

NE 795: Advanced Reactor Materials

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Dr. Benjamin Beeler

Last Time

- Carbides have high fissile density and high thermal conductivity
- He-bonded and Na-bonded designs for liquid metal or gas cooled reactors
- Higher swelling and lower FGR than oxide fuels
- Two primary phases: UC and U₂C₃
- Three stages in burnup that affect fuel temperature
- FGR dependent upon temperature, occurs <3 at% burnup
- Fuel restructures into typically three zones with variable porosity
- Properties dependent upon impurities and composition

Carbide FCCI

- FCCI in fuel pins containing carbide fuel consists of clad carburization, slight reaction with FPs, and formation of intermetallic compounds
- Carbides generally present fewer compatibility problems than MOX fuels
- Chemical Reactions with FPs
- Very little available oxygen leads to FP-C interactions, and we have an expected decrease in C/M ratio with burnup
- Significant FP-cladding interactions are generally not seen
- Some Te intergranular attack, some reaction with iodine
- Generally not a concern

Carbide FCCI

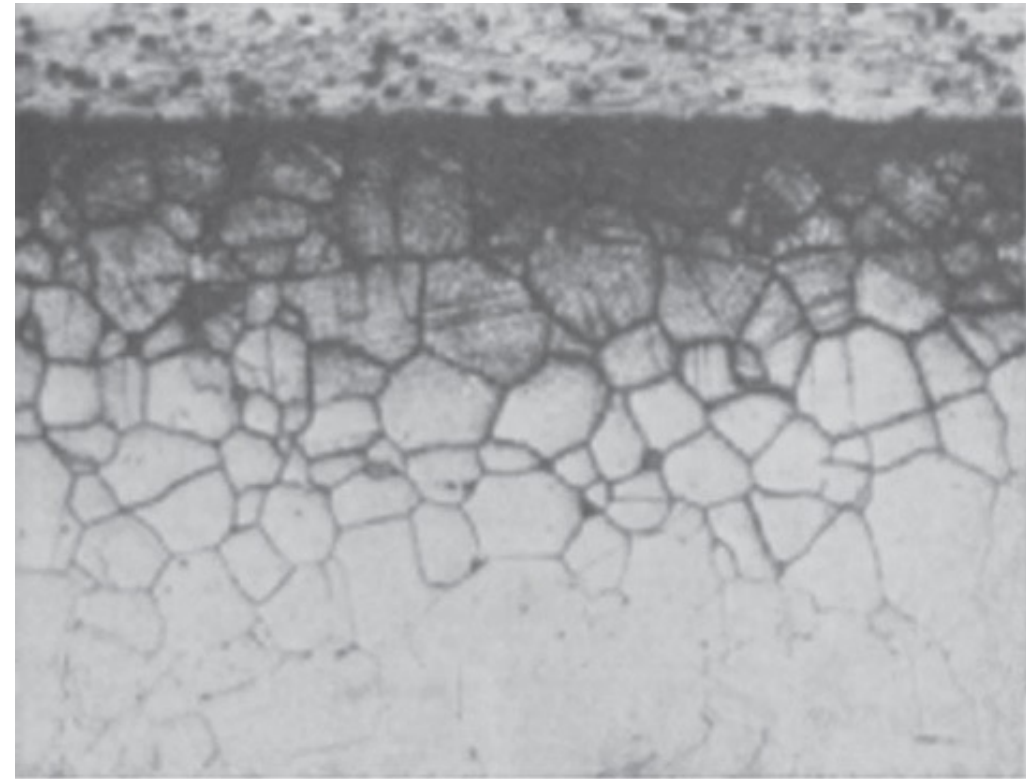
- Low melting phases
- Hypostoichiometric carbide fuels can contain U/Pu metal as a second phase which can form intermetallic compounds with the cladding
- Experimental compatibility tests of (U,Pu)C with cladding have shown intermetallic compounds such as (U,Pu)Fe₂ or (U,Pu)Ni₅ in the fuel and cladding interface
- At typical fuel surface temperatures (~1000K), reaction rates should be slow to create intermetallics
- However, if sufficient hypostoichiometry is present, can react to form intermetallics

