

NE 795: Advanced Reactor Materials

Fall 2023

Dr. Benjamin Beeler

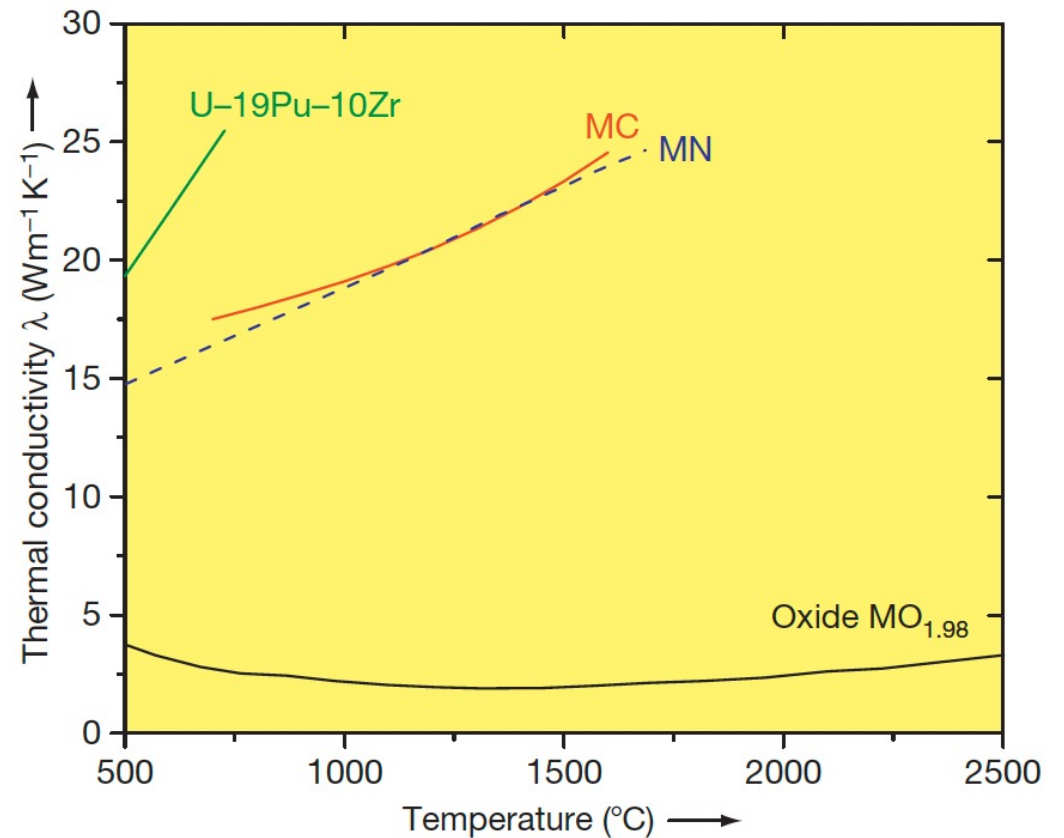
Last Time

- Excess fluorine generated due to fission, yielding oxidizing conditions
- Fission products take different forms (gaseous, precipitates, soluble salts)
- Cover gas helps to remove fission products and control redox potential
- UF_4/UF_3 ratio is an indicator of redox potential
- Three principal corrosion processes: Reactions due to oxides on the metal; Reactions with dissolved impurities; Reactions with necessary constituents of the melt
- Rapid initial corrosion from impurities on surface or in salt; followed by Cr-diffusion-controlled corrosion
- Different materials required for different systems, depending upon irradiation, temperature, salt exposure, etc.

CARBIDES AND NITRIDES

Why Carbides?

- Possible fuel compositions with higher fissile atom density are non-oxide ceramics, for example, uranium–plutonium-mixed carbide or nitride
- These fuels have higher thermal conductivity, high fissile heavy-atom density, and a high melting point compared to metallic fuel
- The higher thermal conductivity of carbide fuel and high melting point makes carbide fuel suitable for operation at high power



Why Carbides?

- The more efficient heat transfer also allows for the possibility of large diameter fuel pins, with more fissile material per pin, and more power generation
- High-specific-power operation permits fewer pins, compared to oxide, and a more compact core, which can reduce plant costs
- A large amount of development work on carbide and nitride fuels was performed from 1960 to 1970, and more than 5000 advanced fuel pins have been fabricated and irradiated
- The practical difficulty of fabrication of carbide fuel hampered carbide development
- The high-purity inert cover gas required for fuel fabrication was expensive and maintenance of C/M ratio was difficult

Carbide Reactor

- The Indian FBR program started with the introduction of plutonium-rich mixed uranium–plutonium carbide as the driver fuel for a small loop-type fast breeder test reactor
- The reactor became critical in the year 1985, is still in service, and it is the only reactor operating on a full core of carbide fuel
- A larger reactor is being constructed in India based on this design
- Carbide fuel cannot be used in LWR because of its incompatibility with the coolant
- However, it can be safely used with liquid metal (Na or lead) or gas (CO₂ or He) coolants in Gen-IV reactors
- Carbide fuel has a breeding ratio of at least 1.30, a doubling time of 15 years or less, and a burnup limit of more than 15 at.%

US Interest in Carbide Fuels

- Many laboratories in the world were engaged in studies on the development of carbide fuels based on uranium and plutonium and thorium
- After the oil crisis in 1974, a national advanced liquid-metal-cooled FBR fuels development program was initiated that built upon early years of carbide fuel development
- Both carbide and nitride fuels offer a middle ground for LMFBR performance because of their higher thermal conductivity, fissile-atom density, and chemical compatibility with liquid sodium, and much higher melting point than metallic fuels

