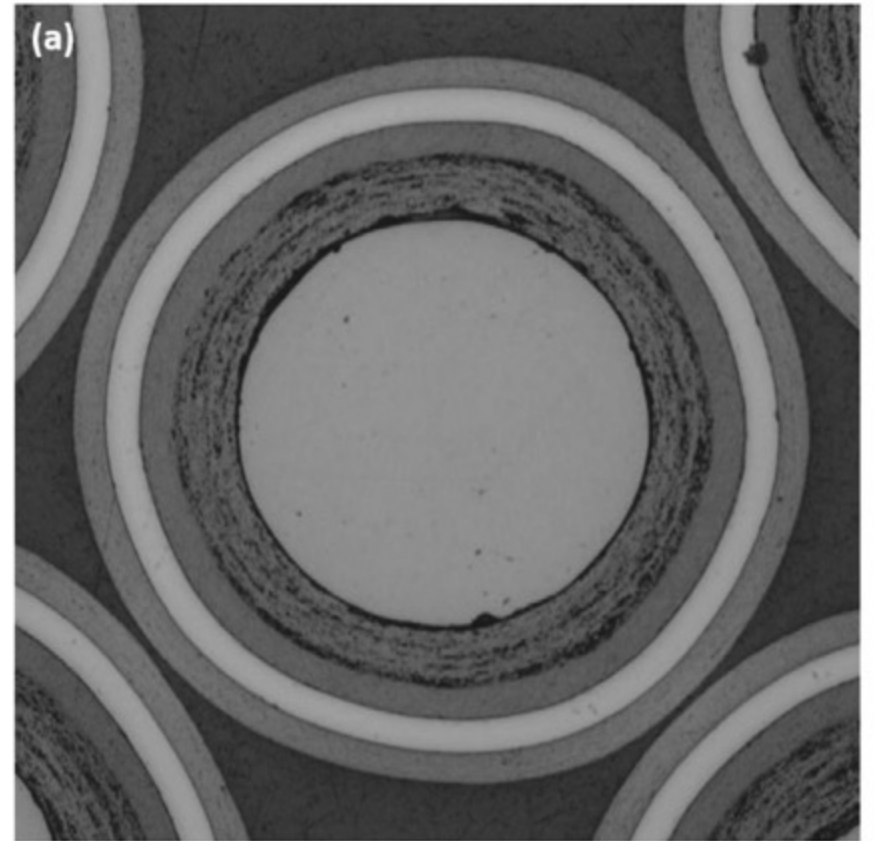
FUEL KERNEL

Fuel Kernel

- Coated particle fuel allows flexibility in kernel material
- The porous buffer layer mechanically decouples the kernel from the outer coating, accommodating some degree of kernel swelling
- Choice of kernel material is influenced by fabrication concerns, kernel behavior under irradiation, and reactor design
- Early designs primarily included fertile carbide fuels (ThC)

- Carbide kernels have excellent high-temperature compatibility with the surrounding graphite fuel elements
- However, oxide kernels simplify the overall fabrication process (don't have to worry about oxidation) and maintain better chemical stability during the high temperature heat treatment of fuel pebbles during manufacture

Fuel Chemistry

- An important consequence of UO_2 fission is the creation of free oxygen since only a part of the O_2 recombines with the fission products
- In the TRISO particle, a portion of this free oxygen combines with carbon from the buffer/PyC coatings to form CO and CO_2 gases
- Identification of those compounds (solid and gaseous) that can form in fuel during normal and off-normal conditions and which elements remain in elemental form, is known as fuel chemistry

- Changes in fuel chemistry may lead to many important mechanisms affecting fuel performance, e.g., kernel size (swelling), kernel migration (amoeba effect), stresses in the coatings (particle pressurization due to fission products and carbon oxide gases), thermal conductivity, creep properties modification, etc.
- The oxygen potential, the pressure of oxygen in the gas phase within the fuel, is the critical parameter determining which elements in their competition for oxygen form oxides
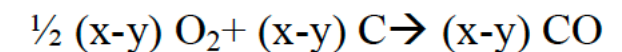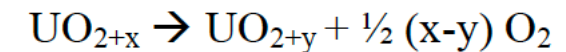
Oxygen Potential

- Calculation of the oxygen potential is complex since it generally varies with distance from the particle center and with temperature, fuel burnup, fission product yields, chemical state of fission products including solid and gas phases, and the effectiveness of the coating layers to absorb fission products and oxygen