Table 4 Reaction between UC and metals and alloys

Al	UC reacts with Al to produce UAl ₃ and UAl ₄ in 24 h at 620°C
Be	Pseudobinary between UC and UBe ₁₃ , UC–Be ₂ C. UC dissolves 20 mol% Be ₂ C at 1700°C
Bi	No reaction at 950°C
Co	Possible pseudobinary, little solubility
Cr	UC–Cr pseudobinary, eutectic at ~1100°C. No mutual solubility between UC and Cr
Cu	UC–Cu pseudobinary
Fe	Pseudobinary UC–Fe, eutectic at 1100°C
Hf	Complete solubility of HfC–UC; probable increase in m.p. (HfC m.p. 3900°C)
Mo	UC + Mo → Mo ₂ C at 1000°C
Na	No reaction at 871°C
Nb	Complete solubility of NbC–UC; NbC melts 3485°C. Nb–UC compatible
Ni	UC–U ₆ Ni pseudobinary
Pb	No reaction
Pu	Large range of solubility of Pu in UC and possibly of Pu in U ₂ C ₃
Re	Simple eutectic at 1850°C
Si	UC + 3Si → USi ₃ + C at 1000°C
Sn	No reaction
Ta	Continuous TaC–UC solid solution; Ta + UC → TaC + U
Th	Continuous ThC–UC solid solution
Ti	UC dissolves < 2 mold % TiC
V	UC dissolves 4–9 mol% VC; VC dissolves no UC
W	UC dissolves ~10 °mol% W; W dissolves no UC
Zn	UC wetted-condition not states
Zr	Continuous solid solution between UC and ZrC, rising to ZrC m.p. of 3500°C
Stainless steel (18Cr, 8–12Ni)	No reaction at 800°C for 6 months. 0.10 mm penetration in 6 days at 1100°C. Liquid phase at ~1200°C
Zircaloy-2	Reacts in 1 h at 1200°C but not at 800°C – possible ZrC diffusion barrier
Nb – 40 °at% Ti	Molten phase at 1200°C
Inconel	0.008 mm corrosion in 100 h at 800°C

