NE 591: Advanced Reactor Materials

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Dr. Benjamin Beeler

Last Time

- QE overview
- Carbides have higher U density and better thermal conductivity than UO2, and a higher melting point than metallic fuel
- Carbide fuels are used as a breeder or burner fuel, with a Na or He bond

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 determines rate of heat transfer out of fuel and into the cladding
- 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

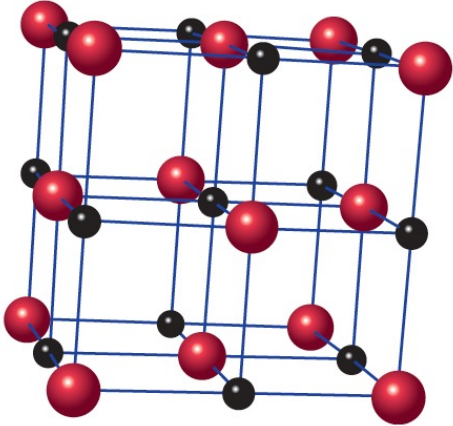| Properties	$(U_{0.3}Pu_{0.7})C$	$(U_{0.8}Pu_{0.2})C$
Solidus temperature (K)	2148	3023
Thermal conductivity ($W\,m^{-1}\,K$) at 1273 K	12.0	19.0
Coefficient of thermal expansion (300–1800 K)	13.8×10^{-6}	10.9×10^{-6}
Hardness (MPa) at 1250 K	1200	1400

Phase Diagrams of Carbides
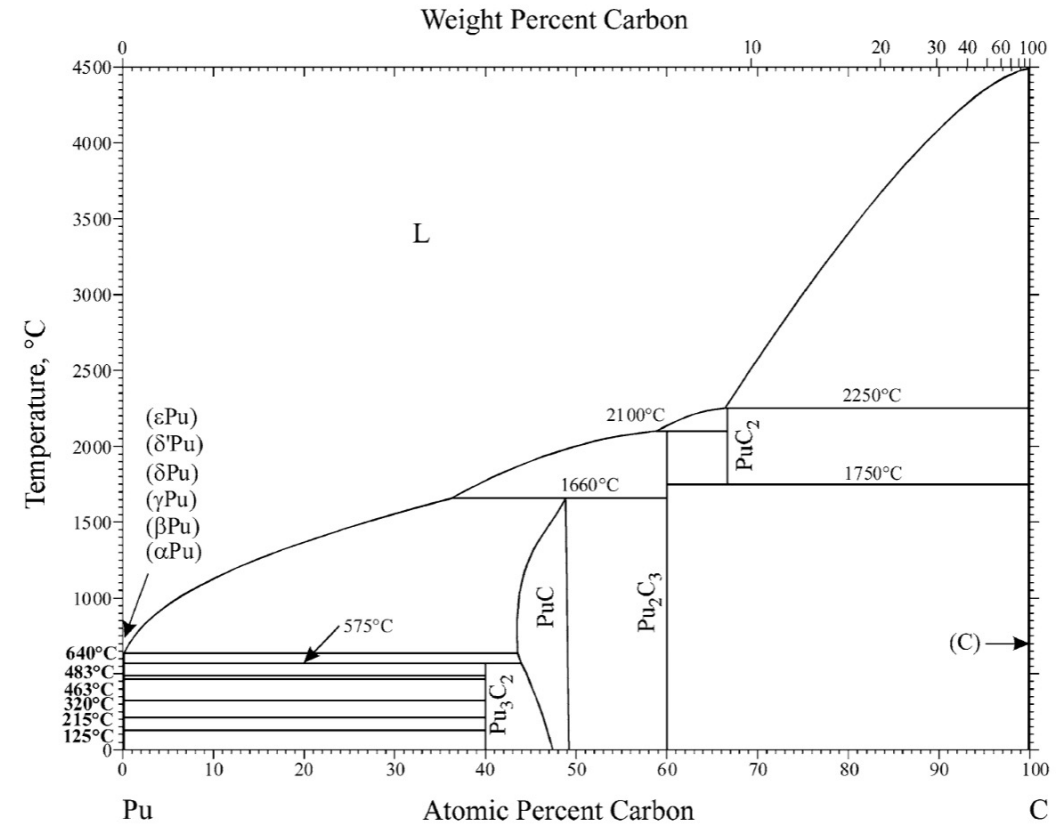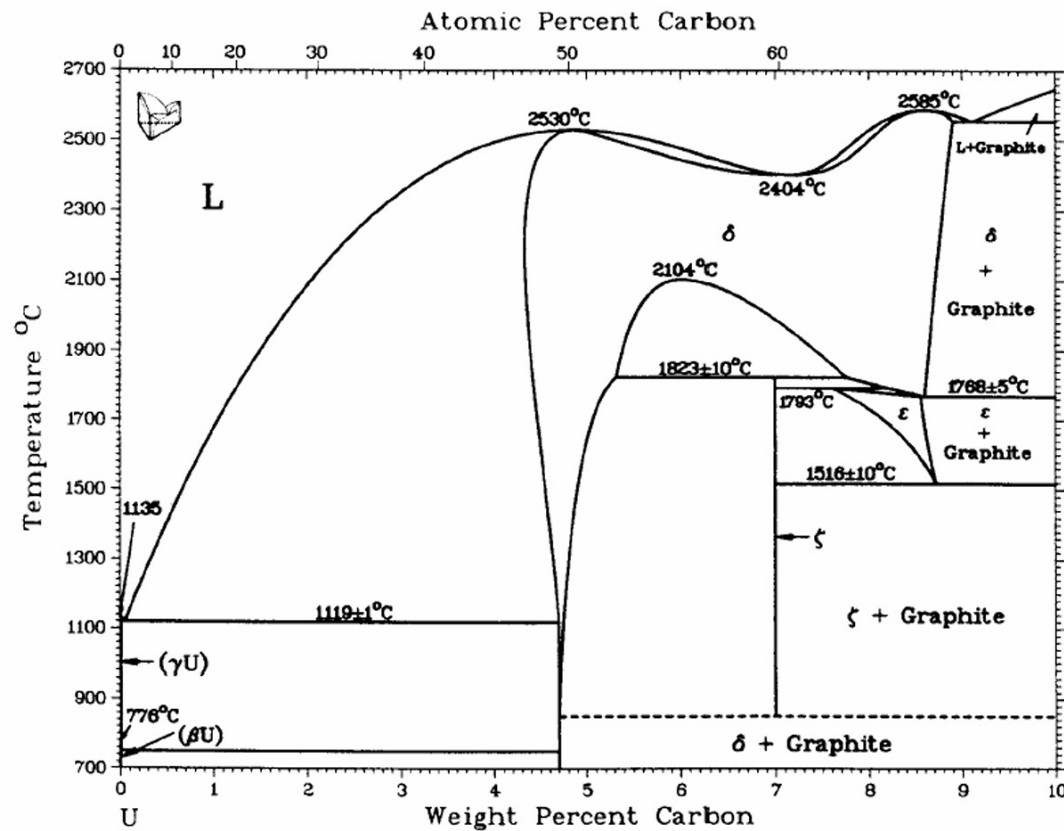
U/Pu-C Chemistry