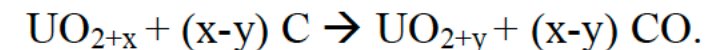- The oxygen potential is represented by:

$$\mu(O_2) = RT \, Log \, P(O_2)$$

- where P(O2) is the oxygen partial pressure, R is the gas constant, T is the temperature

- In fresh fuel (simpler case), where we assume the fuel reaches thermodynamic equilibrium with its surrounding coatings, the main product of the reaction between UO2+x (x>0) and carbon is gaseous carbon monoxide, CO, by the following reactions:

$$UO_{2+x} \rightarrow UO_{2+y} + \tfrac{1}{2}(x-y)\,O_2$$

$$\tfrac{1}{2}(x-y)\,O_2 + (x-y)\,C \rightarrow (x-y)\,CO$$

- which can be rearranged as:

$$UO_{2+x} + (x-y)\,C \rightarrow UO_{2+y} + (x-y)\,CO.$$

- Utilizing an equilibrium rate constant K,

$$Log \, P(CO) = Log \, K_p + \tfrac{1}{2} Log \, P(O_2)$$

Oxygen Potential

- Reactions to generate CO2 are also possible, but at applicable temperatures and values of the oxygen potential, CO production dominates

- As the oxygen potential, i.e., oxygen partial pressure, is increased we are generating more CO

- The result of CO formation is internal pressurization of the particle which may lead, in extreme conditions, to particle failure

- To limit this pressurization other fuel kernel concepts have been and are being studied, of particular interest is the oxycarbide fuel (or UCO) comprising a mixture of UC2 and UO2

- Gas formation is effectively reduced within the UCO particle as compared to a UO2 particle due primarily to their lower oxygen inventory

- Additionally, there is a gettering effect of the UC2 on the oxygen released during UO2 fission which forms a condensed oxide rather than CO gas

CO Pressurization

- The result of CO formation is internal pressurizing of the particle that increases with burnup and adds to the pressurization from fission gases

- At lower burnup (≤ 6 % FIMA), pressurization of the particle arises principally from fission-gas release from the fuel kernel

- At higher burnup (9% FIMA, at 1450 K), the pressure resulting from fission gases can represent half of the contribution of CO in an HTGR TRISO coated particle

- The suppression of excessive CO formation during oxidation of a UO2 based particle remains an important design objective at moderate and high burnup

- The failure of the SiC layer may happen because of over-pressurization due to CO formation

- CO pressures are suspected of being partly responsible for the mechanical weakening of the IPyC coating, and corrosion of the SiC layer by CO can occur as a result from failure of the IPyC coating

Uranium Oxycarbide (UCO)

- Work in the US retained the carbide kernel design, because the HTGR designs of required high peak fuel temperatures and high power densities that would result in excessive kernel migration

- UC fuel, no worries about CO production

- However, it was found that rare earth fission product elements migrating from carbide kernels during irradiation could chemically attack the SiC layer of TRISO particles and compromise the structural integrity