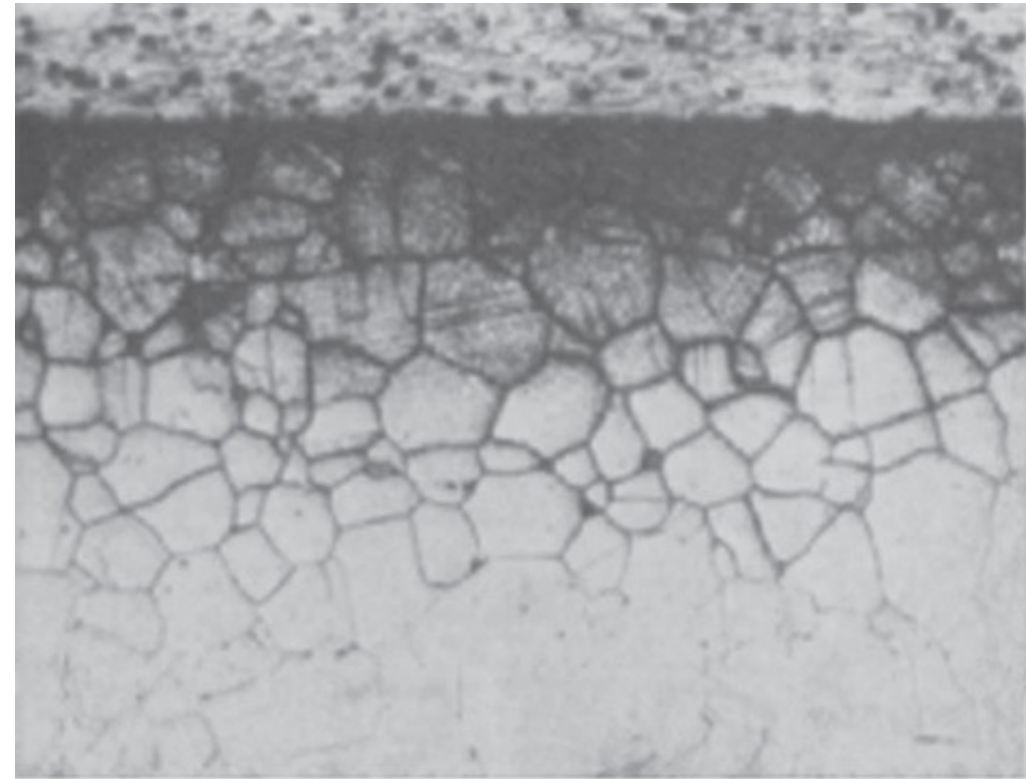
Cladding Carburization

- Carbide fuels are designed to be hyperstoichiometric, which results in a two-phase UC/U₂C₃ microstructure
- The presence of excess carbon prevents the formation of intermetallic phases, but carburizes the cladding
- The decarburization of fuel and the carburization of cladding are governed by the dissolution of carbon atoms from the fuel and then diffusion into cladding
- Cr forms very stable carbides, and carburization often takes the form of Cr₂₃C₆ precipitation



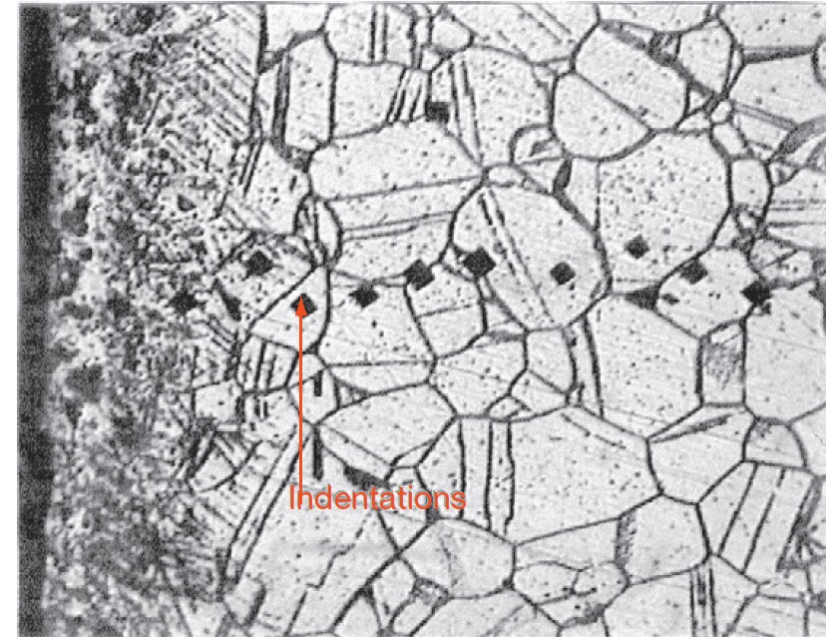
Cladding Carburization

- Cr₂₃C₆ precipitation starts at the grain boundaries, and then can proceed along preferred crystallographic planes
- The carburization proceeds deeper into the material
- The grain boundary carbides can lead to intragranular failure of the steel after only a moderate burnup
- Austenitic stainless steels are very susceptible to carburization and are deemed too brittle if carbon content reaches 0.6 wt. %