- Uranium forms three compounds with carbon: UC, U2C3, and UC2
- U2C3 has a fixed stoichiometry (is a line compound)
- UC is stable over a wide temperature and composition range, with a melting point of ~2800 K
- UC2 is stable in two phases, alpha-UC2 and beta-UC2
- U2C3 decomposes into UC+alpha-UC2 on heating from 2096 to 2110K and into UC+C below 1400 K

- The Pu–C system has four compounds: Pu3C2, PuC1–x, Pu2C3, and PuC2
- The compound Pu3C2 decomposes into Pu+PuC at 848 K
- The differences in the UC/PuC diagrams are mainly due to (i) the presence of Pu3C2 compound, (ii) the low stability of PuC compared to UC, and (iii) the high stability of Pu2C3 compared to U2C3

U/Pu-C Phase

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

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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

Th_2C_3
855.13 ≤ a ≤ 856.09 pm in a narrow homogeneity range

U_2C_3
808.99 pm

Np_2C_3
810.3 pm

Pu_2C_3
812.1 ≤ a ≤ 813.4

Am_2C_3
827.57 pm

Cm_2C_3
839.4 pm

Th_2C_{3-y} ($0 \leq y \leq 0.05$)
Under high
$p > 2.8\,GPa$

$U_2C_3 \rightarrow UC + UC_2$
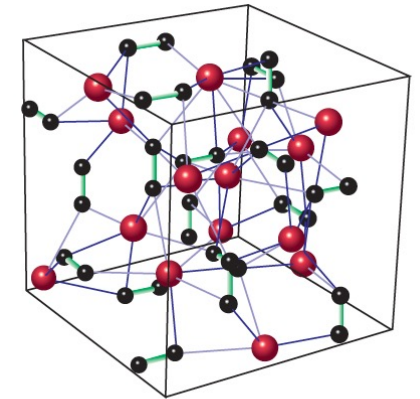($> 2093\,K$)

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$C/Pu = 1.45-1.5$
Stable under 2300 K

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

Phase Properties

- UC and PuC are highly dense with fcc octahedral holes occupied by carbon atoms

- The brittleness of carbides 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 carbon bonds not wanting to form octahedral ligands

- The high density and low FP solubility of UC leads to higher swelling than UO_2

- The U_2C_3 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

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, Na-bonded fuel, or He-bonded particle fuels

