

NE 591: Advanced Reactor Materials

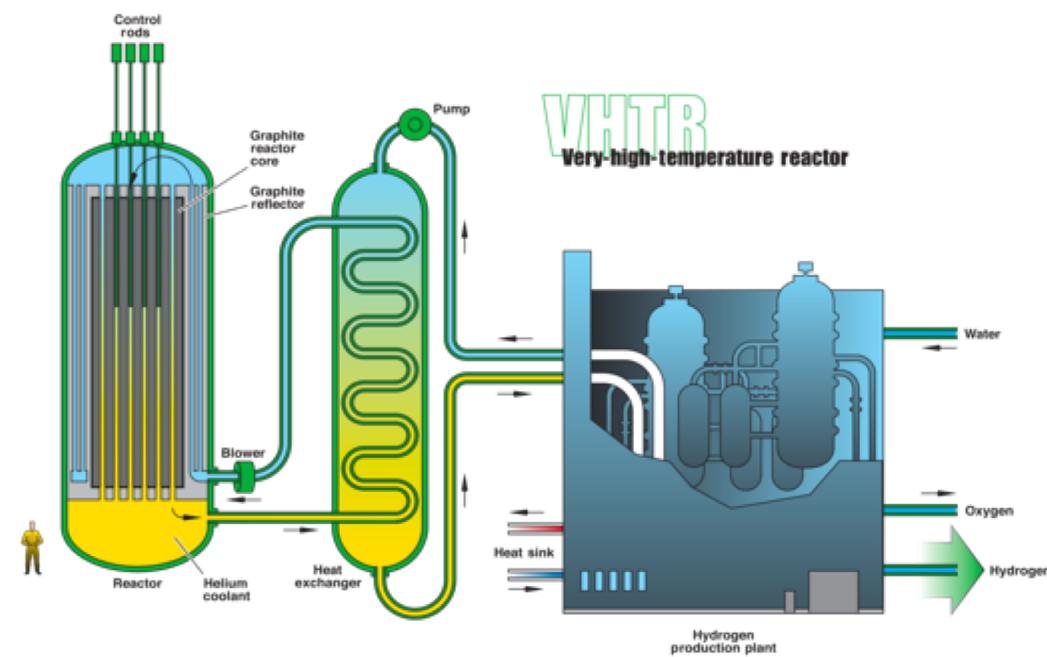
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HIGH TEMPERATURE GAS REACTORS AND TRISO PARTICLES

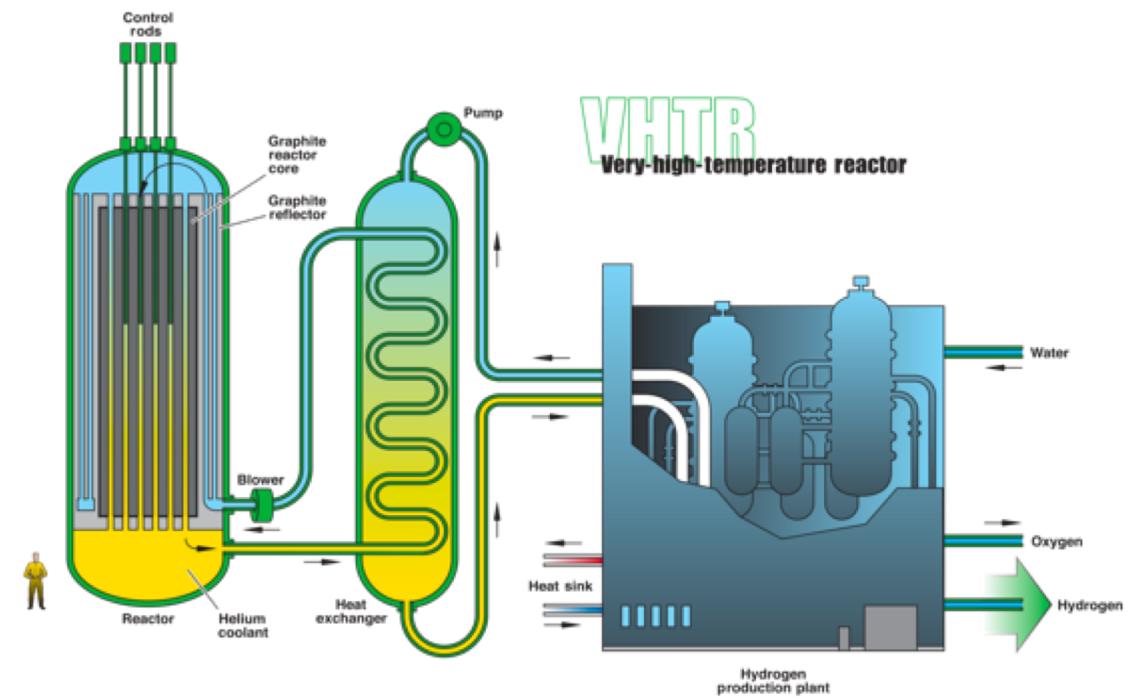
High Temperature Gas Reactor

- The HTGR has a long history going back to the earliest days of nuclear energy development
- Commercial gas-cooled nuclear power for electricity production started in 1956 with the operation of the first 50 MWe unit in the UK
- The design, which came to be known as Magnox, featured carbon-dioxide as the pressurized coolant and magnesium alloy cladding for the fuel
- To raise thermal efficiency, later designs switched to stainless steel cladding, enriched uranium oxide fuel, higher CO₂ pressures, and higher operating temperatures, in what came to be known as the Advanced Gas Reactor (AGR)