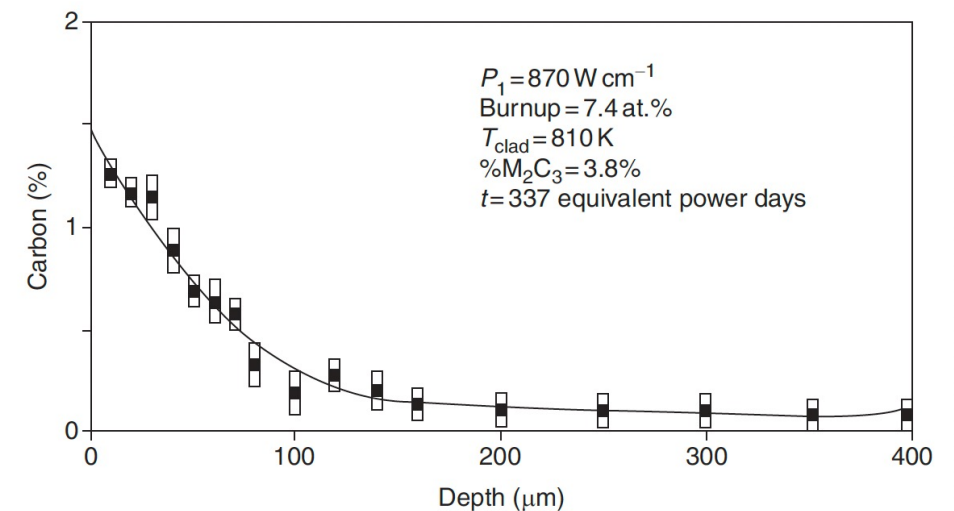
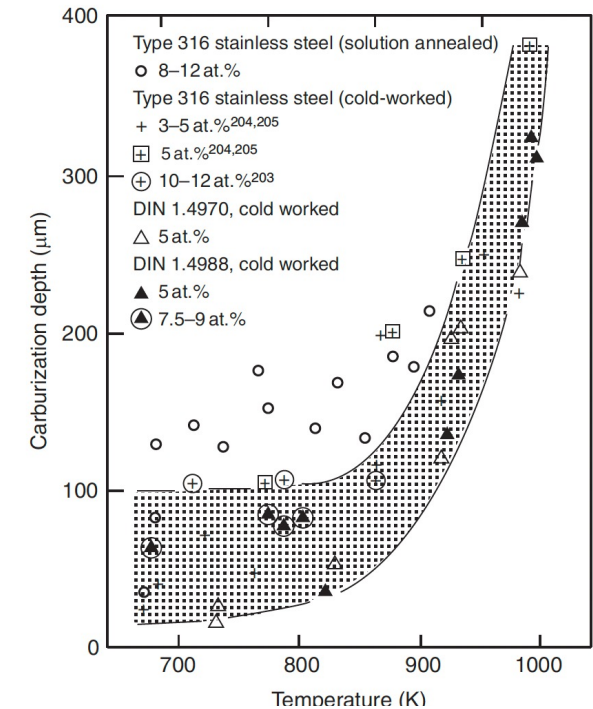
Cladding Carburation

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



Cladding Carburization

- Cladding temperature plays a critical role in carburization
- The temperature gradient in the fuel causes carbon to migrate to colder zones in the fuel, increasing the C/M ratio at the pellet surface
- Carburization depth shows a strong dependence on cladding temperature
- Carbon penetration seems to follow a diffusion process with a constant surface concentration



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 carbon 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.%).