Fuel type	Reactor	Country/ organization	Bond	Density (% TD)	Burnup (at.%)	Clad
MC	RAPSODIE	France/CEA	Na	91.5	12	–
MC	BOR60	USSR	Na	–	–	OX16H15M3G
MC	EBR II	United States	Na	–	12	PE16
MC	RAPSODIE	TUI	He	86	5	–
MC	KNK II	FZK, Germany	He	85	7	1.4970
MC	EBR II	United States	He	80/87	12	316.20 cw
MC	EBR II	United States	He	81/87	16–20	316.20 cw
UC/MC	BOR 60	USSR	He	–	10	OX16H15M3G-
MC	FFTF	United States	He	80	10	D9
MC	PX	CEA/TUI	He	80/82	–	15/15 Ti
MC	FFTF	DOE/PSI	He	–	10	D9
MC	FBTR	India	He	91/86	16	SS316 cw

Properties	(U _{0.8} Pu _{0.2})O ₂	(U _{0.8} Pu _{0.2})C	(U _{0.8} Pu _{0.2})N	U–19Pu–10Zr
Theoretical density (g cm ⁻³)	11.04	13.58	14.32	15.73
Melting point (°K)	3083	2750	3070	1400
Thermal conductivity (W m ⁻¹ °K)				
1000 K	2.6	18.8	15.8	40
2000 K	2.4	21.2	20.1	
Crystal structure	Fluorite	NaCl	NaCl	Multiphase
Breeding ratio	1.1	1.2–1.3	1.2–1.3	1.4–1.5
Swelling	Moderate	High	High (?)	High
Handling	In air	Inert atmosphere	Inert atmosphere	Inert atmosphere
Compatibility				
Clad	Average	Carburization	Good	Eutectics
Coolant	Average	Good	Good	Good
Dissolution and reprocessing amenability	Demonstrated on industrial scale for aqueous and pilot scale for pyro-processes	Dissolution not simple. Process not yet demonstrated on industrial scale	Dissolution easy but risk of C ¹⁴ in waste management	Pyro-reprocessing demonstrated on pilot plant scale
Fabrication/irradiation experience	Large	Limited	Very little	Limited
	Good			

Carbide Pin Designs

- There are two concepts available for the carbide fuel pin depending upon the type of bond between the fuel pellet and the cladding material: He-bonded and Na-bonded carbide fuels
- The average operating fuel temperature of the He-bonded pin is high because of low thermal conductivity of the He bond compared to the Na bond
- This design requires a larger fuel–clad gap and 85% smear density to accommodate the swelling of the fuel
- The fission gas release in a He-bonded pin will be higher compared to that from a sodium-bonded pin, due to the higher temperatures
- Na-bonded carbide fuel pins also require a reduced smear density compared to oxide fuels to account for fuel swelling
- The purity of the Na bond is very important, requiring strict tolerances on O content

Carbide Fuel Details

- A hyperstoichiometric ($C/M > 1$, carbon to metal ratio) fuel composition is chosen so that it contains some amount of sesquicarbide M_2C_3 phase ($M=U+Pu$), which accounts for the decrease in (C/M) ratio with burnup
- A sufficiently low C/M ratio may result in the formation of actinide metal phases, which may form low-melting eutectics with the cladding and limit the life of the fuel pin
- FCMI can potentially exist, depending upon the operating temperature of the fuel
- O and N impurities play important roles, as they act as 'carbon equivalent', which affect the carbon potential of the fuel
- Also have high Pu and low Pu designs, which impact properties and impurity sensitivity

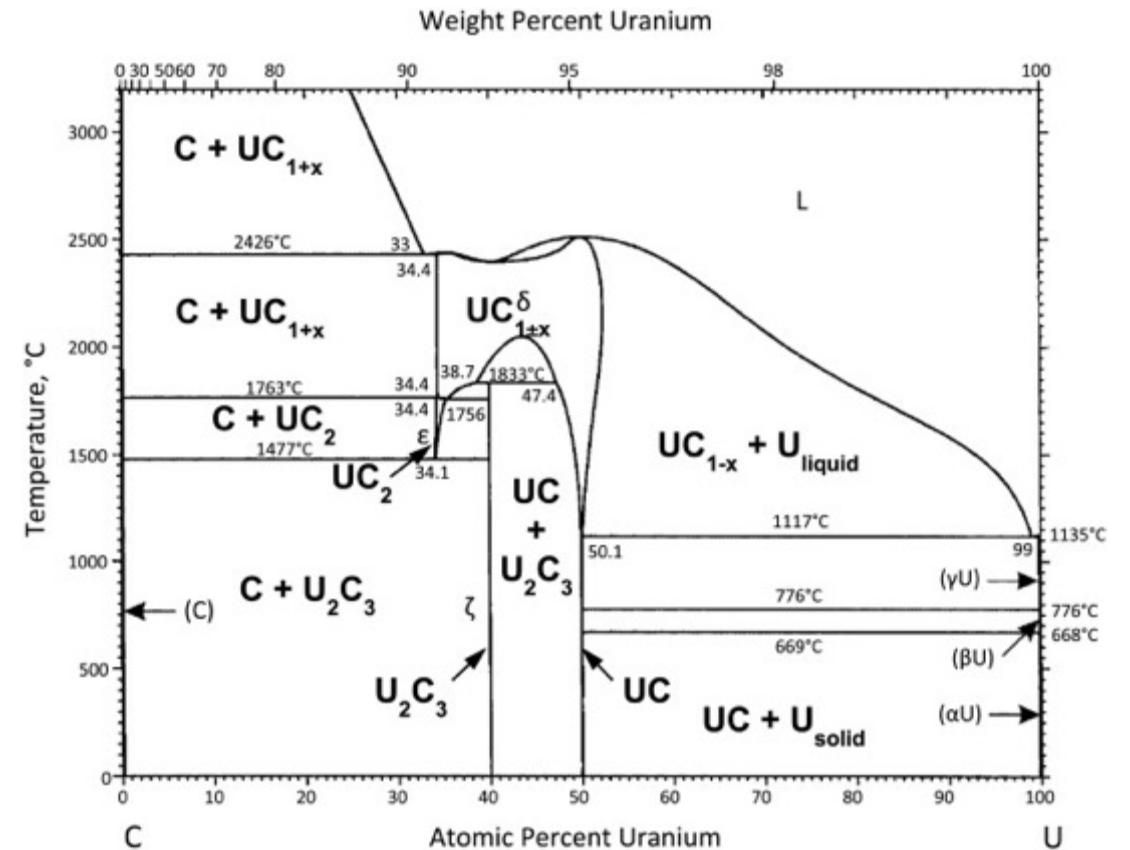
	$(Pu_{0.7}U_{0.3})C$	$(Pu_{0.2}U_{0.8})C$
Plutonium (wt%)	66 ± 1	21.3 ± 1
Pu/(U + Pu)	0.70	0.225
Oxygen (ppm)	≤ 6000	360
Oxygen + nitrogen (ppm)	≤ 7500	~ 400
M_2C_3 (wt%)	5–20	12.5 ± 1.4
Density (% TD)	90 ± 1	80 ± 1
Grain size	$\sim 10\text{--}12 \mu\text{m}$	$12 \mu\text{m}$