(d) 60 μm
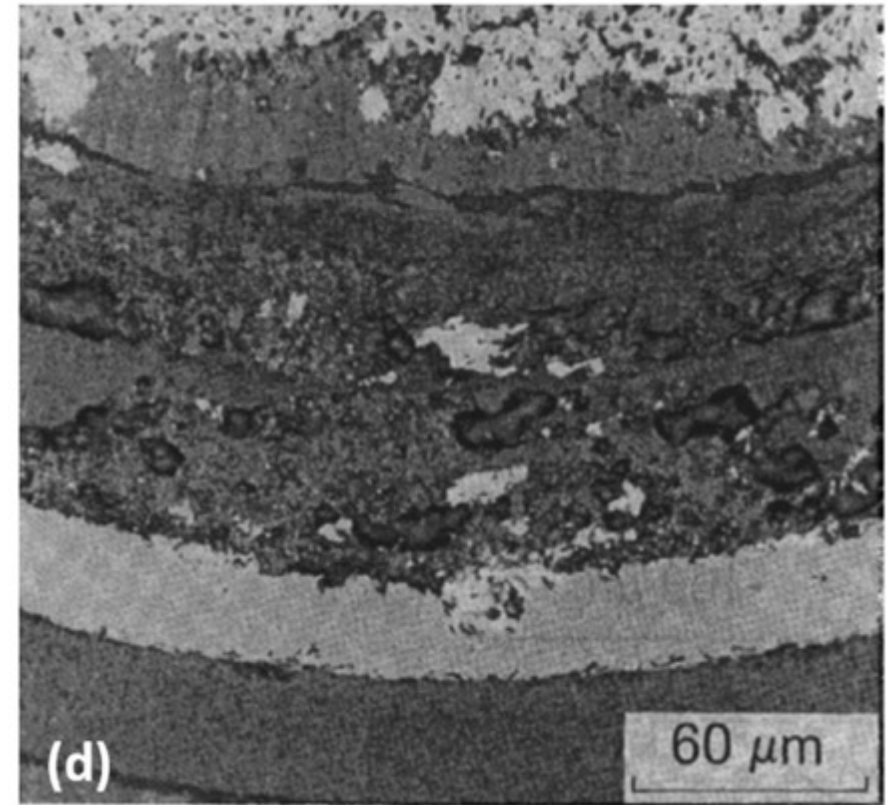
UCO

- We have two fuel kernel problems:
  – CO production (UO2)
  – fission product release (UC)
- This led to the suggestion of a kernel comprised of a mixture of both oxide and carbide phases
- Thus, a design was made to include sufficient UC2 to getter the excess oxygen produced by UO2 fission

- UCO avoids the formation of CO, while still taking advantage of the retention of the metal oxide fission products in the predominantly UO2 kernel
- The success of UCO kernels by the US program led to the adoption of UCO fuel as the reference fissile particle design by the early 1980s, with an approximate UO2/UC2 mixture of 80/20
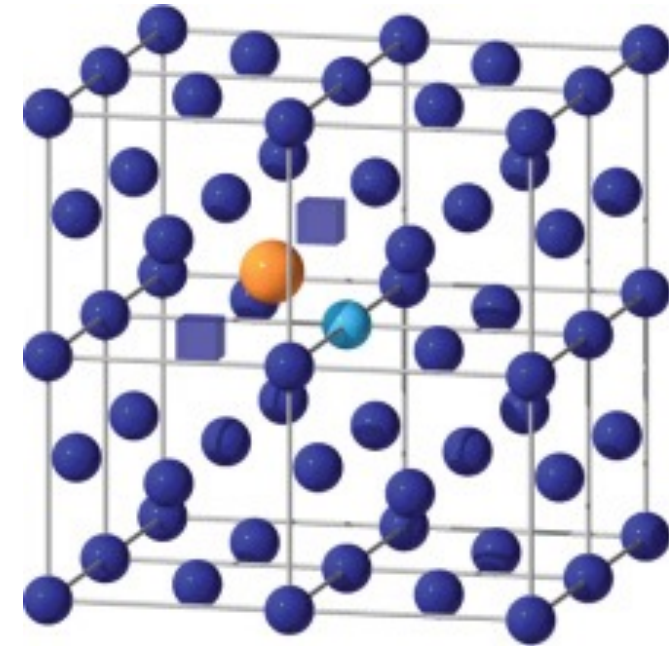
Fission Products

- The rate of change of each nuclide is a function of three processes:
    - depletion of heavy nuclei by fission and corresponding production of lighter nuclei (fission products)
    - production by radioactive decay (actinides and fission products) and/or by neutron capture (actinides)
    - loss by radioactive decay (actinides and fission products) and/or by neutron capture (actinides)
- Element inventory for a UO2 kernel @ 5.5% FIMA on the right

| Element	Amount (10^{-8} moles)	Element	Amount (10^{-8} moles)
UO_2	411	Zr	6.49
C	755	Ru	3.63
Kr	0.74	Ba	1.57
Xe	5.32	La	1.46
Sr	1.78	Ag	0.13
Se	0.12	Br	0.04
Rb	0.70	Y	0.91
Mo	5.74	Tc	1.47
Rh	1.03	Pd	1.08
Cd	0.06	Sn	0.06
Sb	0.03	Te	0.57
I	0.29	Cs	4.79
Ce	2.75	Pr	1.35
Nd	4.62	Sm	0.52
Eu	0.07	Gd	0.02