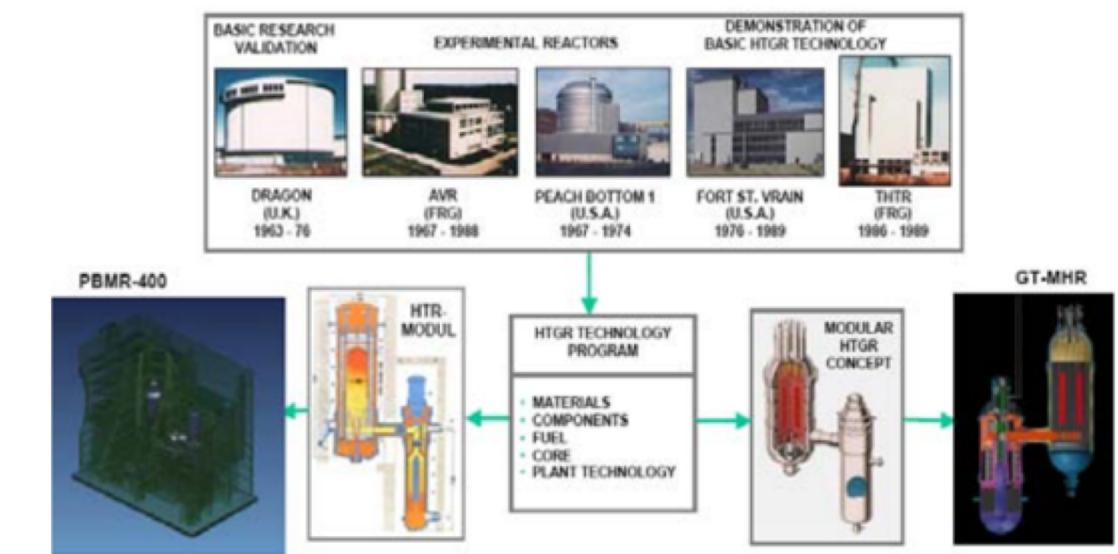
HTGRs

- The use of helium (He) as a coolant was advocated as early as 1944 in a 5 MWt experimental reactor project, also featuring an indirect gas turbine cycle
- Later, the prototype DRAGON reactor was put into operation in the UK in 1965 and featured a steel pressure vessel, coated fuel particles of highly-enriched uranium-thorium carbide and a helium outlet temperature of 750°C

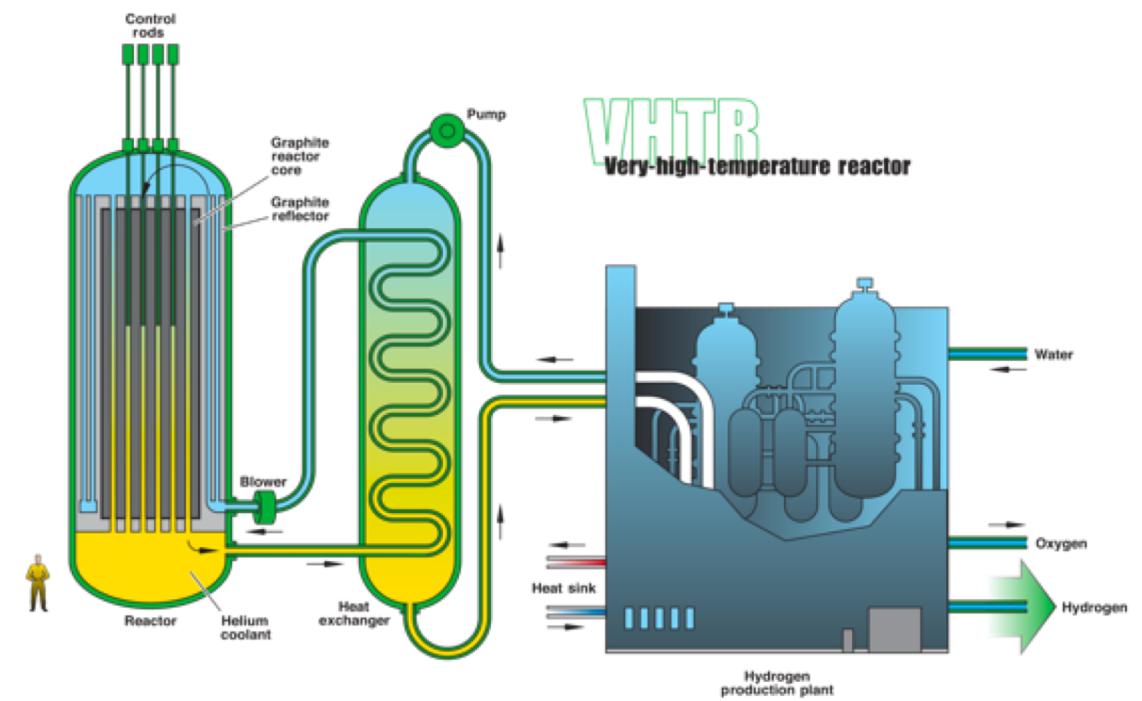
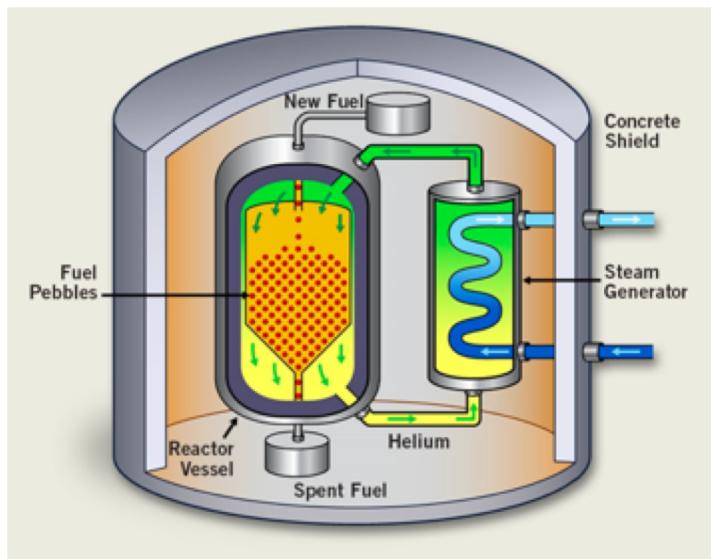


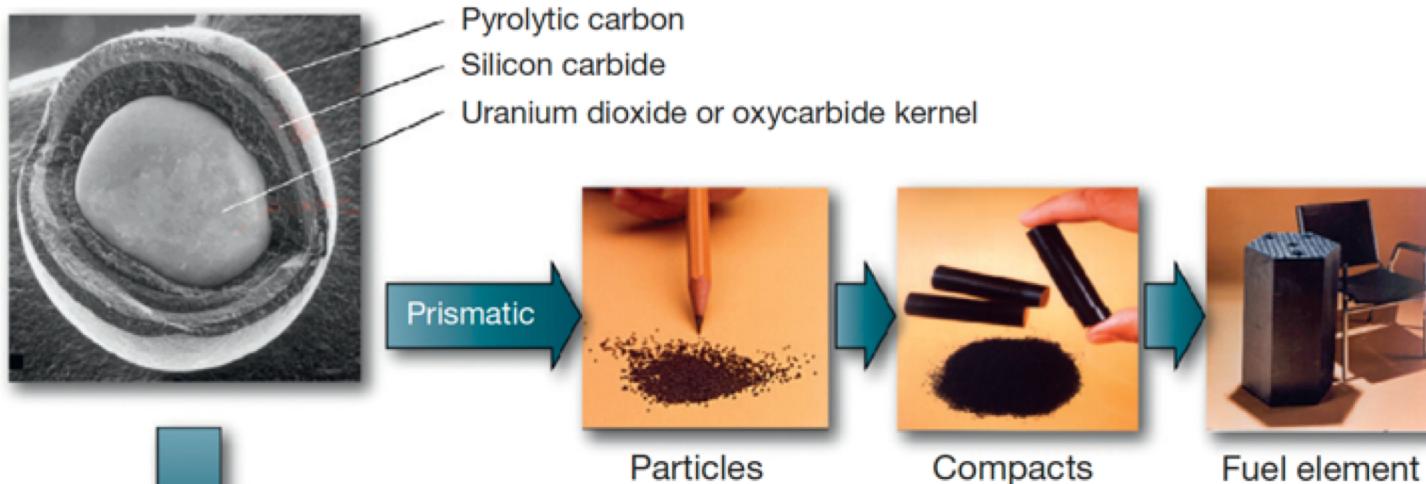
HTGRs

- The substitution of He instead of air or CO₂ provided excellent neutronic and thermal characteristics together with a graphite moderator
- There are two mainstream HTGR design concepts; the prismatic core design and the pebble bed core design, both of which possess common advantages of the HTGR design such as inherent safety and high efficiency