Carbide Fuel Details

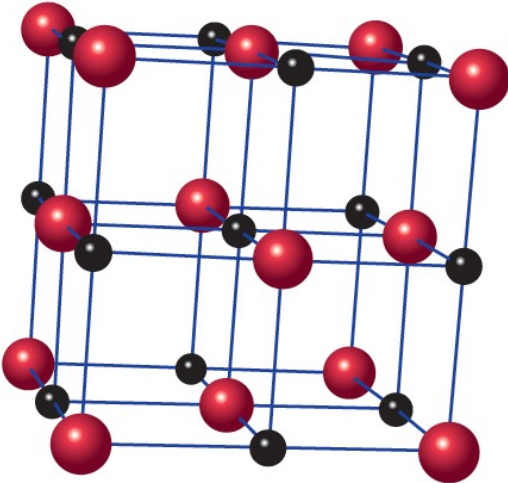
- Carbide fuels have higher swelling and lower fission gas release than oxide fuels
- This is due to the lower fuel temperatures (higher thermal conductivity), and the microstructural evolution of fission gases
- However, carbide fuels go to significantly higher burnups, leading to larger fission product inventories
- Burnup limits are imposed by cladding stresses/damage due to fission gas pressure and FCMI

U(Pu)-C Phases

- Uranium forms three compounds with carbon: UC, U_2C_3 , and UC_2 , with only U_2C_3 being stoichiometric
- UC is stable over a wide temperature and composition range
- UC_2 is stable in two high temperature phases
- The Pu–C system has four compounds: Pu_3C_2 , PuC_{1-x} , Pu_2C_3 , and PuC_2
- UC and PuC are face-centered cubic structures (NaCl-type)



U/Pu-C Phase

Compound and lattice parameters	Composition and temperature range	Space group	Structure ● - Actinide; ● - C
$\text{ThC}_{1\pm x}$ 508.8 pm (Th) to 534.4 pm ($\text{ThC}_{0.98}$ in equilibrium with ThC_2)	$\text{C/Th} = 0 - 1.96$ Eutectic $\text{ThC}_{1\pm x} = 1980 \text{ K}$ Congruent $T_m = 2780 \text{ K}$ for $\text{C/Th} = 0.975$	NaCl-fcc $\text{O}_h^5 - Fm\bar{3}m(\text{Nr.225})$	
PaC 506.08 pm	—		
$\text{UC}_{1\pm x}$ 4.9605 Å ($\text{UC}_{1.0}$) 4.9563 Å ($\text{UC}_{0.93}$)	$\text{C/U} = 0.82 - 1.86$ $T_m = 2780 \text{ K}$ for $\text{C/U} = 1$		
$\text{NpC}_{1\pm x}$ 499.1 pm for $\text{NpC}_{0.82}$ to 501.0 pm for $\text{NpC}_{1.0}$	$0.82 \leq \text{C/Np} \leq 1.0$		
PuC_{1-x} $a = 498.13 - 1.50$ $(1 - \text{C/Pu})\text{pm}$	$\text{C/Pu} = 0.74 - 0.94$ $T_{\text{peritectic}} =$ $1910 \pm 20 \text{ K}$		

Phase Properties

- The brittleness of the monocarbides is due to alternate close-packed planes of metal and nonmetal atoms, restricting the slip and thereby hardening the crystal
- Many fission products are not soluble in the monocarbide lattice due to the nature of the carbon bonding
- The high density and low FP solubility of UC leads to higher swelling than UO₂
- The U₂C₃ phase has more open space in the structure, and generally has less swelling than UC
- An increase in O and N impurities results in an increase of carbon activity and CO pressure of the fuel
- O impurities are also known to contribute to the actinide redistribution in carbide fuels and fuel restructuring during burnup

U/Pu₂-C₃

- This structure is more complex than that of the mono- and dicarbides, and is often difficult to form
- U₂C₃ is produced by a complex preparation procedure and decomposes into a mixture of mono- and dicarbides at high temperatures

Th₂C₃
 $855.13 \leq a \leq 856.09$ pm
 in a narrow
 homogeneity range

U₂C₃
 808.99 pm

Np₂C₃
 810.3 pm

Pu₂C₃
 $812.1 \leq a \leq 813.4$

Am₂C₃
 827.57 pm

Cm₂C₃
 839.4 pm

Th₂C_{3-y} ($0 \leq y \leq 0.05$)
 Under high
 $p > 2.8$ GPa

U₂C₃ → UC + UC₂
 (>2093 K)