Fission Products

- Fission products in UO2 are primarily located as substitutional atoms, commonly paired with additional vacancies
- A large number of fission products are highly insoluble in UO2, including Xe, I, and Br
- Some solubility exists for transition metals such as Zr and alkaline metals such as Sr, and high solubility exists for some rare earth elements, such as Ce
- Fission products in the fuel lattice can diffuse out of the UO2 to grain boundaries
- The diffusion mechanism depends on the nature of the fission product trap sites and on the fission product intrinsic characteristics
- Irradiation effects can greatly enhance or reduce this diffusion by trapping mechanisms on extended defects
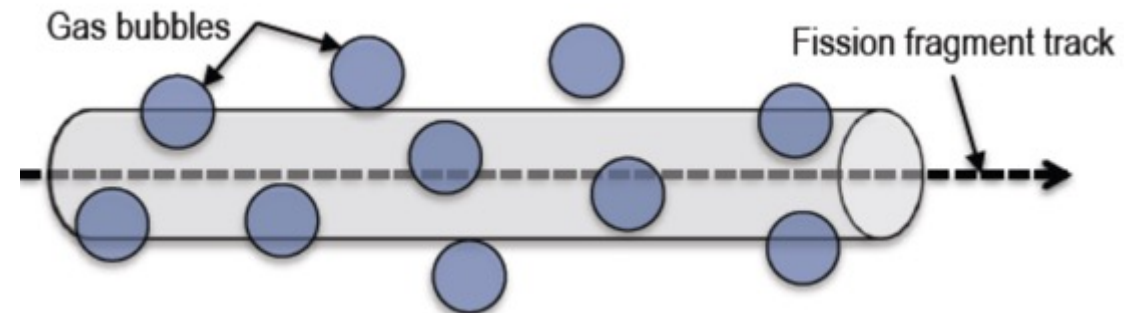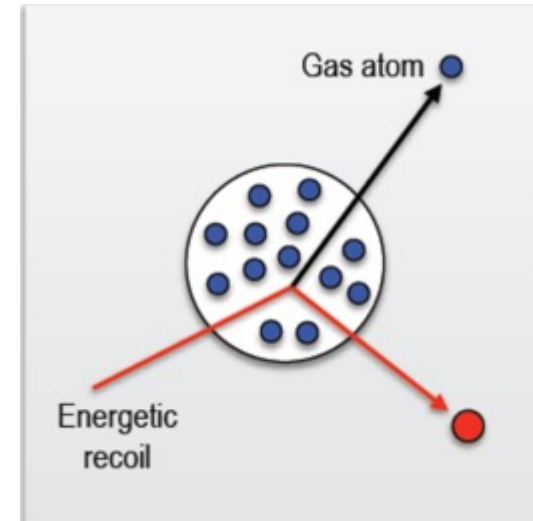
Fission Products

- The fission gases precipitate primarily as intragranular bubbles which can grow by gas-atom and vacancy absorption

- Fission gases can migrate to grain boundaries by atomic or bubble diffusion to form intergranular bubbles where they can grow by addition of gas and vacancies

- Fission-rate helps to strongly limit bubble size and maintain a substantial fission-gas atom population in the fuel lattice by re-solution of gas from bubbles

- Once intergranular-bubble growth becomes significant causing interconnection of porosity, a path from within the kernel to the buffer is created leading to fission-gas release by a percolation mechanism
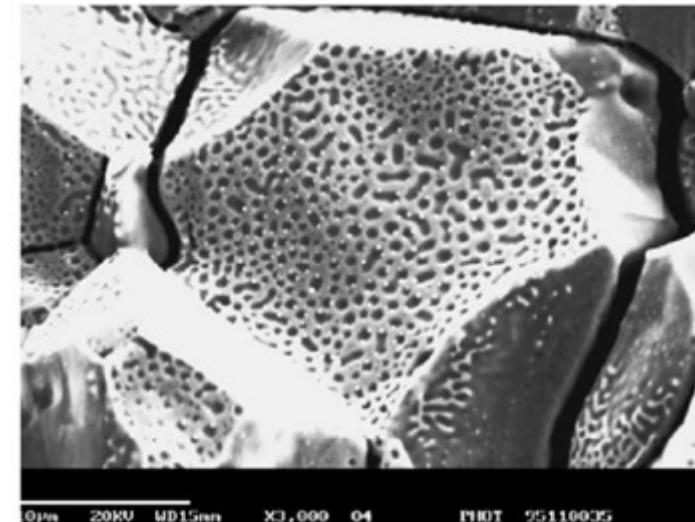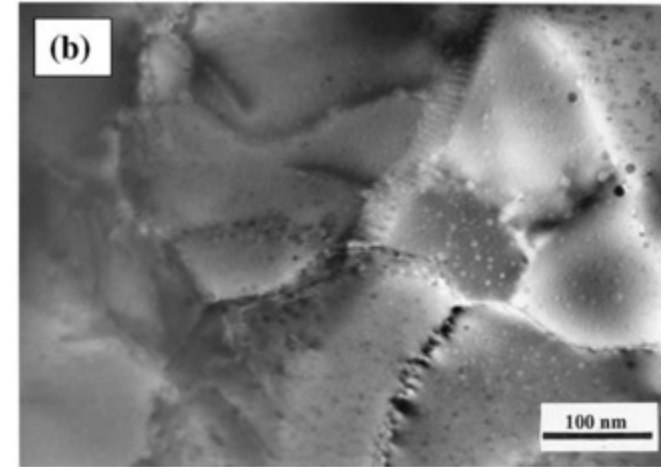
Bubble Resolution