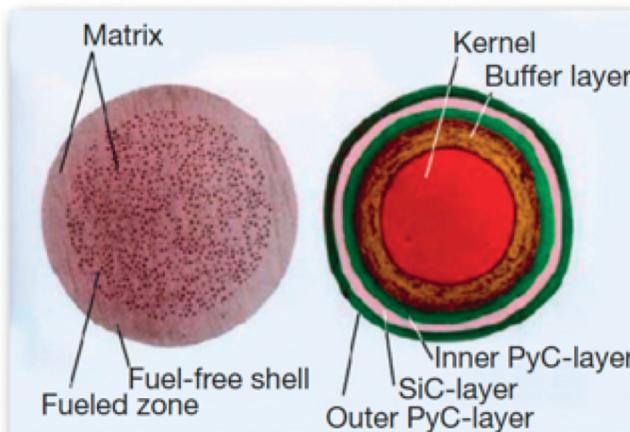


Two types of HTGRs

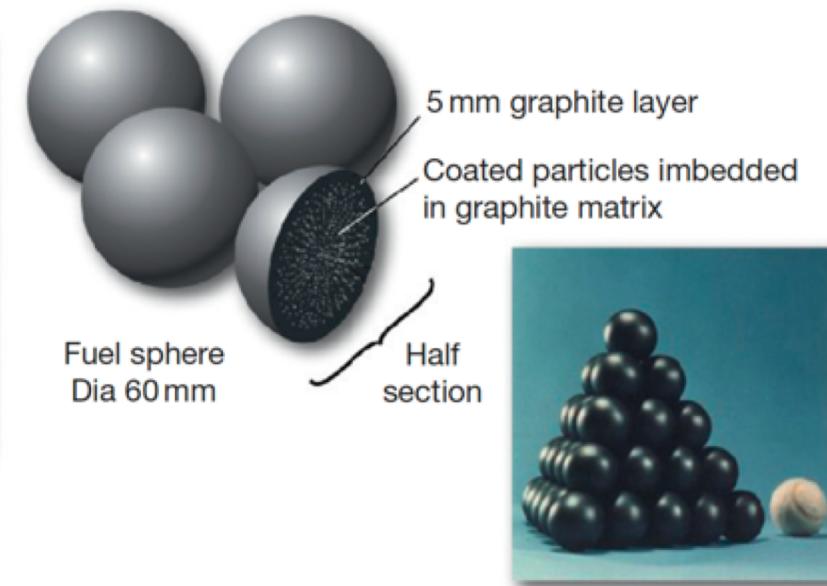




TRISO-coated fuel particles (left) are formed into fuel compacts (center) and inserted into graphite fuel elements (right) for the prismatic reactor



TRISO-coated fuel particles are formed into fuel spheres for pebble bed reactor



HTGRs

- The main features of HTGRs are enhanced safety, high thermal efficiency, economical competitiveness, and proliferation resistance and these make this technology a potential candidate for the nuclear power plant deployment
- One of the driving forces behind the HTGR philosophy is its utilization in the production of process heat: the high outlet gas temperatures may be utilized as a thermal heat source in endothermic chemical processes
- Net thermal efficiencies greater than 45% are within the reach in some of the designs of HTGRs
- The enhanced safety of the HTGR fuel is based on its coated fuel particle design consisting of uranium oxide/carbide particles coated with layers of pyrolytic carbon and silicon carbide
- Coated particles are so designed that they can withstand high internal gas pressure without releasing any fission products to the environment

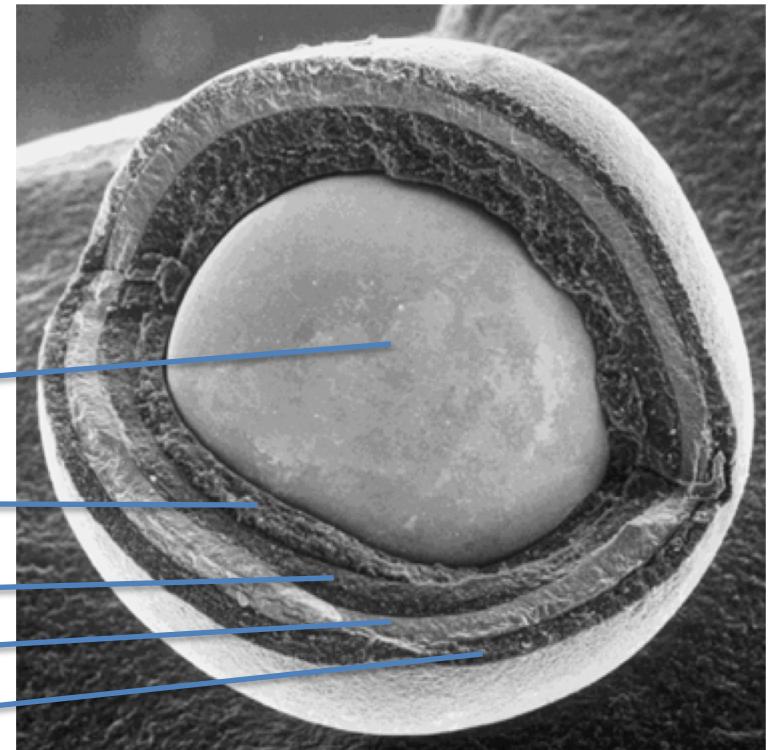
HTGRs

- Difference from LWRs
 - helium cooled
 - much higher temperatures
 - thermal/fast options
 - extensive utilization of graphite
 - flexibility of fuel