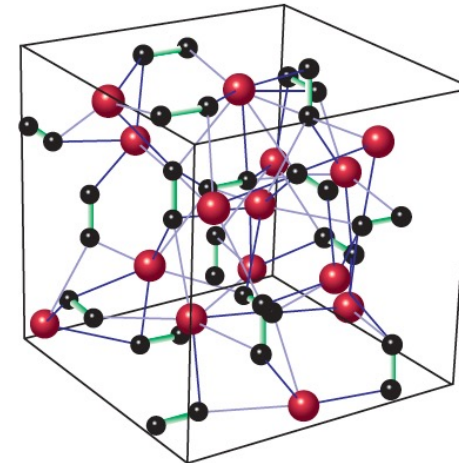
–

C/Pu = 1.45–1.5
 Stable under 2300 K

–

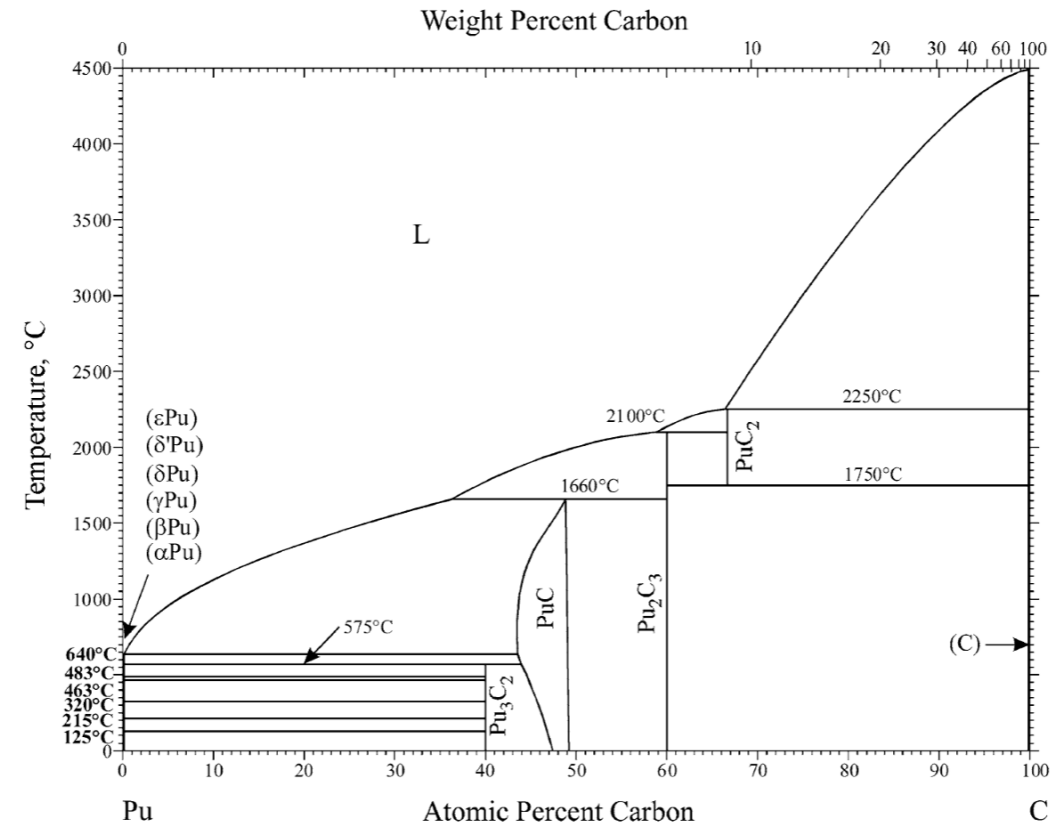
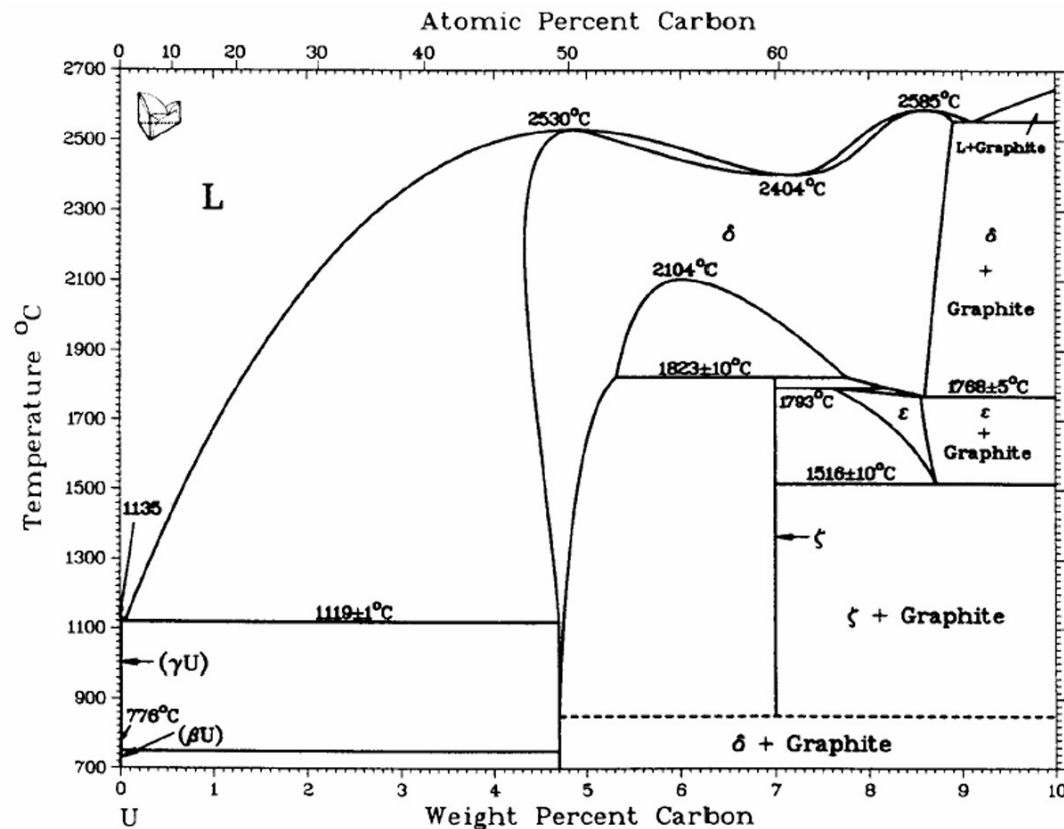
–

bcc – eight molecules
 per unit cell
 $T_d^6 - I \bar{4}3d$ (Nr.220)