- 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
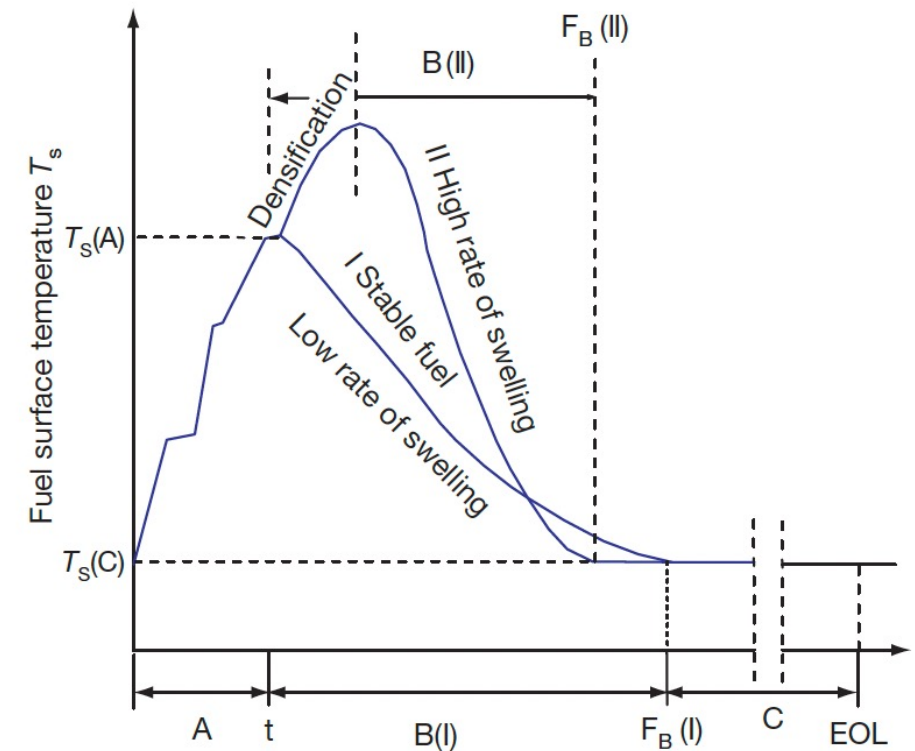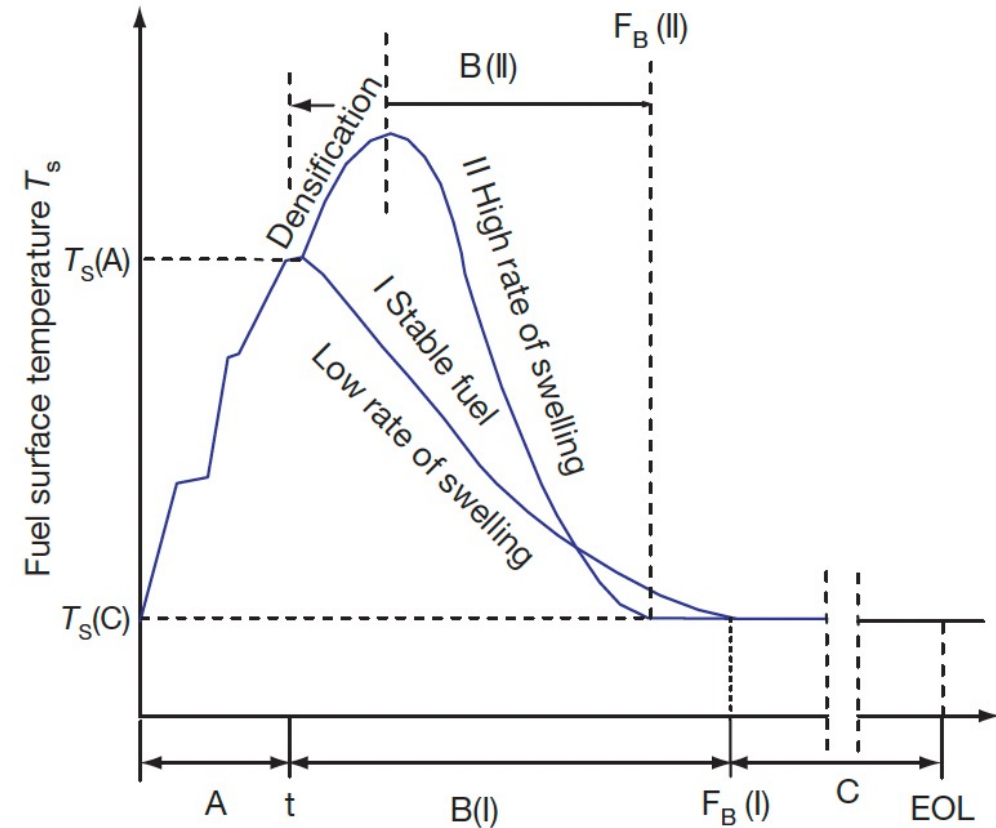
Burnup Stages

- 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
- Stage A lasts for a few days