- ## Homogeneous resolution
  - – individual gas atoms are ejected from the gas bubble through collisions with energetic fission fragments or recoil uranium atoms

- ## Heterogeneous resolution
  - – bubble are almost completely destroyed by the passage of a fission fragment

Fission Product Chemistry

- Rare earth elements have high solubility in UO2 and form rare earth oxides (REOs)

- Zr, Nb and Sr have significant solubility in UO2 and oxidize to form ZrO2, Nb2O3 and SrO

- Fission products that either have lower solubility or are less likely to form stable oxides, such as Ba, Te and Mo, diffuse to the grain boundaries and form perovskite or intermetallic precipitates

- These grain boundary inclusions can allow for release from the fuel kernel

- Ag and Pd are known to form intermetallic precipitates and are readily release from the fuel kernel
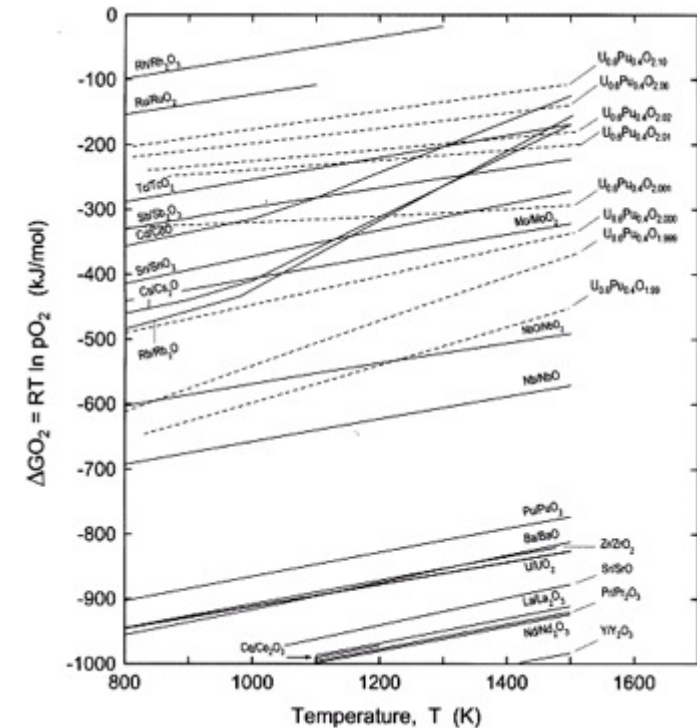
Ellingham diagram showing the temperature dependence of the stability of compounds

Fission Product Carbides

- In the UCO-type fuel kernel, oxygen liberated during the fission process of UO2, first oxidizes the carbide UC2 phase and then the RE fission products because of their high affinity for oxygen

- Those fission product elements with lower affinity for oxygen (Sr, Eu, Zr, Ba) exist as carbide compounds