Phase Diagrams of Carbides

- The differences in the UC/PuC diagrams are mainly due to (i) the presence of Pu_3C_2 compound, (ii) the low stability of PuC compared to UC, and (iii) the high stability of Pu_2C_3 compared to U_2C_3



Key Properties

- The thermophysical properties that are of importance and affect the fuel performance are solidus/liquidus temperature, thermal conductivity, coefficient of thermal expansion, elastic/fracture properties, creep, and hardness at ambient and at high temperatures
- The solidus/liquidus temperatures along with thermal conductivity limit the fuel operating temperature in terms of linear heating rate
- Thermal conductivity varies as a function of density, porosity (shape, size, and distribution), composition, presence of a second phase, grain size, etc.
- Coefficient of thermal expansion is an important design parameter, the stresses generated in the fuel and by the fuel in the cladding are partly due to the difference in the CTE between the fuel and the cladding

Key Properties

- The elastic and fracture properties of the fuel are primarily responsible for the extent and severity of FCMI
- Both thermal-induced and irradiation-induced creep of the fuel also determine the extent of FCMI
- Mechanical and creep properties depend on composition, second phases, grain size, etc.
- Pu lowers melting point, decreases thermal conductivity, increases expansion, and softens the fuel

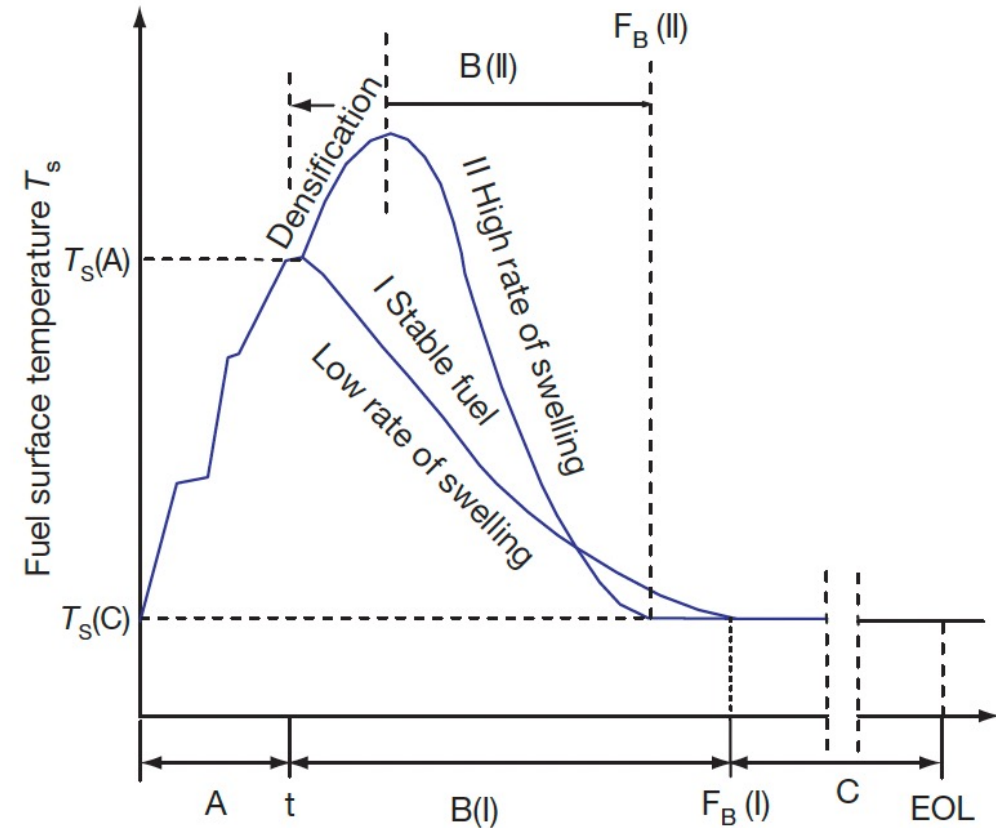
<i>Properties</i>	<i>(U_{0.3}Pu_{0.7})C</i>	<i>(U_{0.8}Pu_{0.2})C</i>
Solidus temperature (K)	2148	3023
Thermal conductivity (W m ⁻¹ K) at 1273 K	12.0	19.0
Coefficient of thermal expansion (300–1800 K)	13.8×10^{-6}	10.9×10^{-6}
Hardness (MPa) at 1250 K	1200	1400

In-pile behavior

- The in-pile fuel behavior depends to a large extent on the fuel operating temperature, which in turn depends on the type of pin or bond concept, namely, He-bonded fuel or Na-bonded fuel
- A large number of mixed carbide fuels have been irradiated in the US, Europe, Russia, India, and Japan
- The performance analysis of the mixed carbide fuel can be best understood based on their burnup period, the structural changes occurring during the burnup, and subsequently the swelling of the pin