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

Burnup Stages

- Stage B-cont.
- 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
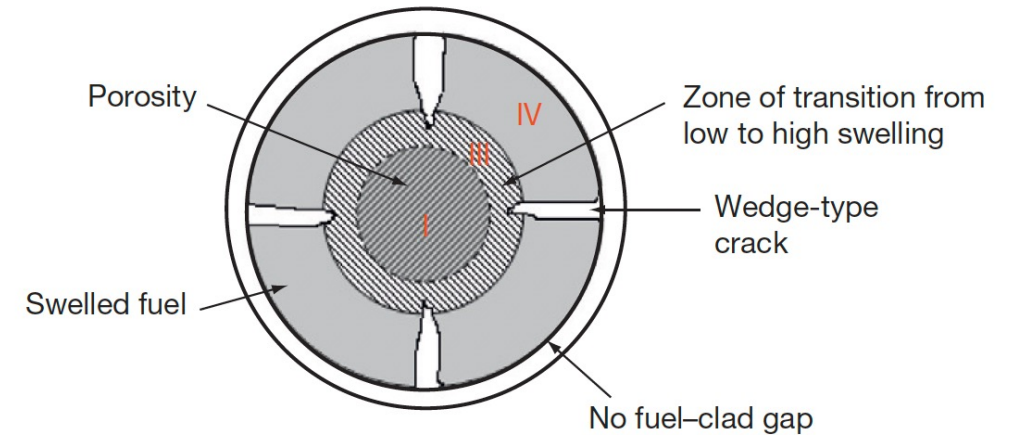- Stage B ends after a burnup of approximately 3 at.%

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Burnup Stages

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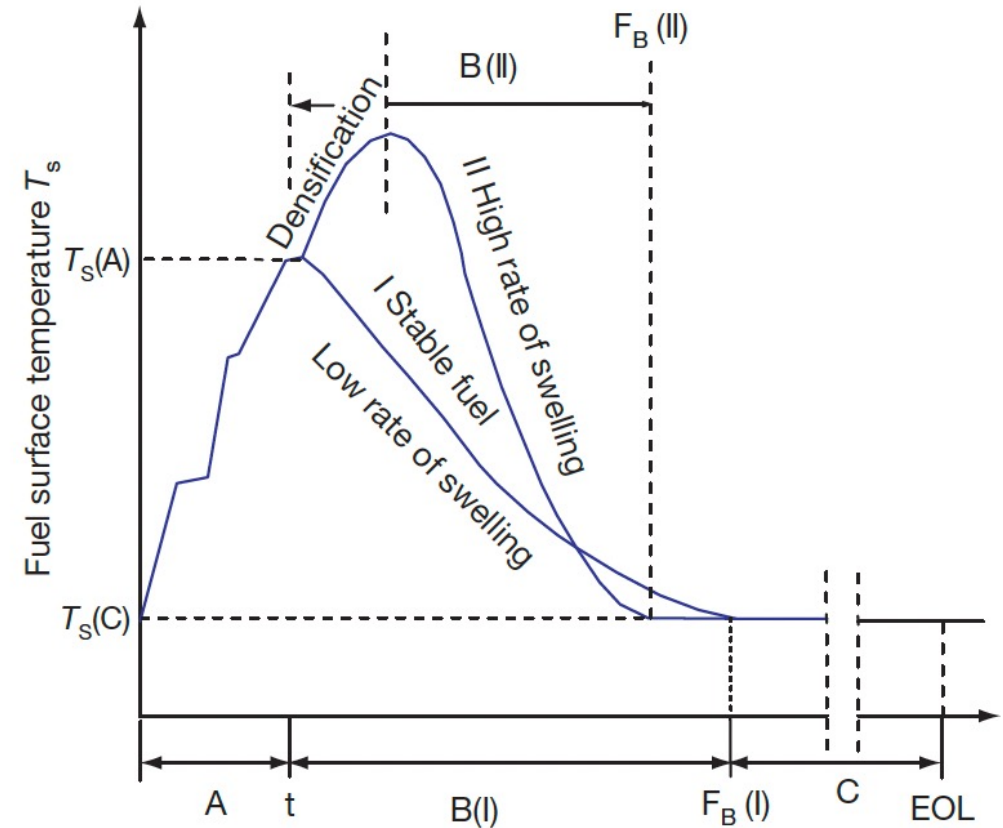
Fuel Restructuring

- 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 2 is an intermediate zone that only exists at very high heating rate (>1200W/cm)

- Zone-IV is the coolest zone of the fuel cross section, which is next to the fuel cladding

Porosity — IV — Zone of transition from low to high swelling

III

I — Wedge-type crack

Swelled fuel — No fuel–clad gap

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

Na Bonded Pin Performance

- For the sodium-bonded fuel pin, the smear density is lower than that of He-bonded fuel

- This allows for the manufacture of a denser fuel with less initial porosity

- In the beginning (stage A), the fresh fuel fractures, reducing thermoelastic stresses and drastically changing temperature gradient of the fuel

- There is no abrupt change in fuel temperature in this concept

- The lower temperature of the sodium-bonded pin keeps the swelling rate of the fuel low

- The decrease in thermal conductivity with burnup is compensated by a slow decrease in linear heating

- FCMI can be avoided till end of life by proper selection of initial fuel–clad gap

- Na bond acts like a medium for transfer of C from the fuel to clad, causing clad carburization

He Bonded Pin Performance

- He bonding is the most preferred bonding concept of carbide fuel, due to cost and the potential for Na bond deterioration at high burnup

- The in-pile performance of the He-bonded pin depends to a large extent on the porosity of the as-fabricated fuel

- The initial temperature rise is much higher at the beginning of life because of the lower thermal conductivity of the He bond compared to Na bond