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

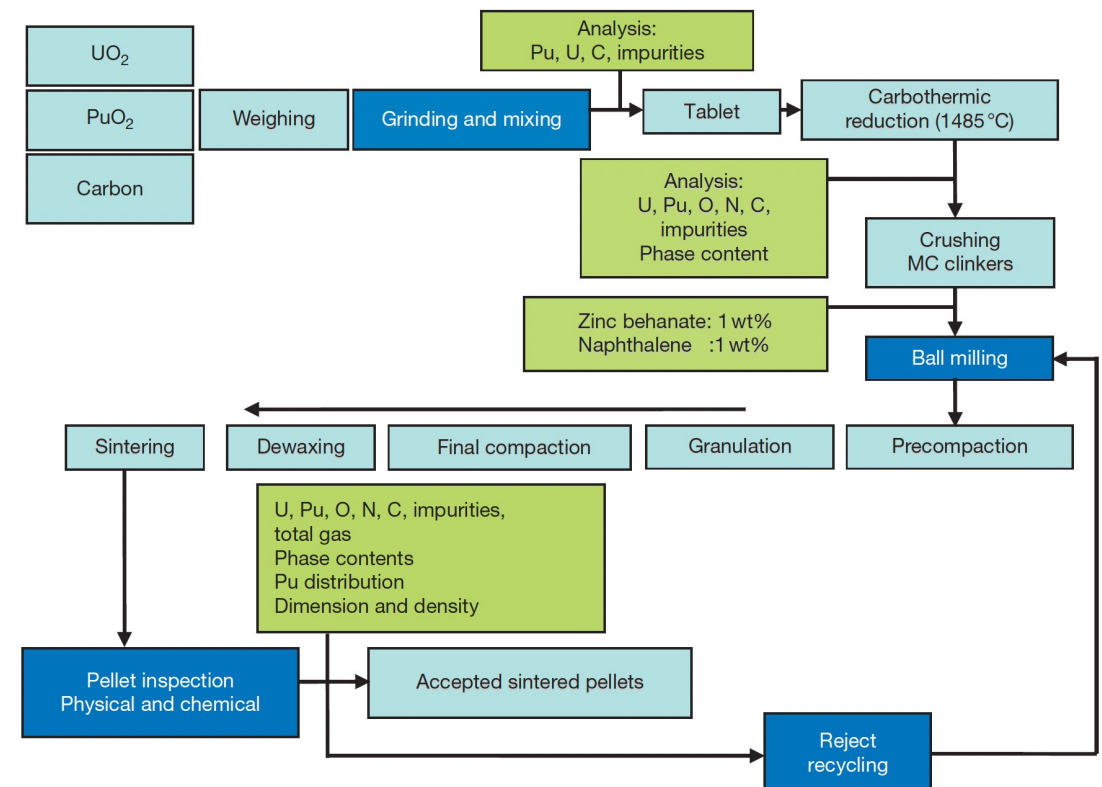
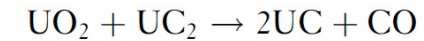
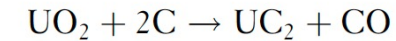


Fabrication Techniques

- 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 $\text{PuH}_2 + 0.85\text{C} \rightarrow \text{PuC}_{0.85} + \text{H}_2(\text{g})$
- For UC, the reaction between uranium metal and a hydrocarbon gas (methane) is carried out with careful control of the hydrocarbon flow

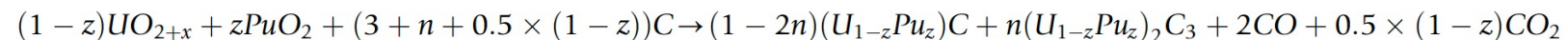
Carbothermic Reduction

- Uranium monocarbide is mainly produced by carbothermic reduction of UO_2 and carbon following the reaction
- A mixture of UO_2 and carbon is blended together and the mixture is compacted at 300–600 MPa along with an organic binder
- The pellets are heated in a vacuum induction furnace and ground to a powder for compaction