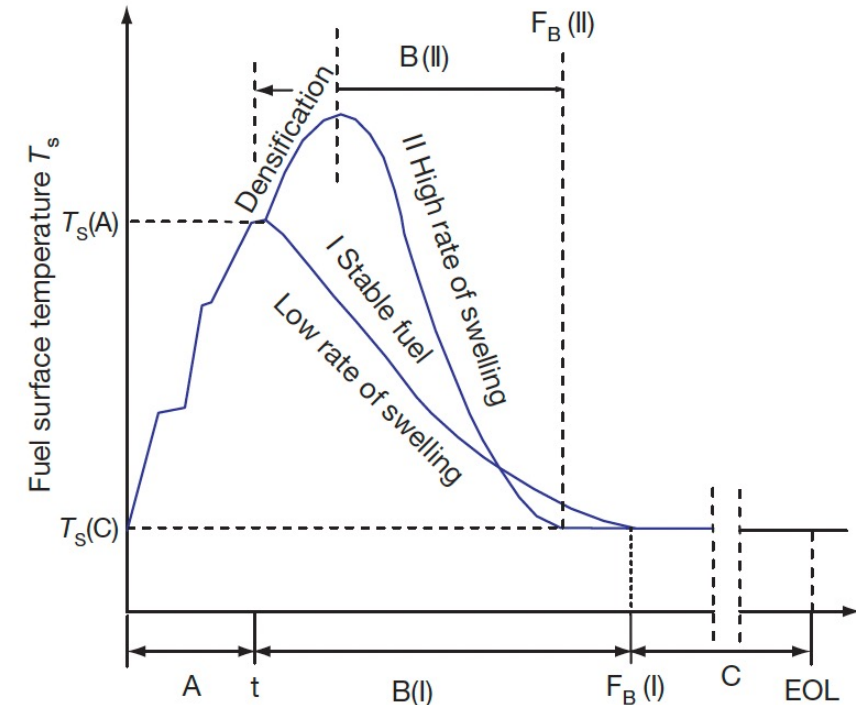
Burnup Stages

- Stage A: At the BOL, the fuel undergoes cracking, which results in the movement of the fragmented fuel toward the cladding surface
- The fuel-clad gap partly reduces but does not close
- Fuel sees a dramatic increase in temperature due to cracking
- Stage A lasts for a few days



Burnup Stages

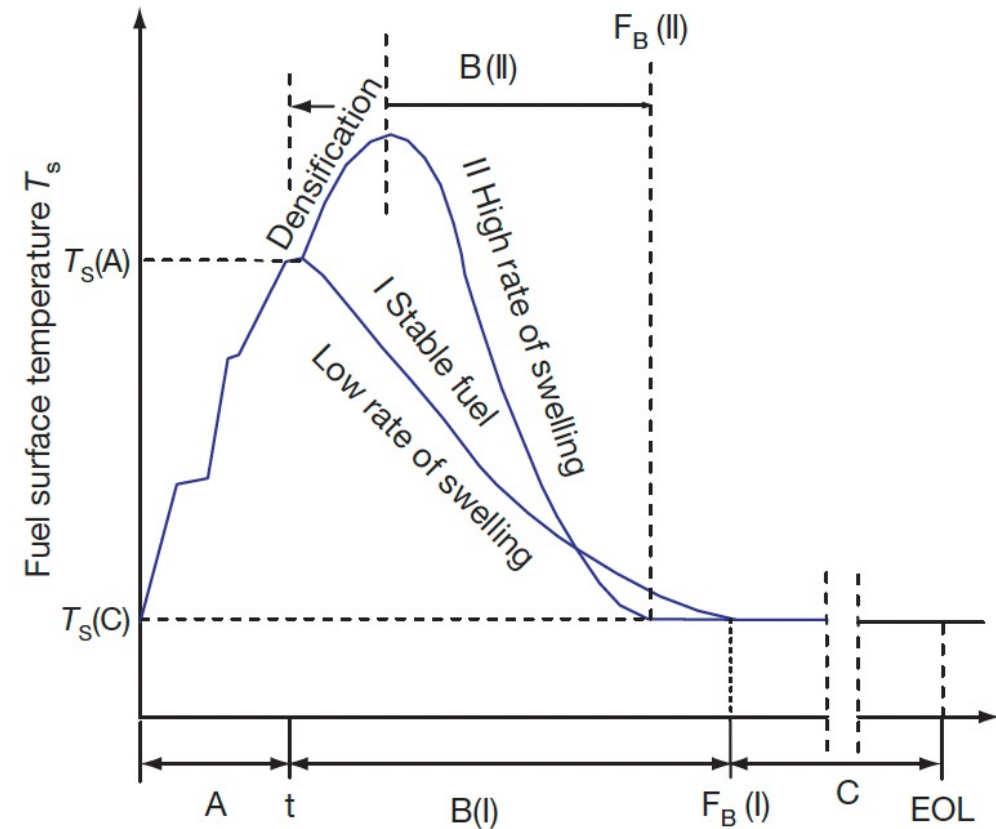
- Stage B: Fuel undergoes unrestrained free swelling, crack healing, or resintering
- Resintering/densification occurs for thermally unstable or low density fuels, which causes an initial increase in gap size resulting in the rise in the fuel surface temperature
- In stage B, free swelling occurs and crack healing starts, which results in the relocation of fuel fragments further from the center of the fuel to the periphery
- Swelling causes fuel-clad gap closure, increase in heat transfer coefficient, and decrease in fuel surface temperature



- Surface roughness of fuel and cladding limits complete gap closure
- FCMI begins due to the swelling of the fuel
- Stage B ends after a burnup of approximately 3 at.%