- The lower thermal conductivity of the He bond requires the reduction of the fuel–clad gap compared to the Na-bonded fuel

- The fuel density for He bonded fuel is lower and has a fabrication porosity of about 15%

- The gap closure in the early burnup period results in lowering of the fuel temperature, and free swelling changes into restrained swelling under the contact pressure developed at the clad–fuel interface

Pin Failure

- The mechanical properties of the fuel and clad (creep, fracture toughness) largely predict the fuel behavior after gap closure

- Cladding breaches due to FCMI or FCCI can be due to loss of ductility of the clad, carburization of the clad, or fuel swelling

- Clad carburization makes the clad surface hard and brittle and cracks form and propagate easily

- It has been observed that the He-bonded pin can be operated safely up to 15 at.% burnup (peak burnup 20 at.%).

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 clad 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

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

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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
- No data on creep of U/Pu-C or Pu-C fuel exists
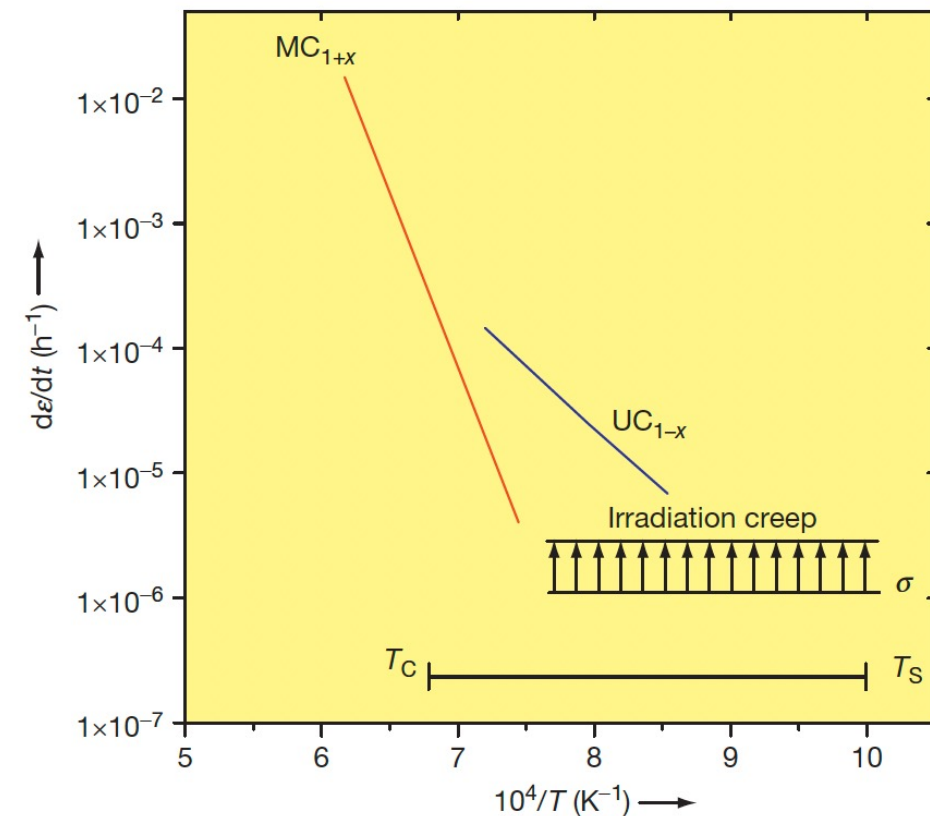
Irradiation Performance

- 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
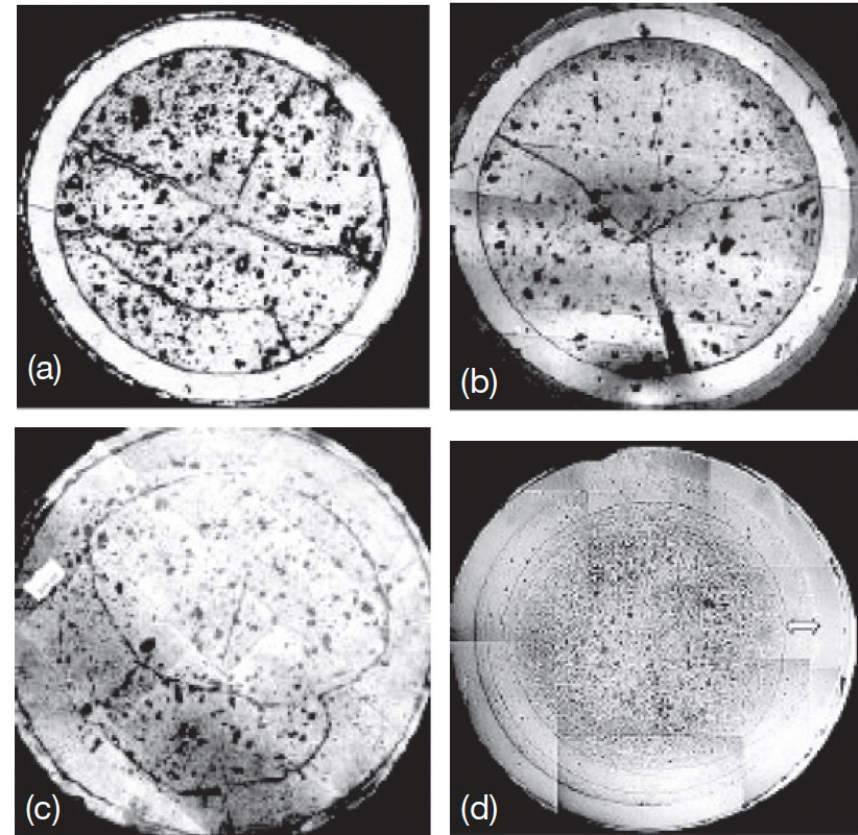
FCCI