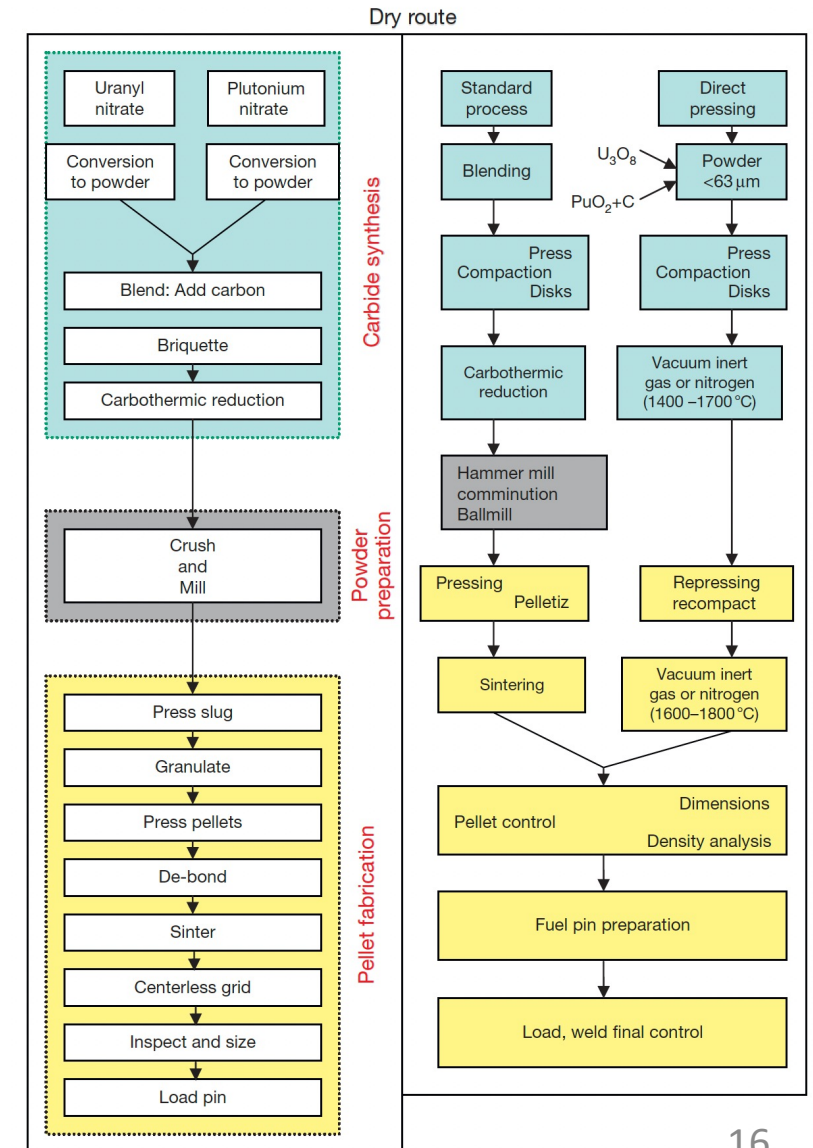
Carbothermic Reduction

- Uranium–plutonium-mixed carbide is also prepared by carbothermic reduction of UO₂–PuO₂
- The physical state and homogeneity of the mixture influences the reaction rate and the quality of the final product
- 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
- Carbothermic reduction temperature also depends on the Pu content of the material