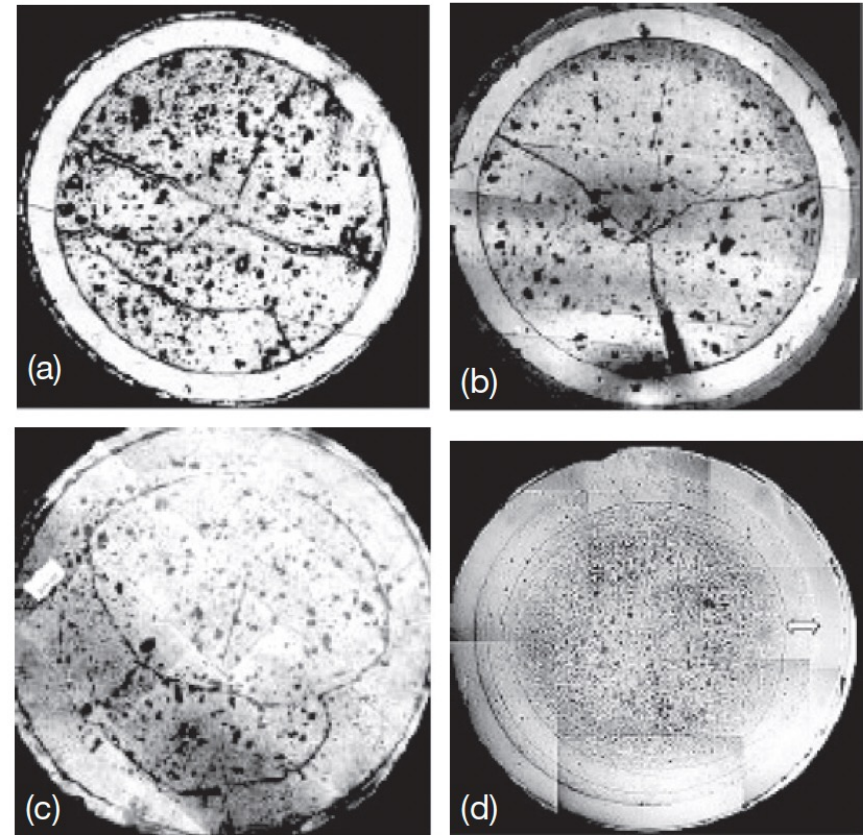
Burnup Stages

- Stage C
- This stage starts after fuel–clad gap closure when a steady minimum surface temperature is reached, and it continues until the end of fuel life
- For carbide fuel, this could be up to 15 at.%
- At this stage, more homogeneous fuel–clad interaction starts



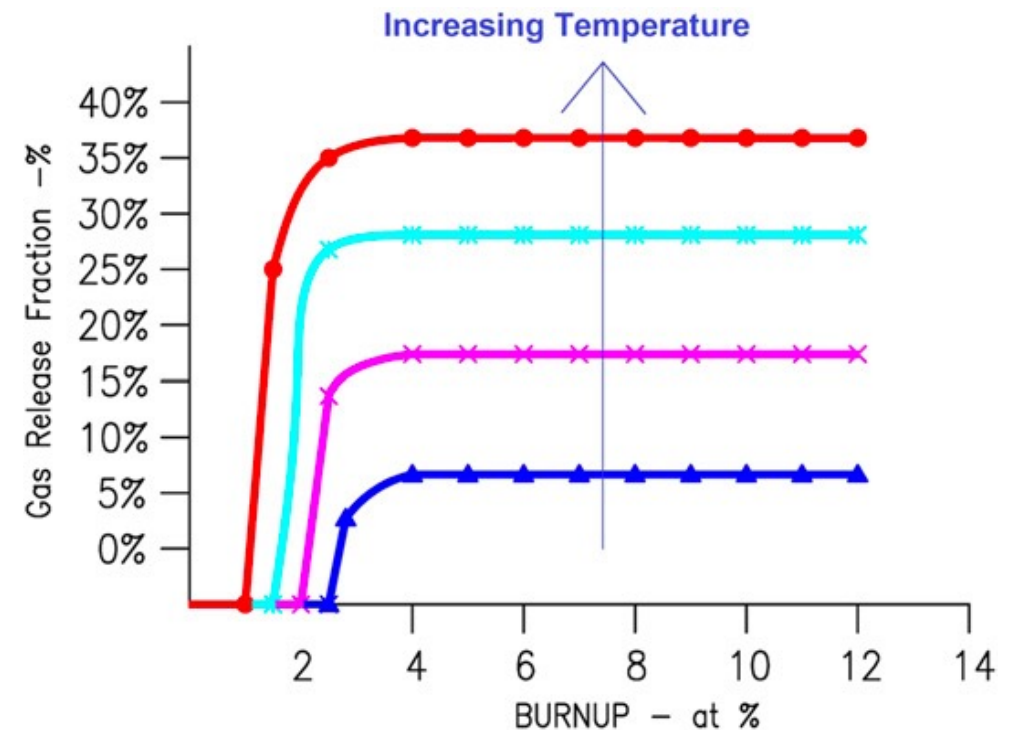
Evolution with Burnup

- Carbide fuel containing 70% and 55% PuC was used as the driver fuel for FBTR
- PIE at burnups of 2.5, 5, 10, and 15.5 at.% shows the evolution of the pin
- After 10 at.% burnup, the gaps had closed at the center of the fuel column
- Circumferential cracks due to thermal stresses formed, and a discrete zone free from any porosity is observed near the outer region



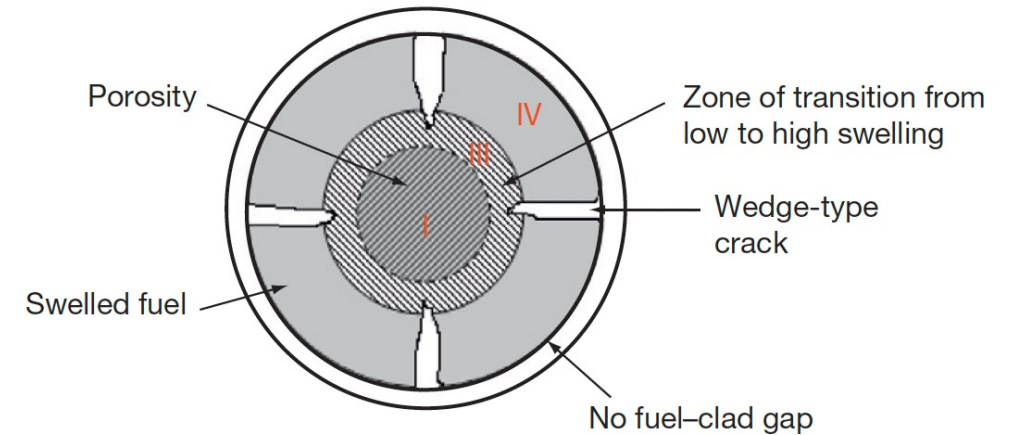
Fission Gas Release

- FGR in carbide fuel pins is lower than oxide fuel pins, mainly due to lower temperatures
- Release rates from carbide are $<1\%$ at temperatures below 900 C but rise to about 5%–10% with temperature rising to 1200 C
- Above 1200 C, gas release is associated with bubble growth and interlinkage at grain boundaries, as in oxide fuels
- Low density fuel releases more FG than high density, due to additional porosity
- Off-stoichiometry also promotes porosity, and thus increases FGR