	Neutron spectrum (fast/thermal)	Coolant	Temperature (°C)	Pressure*	Fuel	Fuel cycle	Size (MWe)	Use
Gas-cooled fast reactors	fast	helium	850	high	U-238 +	closed, on site	1200	electricity & hydrogen
Lead-cooled fast reactors	fast	lead or Pb-Bi	480-570	low	U-238 +	closed, regional	20-180** 300-1200 600-1000	electricity & hydrogen
Molten salt fast reactors	fast	fluoride salts	700-800	low	UF in salt	closed	1000	electricity & hydrogen
Molten salt reactor - advanced high-temperature reactors	thermal	fluoride salts	750-1000		UO ₂ particles in prism	open	1000-1500	hydrogen
Sodium-cooled fast reactors	fast	sodium	500-550	low	U-238 & MOX	closed	50-150 600-1500	electricity
Supercritical water-cooled reactors	thermal or fast	water	510-625	very high	UO ₂	open (thermal) closed (fast)	300-700 1000-1500	electricity
Very high temperature gas reactors	thermal	helium	900-1000	high	UO ₂ prism or pebbles	open	250-300	hydrogen & electricity

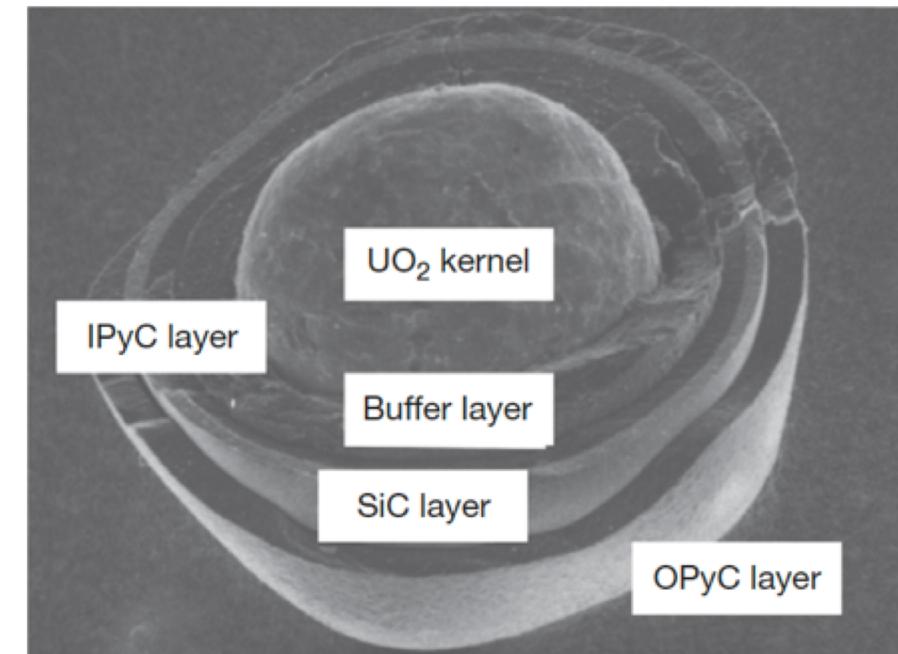
TRISO Particles

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



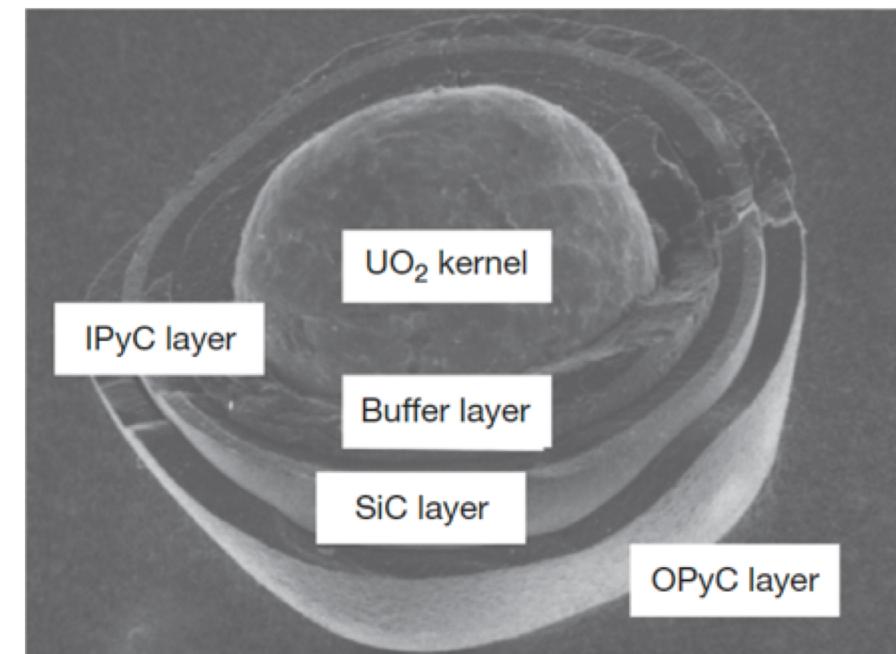
Fuel Kernel + Buffer

- 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

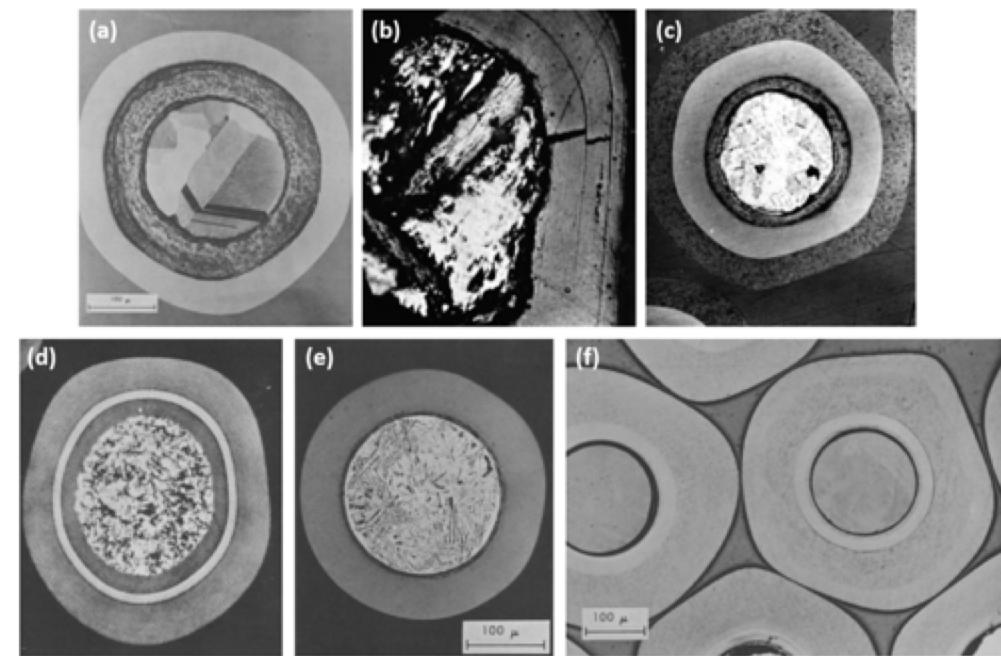
- Surrounding this inner buffer layer is a layer of dense pyrolytic carbon (IPyC), a silicon carbide (SiC) layer, and a dense outer pyrolytic carbon (OPyC) layer
- The pyrolytic carbon layers protect the SiC layer, which is the pressure boundary
- The pyrolytic carbon layers are approximately 40-micron 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