- Carbon activity and partial pressure of CO are important parameters responsible for clad carburization

- In sodium-bonded fuel, carbon transfer from the fuel to the clad takes place by dissolution of carbon in sodium liquid

- In He-bonded fuel pins, carbon transfer takes place through CO

- Out-of-pile testing with Na-bonded fuel showed carburization above 1000 K, with hardening of the SS316 cladding up to 100 μm

- Carburization typically takes the form of carbide precipitation along the grain boundaries and slip lines

- The depth of carburization in Na-bonded fuel was greater than in the He-bonded pins

Indentations

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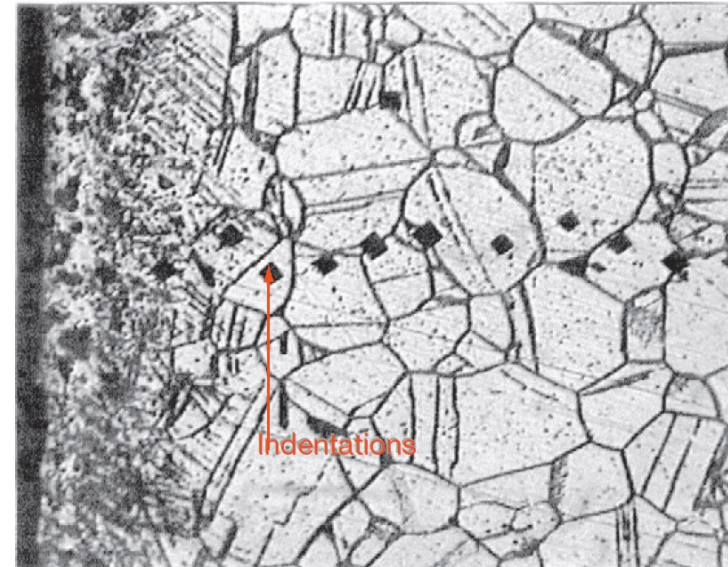
C/M Ratio

- The fission of uranium–plutonium MC results in the formation of different types of fission products
- The fission products generated may form dicarbides or monocarbides depending upon the carbon potential in the fuel
- This may cause decrease in the C/M ratio and result in the formation of metal phase U/Pu, which forms low-melting eutectic with the components of the cladding material

- Thus, a hyperstoichiometric fuel is always preferred for carbides
- The extent of hyperstoichiometry (M2C3 content) in the initial fuel composition is determined by the target burnup, with additional C required for longer burnups
- Thermodynamic calculations have shown that rare earth elements show more solubility in M2C3 than in the MC phase of the fuel, and that lanthanides make stable sesquicarbides and dicarbides

Carbide Fabrication

- Fabrication of carbide fuel on commercial scale is a difficult task and needs additional care because of its pyrophoricity, high radio toxicity, and the concern for criticality restricts the batch size

- Carbide powders formed during carbothermic reduction of oxides are prone to oxidation and hydrolysis

- This requires high-purity inert-gas cover in the fabrication line consisting of glove boxes

Fabrication Techniques

- Melting casting
- In this method, UO2 or U metal chips with graphite are arc-melted and made into the form of a button
- Melting casting route results in large-grained materials compared to that obtained by powder metallurgical methods
- The melting casting method is, however, uneconomical due to the high cost of metal fabrication

- Metal hydriding– dehydriding
- This method is followed for small-scale production of high-purity carbides, where the metal hydride reacts with graphite
- Actinide carbides MC and M2C3 can be prepared from a mixture of hydride and graphite $PuH_2 + 0.85C \rightarrow PuC_{0.85} + H_2(g)$
- For UC, the reaction between uranium metal and a hydrocarbon gas (methane) is carried out with careful control of the hydrocarbon flow

Carbothermic Reduction

- Uranium monocarbide is produced by carbothermic reduction of UO2 and carbon following the reaction

$$UO_2 + 2C \rightarrow UC_2 + CO$$

$$UO_2 + UC_2 \rightarrow 2UC + CO$$
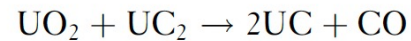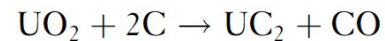
- A mixture of UO2 and carbon is blended together and the mixture is compacted at 300–600MPa pressure along with an organic binder