- As the burnup increases, the UC2 phase in the kernel decreases

- When UC2 has fully disappeared, the oxygen potential then increases and oxygen is available to form oxide compounds with these fission products
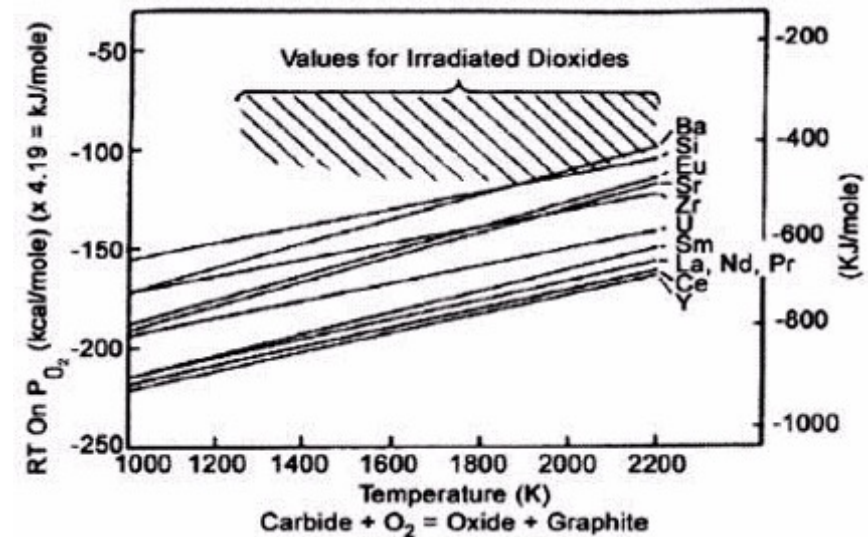
Oxidation diagram for carbides of interest

Fuel Kernel Summary

- Flexible composition, allowing for commercial power, fertile, breeder, and burner options

- Carbide and Oxide options

- Carbides allow for higher power density and higher temperatures, reduce CO production

- Oxides retain fission products

- US utilizes UCO 80(UO_2)/20(UC_2) mix

- UC_2 gets oxidized, then other fission fission products will form oxides

- Will cover some other fuel kernel related failure mechanisms later

SILICON CARBIDE

Silicon Carbide (SiC)

- SiC is a very hard and strong non-oxide ceramic that possesses unique thermal and electronic properties
- Polycrystalline SiC has a strength of 15 GPa and has excellent creep resistance
- SiC's upper limit of stability is around 2500C and has a melting temperature of around 2830C
- SiC also has excellent thermal conductivity
- SiC is a highly covalent material that forms tetrahedra that are centered around either carbon or silicon atoms
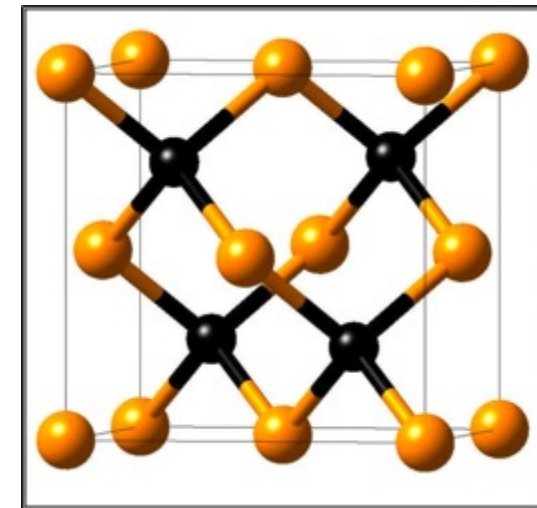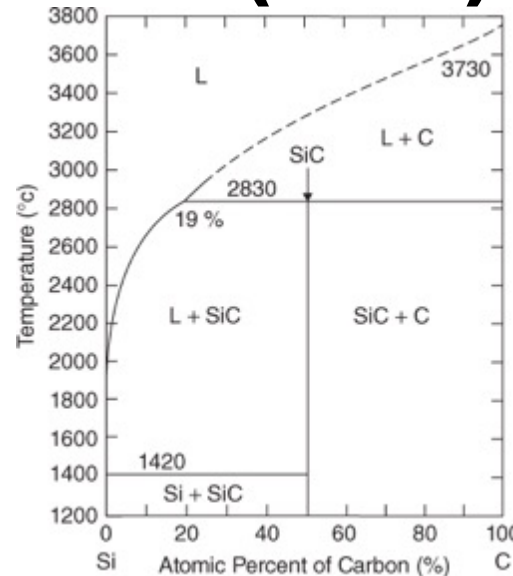
- β-SiC takes the diamond cubic structure with half of the carbons being replaced with silicon; this is a very stable structure that is conducive to phononic heat conduction