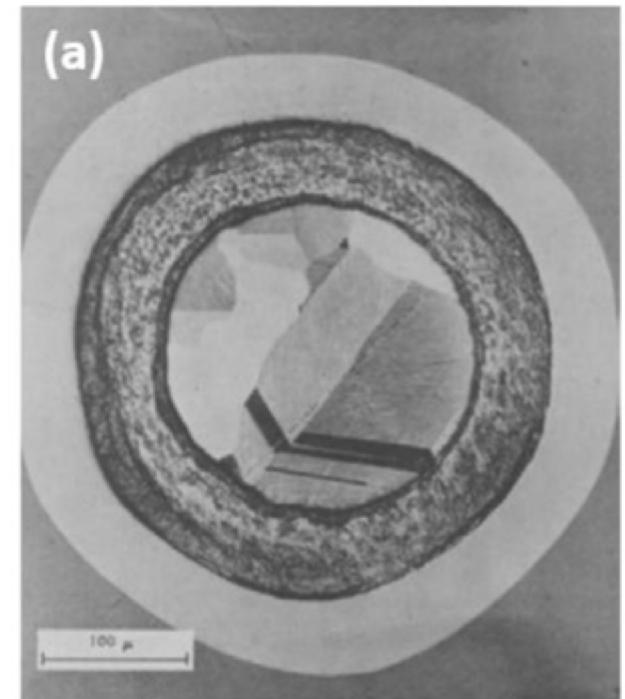
A refractory material or refractory is a material that is resistant to decomposition by heat, pressure, or chemical attack, and retains strength and form at high temperatures



(a) BISO particle, (b) Particles with “laminated” pyrocarbon layer structure, (c) Particle with “Triplex” structure, (d) Fertile (Th,U)C₂ with PyC-SiC-PyC structure, (e) Carbide particle with single PyC coating, (f) “Duplex” (Th,U)C₂ particle

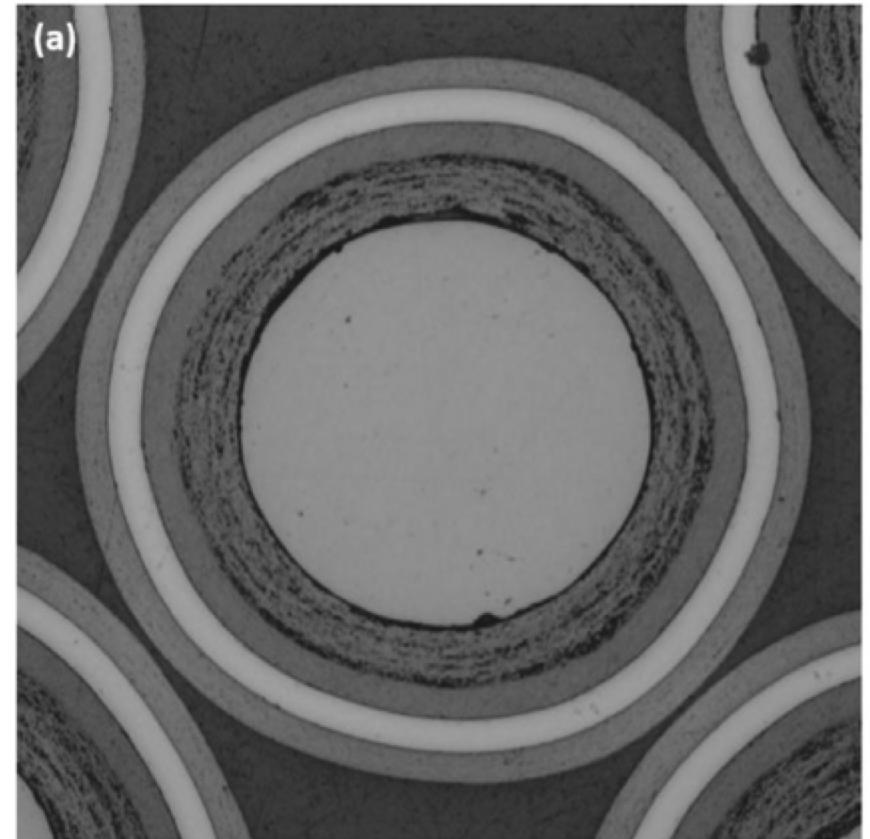
Early Failure

- 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 UO₂ fission is the creation of free oxygen since only a part of the O₂ 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 CO₂ 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

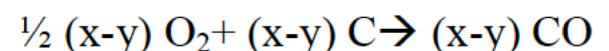
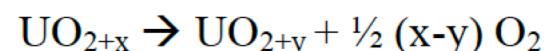
Oxygen Potential

- 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:

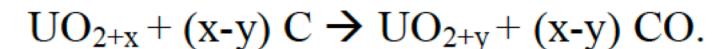
$$\mu(O_2) = RT \log P(O_2)$$

- where $P(O_2)$ 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 UO_2+x ($x>0$) and carbon is gaseous carbon monoxide, CO, by the following reactions:



- which can be rearranged as:



- Utilizing an equilibrium rate constant K,

$$\log P(CO) = \log K_p + \frac{1}{2} \log P(O_2)$$

Oxygen Potential

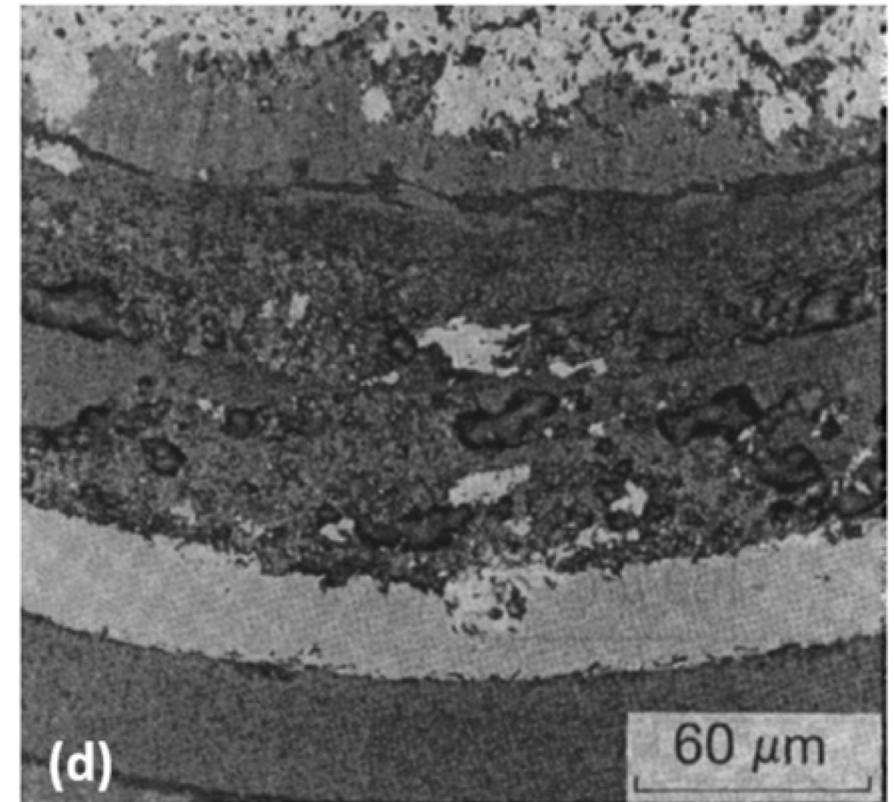
- Reactions to generate CO₂ are also possible, but at applicable temperatures and values of the oxygen potential, CO production dominates
- As the oxygen potential, i.e. oxygen partial pressure, is increased we are generating more CO
- The result of CO formation is internal pressurization of the particle 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 and CO₂ formation is internal pressurizing of the particle that increases with burnup and adds to the pressurization from fission gases
- At lower burnup ($\leq 6\%$ 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 and CO₂ 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 and CO₂ 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

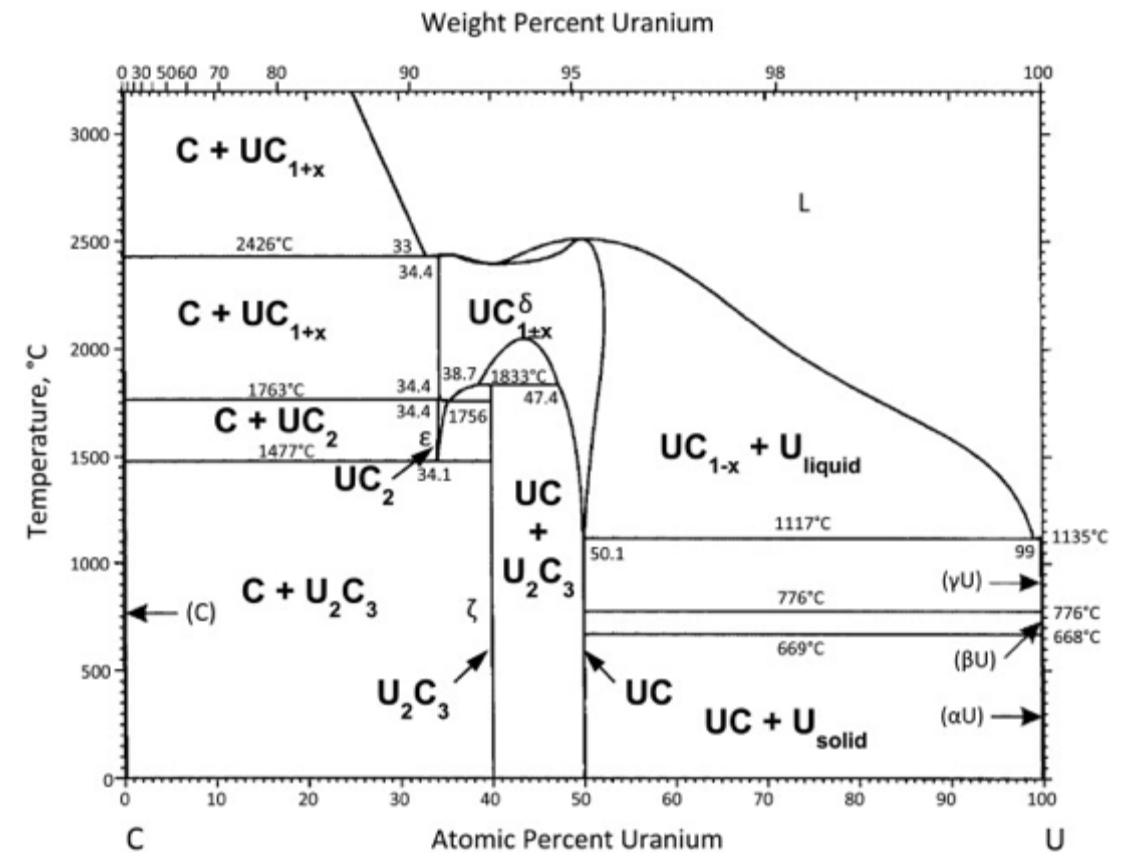


UCO

- We have two fuel kernel problems:
 - CO production (UO_2)
 - 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 UC_2 to getter the excess oxygen produced by UO_2 fission
- UCO avoids the formation of CO, while still taking advantage of the retention of the metal oxide fission products in the predominantly UO_2 kernel
- The success of UCO kernels by the US program lead to the adoption of UCO fuel as the reference fissile particle design by the early 1980s, with an approximate UO_2/UC_2 mixture of 80/20

U-C Phases

- UC₂ has a fcc fluorite structure at high temperature and transforms to a body-centered tetragonal structure at 1820°C
- The UC₂ phase is retained in a metastable form in material rapidly cooled from the melt
- As-cast hyper stoichiometric UC consists of a Widmanstatten pattern of UC₂ platelets on the {100} planes of the face-centered cubic UC matrix