- The pellets are heated in a vacuum induction furnace and ground to a powder for compaction
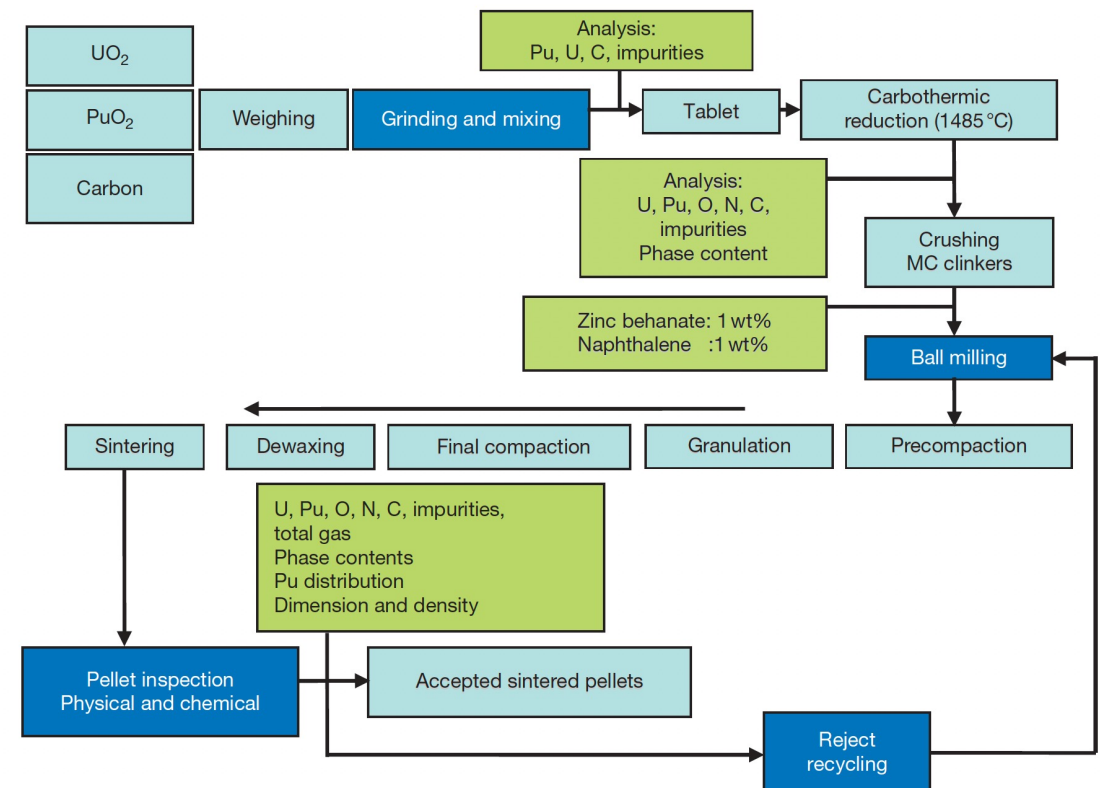
Carbothermic Reduction

- Uranium–plutonium-mixed carbide is also prepared by carbothermic reduction of UO2–PuO2

- The reaction is complicated by the uneven distribution of plutonium in the two carbide phases and the formation of CO2 and CO, especially in hyperstoichiometric feedstock

- Pu can volatilize and evaporate, which needs to be controlled via increased CO partial pressure
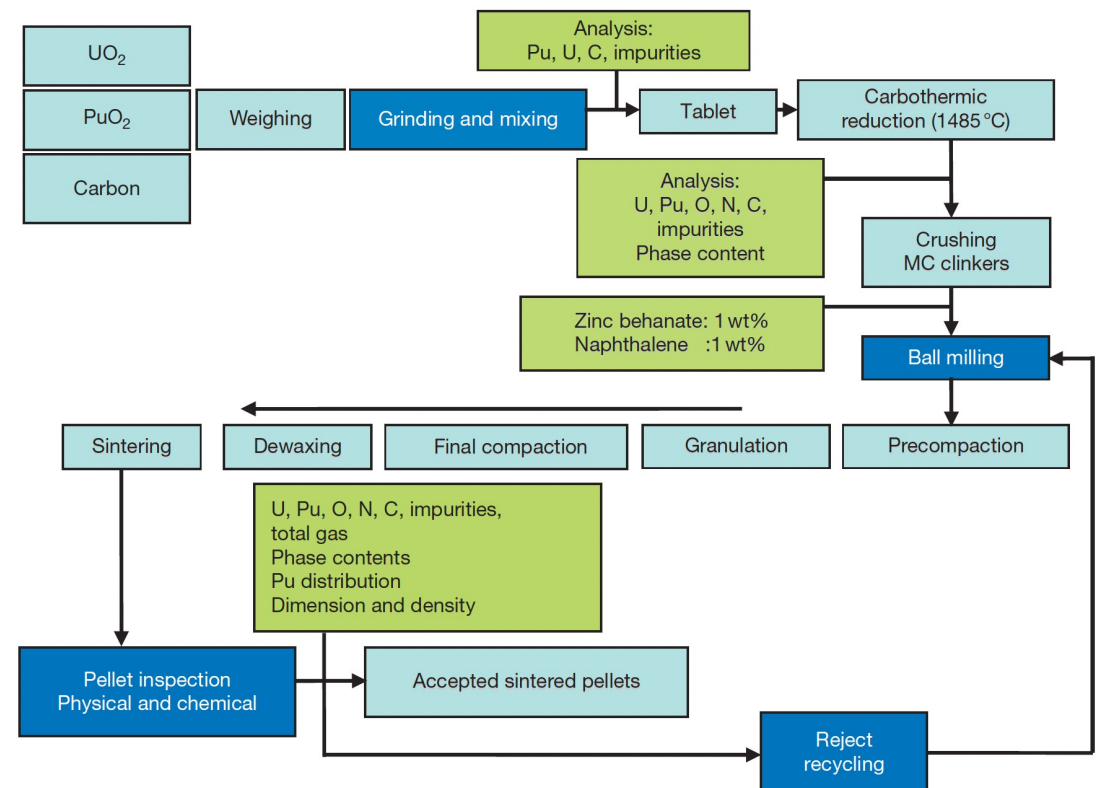
Pressing