Silicon Carbide (SiC)

- Silicon carbide (SiC) has been studied and utilized in nuclear systems for decades, primarily as the micro pressure vessel for high-temperature gas-cooled reactor fuels
- The SiC must be strong enough to withstand the pressure buildup from the fission product gas liberated and CO produced

- The SiC layer must withstand chemical attack from metallic fission products such as palladium
- The SiC must be able to handle the mechanical loads derived from irradiation-induced dimensional changes occurring in the pyrolytic graphite
- The SiC must maintain its properties during irradiation

Radiation Effects in SiC

- The neutron-induced swelling of SiC has been well studied for low and intermediate temperatures (up to 1000 C)

- It is well understood that the presence of significant second phases and/or poorly crystallized phases in these materials leads to unstable behavior under neutron irradiation

- While high purity, stoichiometric, near-theoretical density SiC can show excellent radiation resistance

- Here I will be talking about the good SiC, assuming that the fabrication process has produced appropriately clean coatings

Radiation Effects in SiC

- The microstructural evolution map is shown on the right

- The contribution of the defects themselves to the swelling in SiC is not well understood
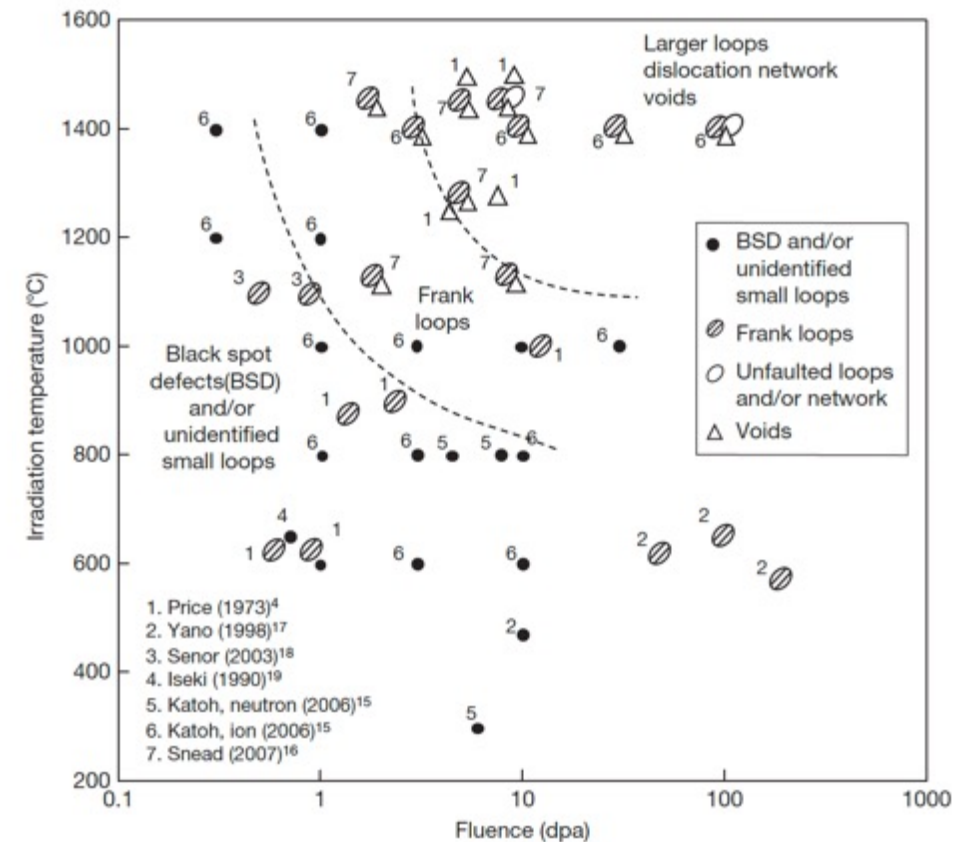
Low T Radiation Effects in SiC

- Below 400 K, neutron irradiated SiC microstructure is described as black spot defects, which are most likely clusters of self-interstitial atoms

- For irradiation temperatures less than about 423 K, accumulation of strain due to the irradiation-produced defects can exceed a critical level above which the crystal becomes amorphous

- The swelling under self-ion irradiation increases logarithmically with dose until amorphization occurs

- The swelling of neutron- and ion-amorphized SiC has been reported to be as high as 10.8% at 343K