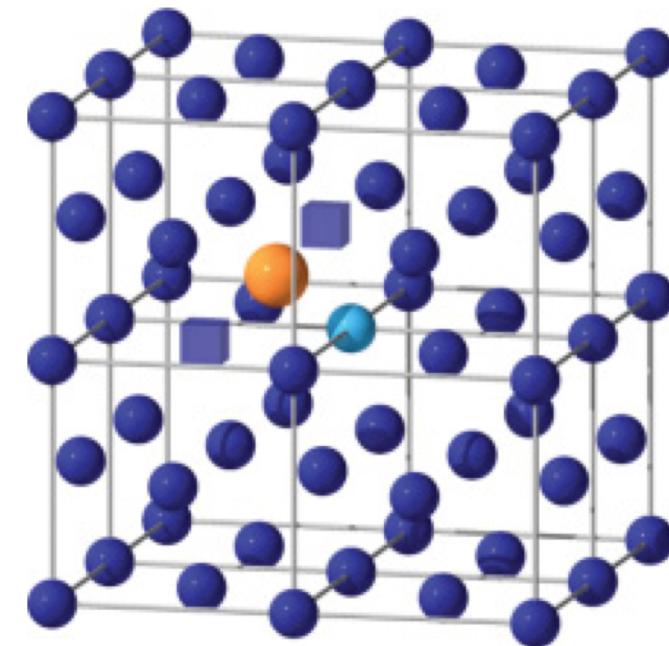
Fission Products

- 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

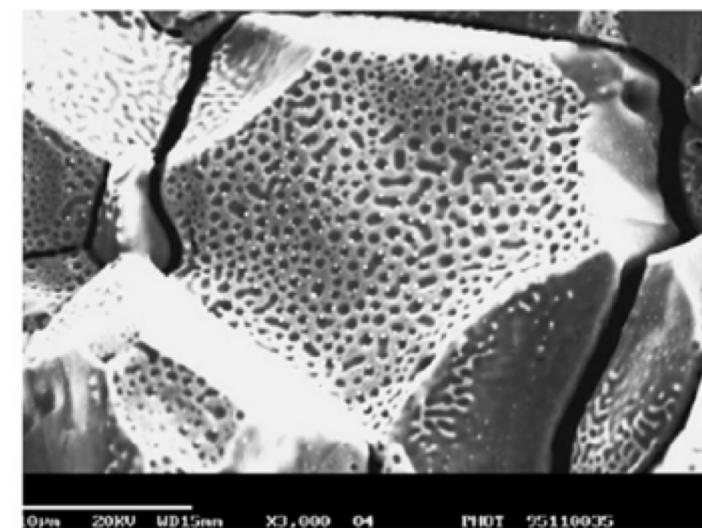
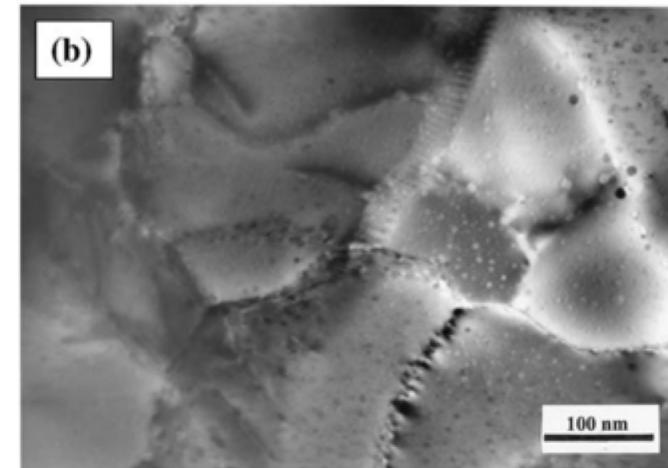
Fission Products

- 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



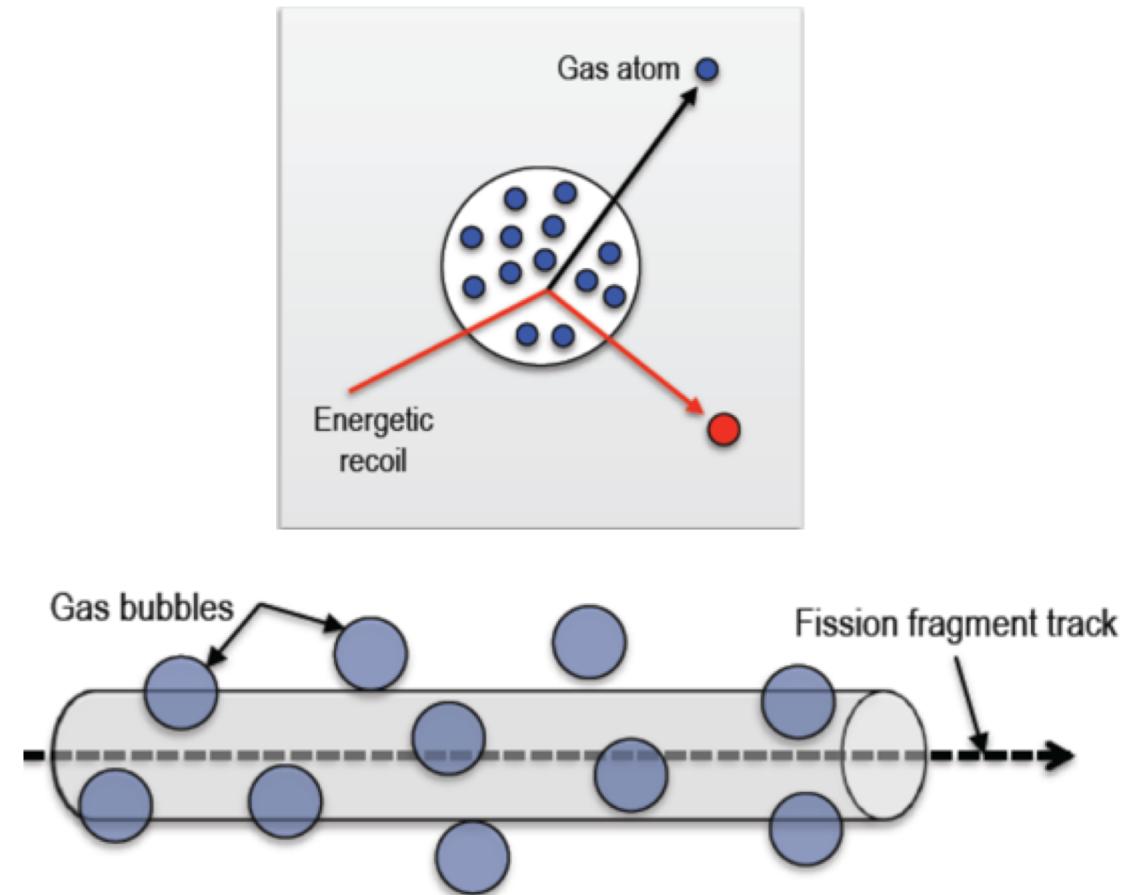
Fission Products

- 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



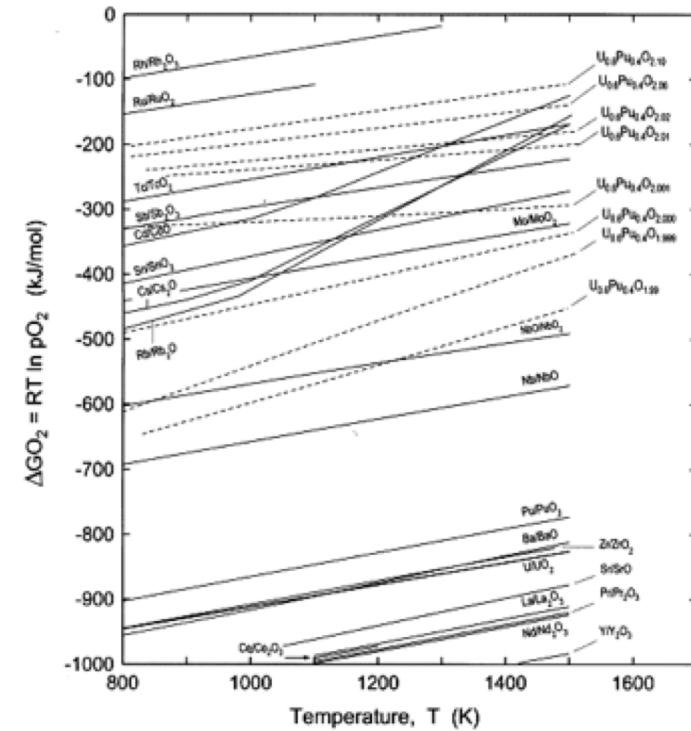
Bubble Resolution

- Homogeneous resolution
 - individual gas atoms are ejected from the gas bubble through collisions with energetic fission fragments or recoil uranium atoms
- Heterogeneous resolution
 - bubbles are almost completely destroyed by the passage of a fission fragment