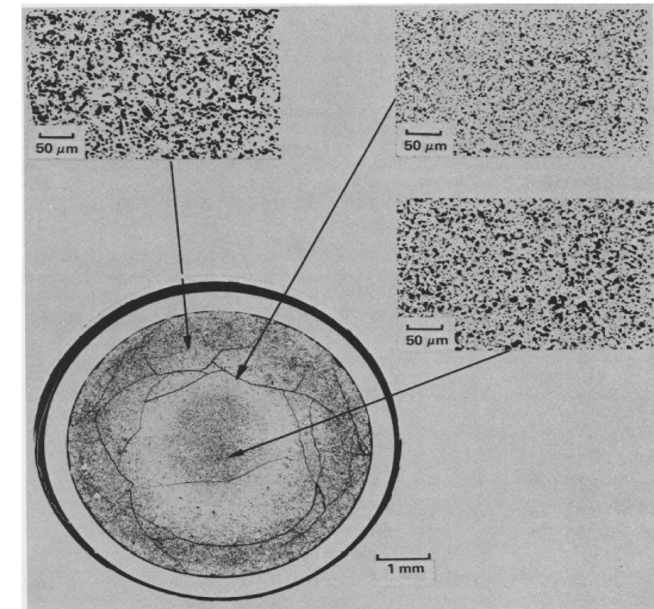


Fuel Restructuring

- The cross section can be divided into four structural zones, become well defined when the fuel sees a burnup of 1.3 at.%.
- Zone 1 is the porous fuel at the center having high temperature and helps in the release of fission gases
- Zone 3 contributes to high microscopic swelling
- Zone-IV is the coolest zone of the fuel cross section, which is next to the fuel cladding
- Zone 2 is an intermediate zone that only exists at very high heating rate (>100 kW/m)

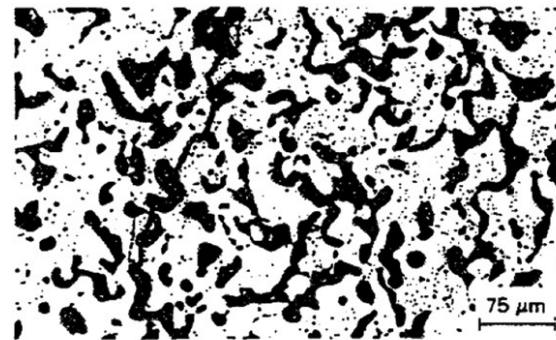


(c) End of stage B, Zone I: cracks transformed to porosity, wedge cracks in Zone III and Zone IV

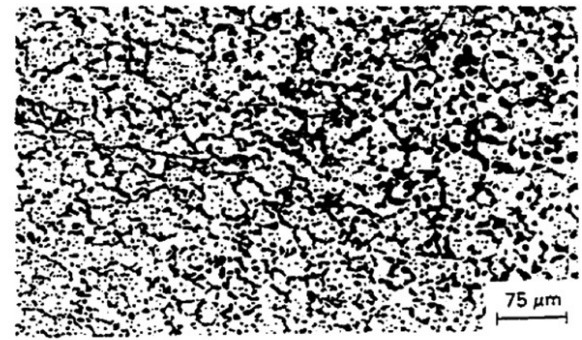


Fuel Restructuring

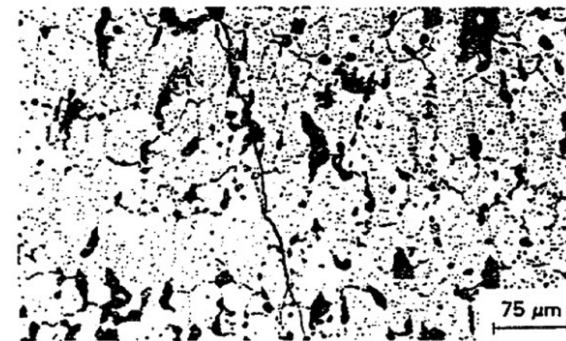
- Zone 1 has large bubbles, interconnected porosity
- Zone 2 exhibits grain growth parallel to the temperature gradient, similar to columnar grains in MOX fuel
- Zone 3 has coaxial grain growth and developed porosity
- Zone 4 typically has a stable grain size and near as-fabricated porosity
- Zone 2 does not always form, expected to form at higher temperatures
- At low LHR (<50 kW/m) no restructuring is observed



Zone I at relative radius $\frac{r}{r_0} = 0.26$



Zone III at relative radius $\frac{r}{r_0} = 0.71$



Zone II at relative radius $\frac{r}{r_0} = 0.56$



Zone IV at Pellet surface

Fuel Creep

- The source of stresses in the fuel under irradiation is the pressure generated by fission gases produced within the fuel
- After the fuel–clad gap closure, free swelling is restrained, and a back stress is generated by the cladding on the fuel
- Unlike close-packed metals, deformation of carbide requires much higher stresses because of the strong covalent bonding existing between the metal atom and the carbon atom
- Two types of creep deformation are operative in the fuel: temperature-dependent thermal creep and irradiation creep
- Thermal creep has been shown to start at 1000C and dominate over radiation-induced creep
- The steady-state creep curve has been determined and is a function of stress, temperature, composition, grain size, and impurity content in the fuel

$$\dot{\epsilon} = Ad^{-m}\sigma^n \exp(-\Delta H/RT)$$

Fuel Creep

- Steady-state creep data of UC_{1-x} and MC_{1+x} at a stress of 20 MPa
- Substantial creep only exists for a limited part of the fuel, and thus most of the fuel acts as a brittle material
- Irradiation-induced creep is independent of temperature, but increases with fluence
- Additional porosity or second phases will change this data
- No data on creep of high-Pu mixed carbide or Pu-C fuel exists