- The conventional powder metallurgy route of carbide fuel fabrication has certain disadvantages, including pick up of O impurity from the cover gas and risks of pyrophoricity

- Direct pressing takes the product of carbothermic reduction and presses them into a low density pellet, which can be sintered into the final product

- This reduces O pickup, reduces dust and impurities, and reduces time/cost

- There is an additional route that involves wet processing of nitrate-based fuels in a sol-gel technique
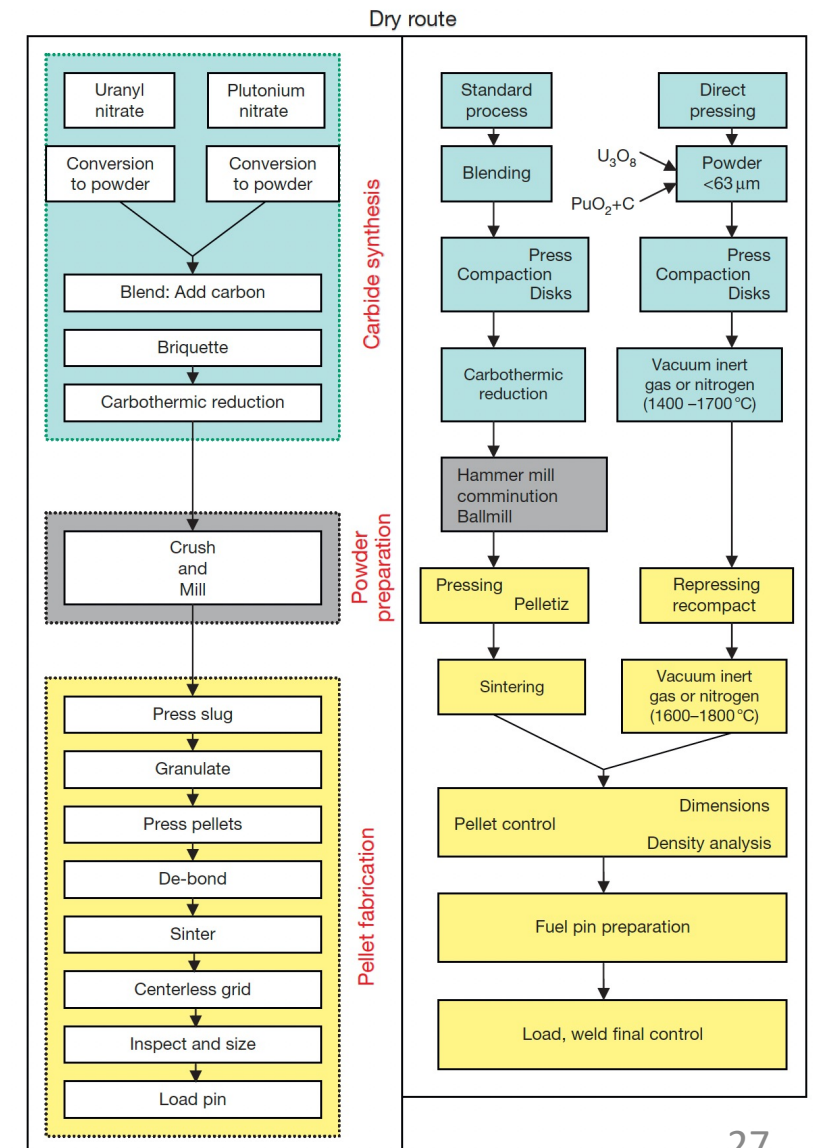
Summary

- Key thermophysical properties includes thermal conductivity, CTE, creep, etc., and vary strongly based upon composition
- Two primary phases: UC and U2C3
- Three stages in burnup that affect centerline temperature
- Fuel restructures into typically three zones with variable porosity
- Carburization of cladding is the key FCCI phenomenon
- Control of C/M ratio via initial hyperstoichiometry prevents low melting metal phases forming
- Carbothermic reduction is primary fabrication route