Fission Product Chemistry

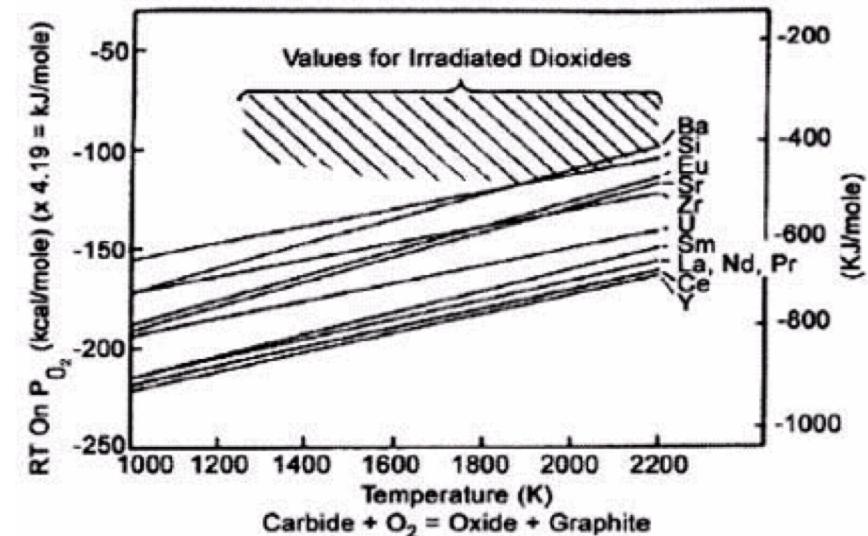
- Rare earth elements have high solubility in UO₂ and form rare earth oxides (REOs)
- Zr, Nb and Sr have significant solubility in UO₂ and oxidize to form ZrO₂, Nb₂O₃ and SrO
- Fission products that either have lower solubility or are less likely to form stable oxides, such as Ba, Te and Mo, diffuse 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

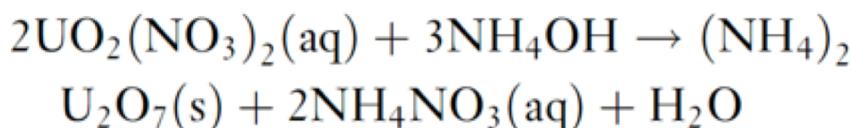
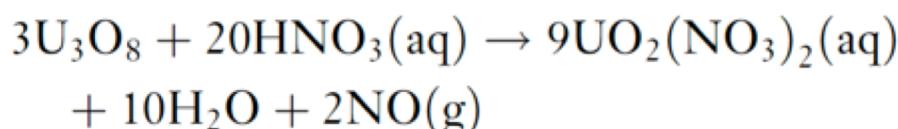
- In the UCO-type fuel kernel, oxygen liberated during the fission process of UO₂, first oxidizes the carbide UC₂ phase and then the RE fission products because of their high affinity for oxygen
- Those fission product elements with lower affinity for oxygen (Sr, Eu, Zr, Ba) exist as carbide compounds
- 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

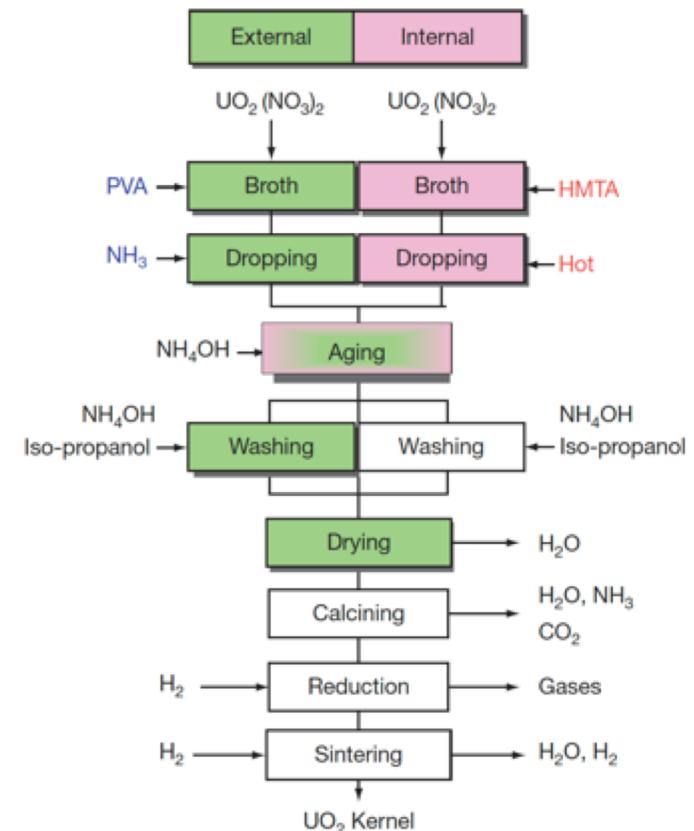
Fuel Kernel Fabrication

- The sol–gel technique for kernel microsphere preparation is based on the following two chemical reactions starting from U₃O₈ powder
- The (NH₄)₂U₂O₇ (ammonium diuranate – ADU) is converted to UO₂ by sintering in hydrogen gas
- For the production of UCO kernels, carbon black is added to the broth and the sintering is performed in CO gas to ensure adequate C/O stoichiometry



Fuel Kernel Fabrication

- The mechanical strength of the coated layers depends on their thickness and sphericity, and thus strongly depend on the diameter and sphericity of the kernels
- Vibrating nozzles from which droplets are emitted with high speed were developed for uniform and spherical kernel fabrication
- A process is applied to prevent the deformation of droplets while they are landing on the ammonia water, where droplets are solidified while falling in ammonia gas blown against them



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(UO₂)/20(UC₂) mix

QUESTIONS?