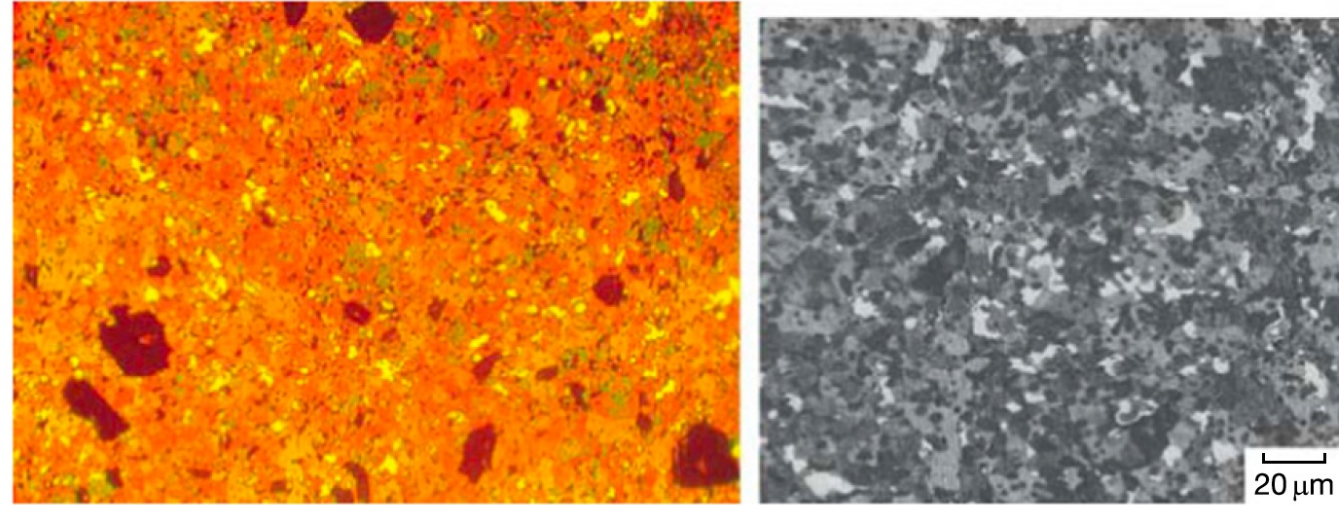
Pressing

- The conventional powder metallurgy route of carbide fuel fabrication has certain disadvantages, including pick up of O/N impurities 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



As-fabricated microstructures

- Carbide pellets are susceptible to surface defects, such as chips and cracks
- As in all sintered materials, residual porosity will be present
- Varying degrees of the M_2C_3 phase will be present and are observable via characterization



Mixed carbide fuel with (a) 70%PuC and (b) 20%PuC showing bright/white areas of sesquicarbide phase

NITRIDE FUELS

Nitride Fuels

- Nitride fuel has been proposed as an advanced fuel for fast reactors and developed since the 1960s and tested in the BR-10, MTR, and EBR-II reactors
- Nitride fuel is often a solid solution of uranium mononitride (UN) and plutonium mononitride (PuN), in which the Pu/(U+Pu) molar ratio ranges from 0.15 to 0.25
- Nitride has potential applications as a fuel for space reactors, large breeder reactors, different Gen IV fast reactors, accelerator-driven systems, and small modular reactors
- UN is now also being considered as an accident tolerant fuel for LWRs

Nitride Fuel Benefits

- Higher fissile density: 40% more uranium in UN than in UO_2 , leading to higher conversion ratios, and potentially higher burn-ups
- Higher thermal conductivity: reduction of the fuel centerline temperature, increase in the margin for fuel melting, delay the migration of fission products and actinides
- Reprocessing: readily dissolve in nitric acid (HNO_3), making this fuel compatible with the PUREX process
- Stability: chemically compatible with most potential cladding materials, good irradiation stability
- Potential for longer fuel cycle: neutronic behavior of UN can extend cycles from 18 to 25 months, reducing costs and down time

Nitride Properties

- Best of both worlds fuel; with high melting point, high fissile density, and high thermal conductivity

	<i>Oxide fuel</i>	<i>Metallic fuel</i>	<i>Nitride fuel</i>
Chemical composition	$(\text{U}_{0.8}\text{Pu}_{0.2})\text{O}_2$	U-19Pu-10Zr (wt.%)	$(\text{U}_{0.8}\text{Pu}_{0.2})\text{N}$
Theoretical density (TD) (g cm^{-3})	11.1	15.9	14.3
Metal atom density (g cm^{-3})	9.75	14.3	13.5
Thermal conductivity ($\text{W m}^{-1} \text{K}^{-1}$)			
at 773 K	4.1	18	15
at 1273 K	2.9	31	18
Melting temperature (K)	3083	1330	3053 ^a

Drawbacks of Nitrides

- Fabrication: the production of MA or Pu-containing nitride fuel is not straight forward and requires some difficult production steps
- Oxidation resistance: the nitride pellets readily oxidize in superheated steam
- Nitride powder is pyrophoric, requiring strict atmospheric controls during fabrication and handling
- Fuel enrichment: the nitrogen component has to be highly enriched in ^{15}N to increase the neutron economy and avoid the (n, p) formation of ^{14}C from ^{14}N , which significantly increases costs
- Fuel fabrication and N enrichment have led to slower development of MN fuels than MC fuels

Irradiation History of Nitrides

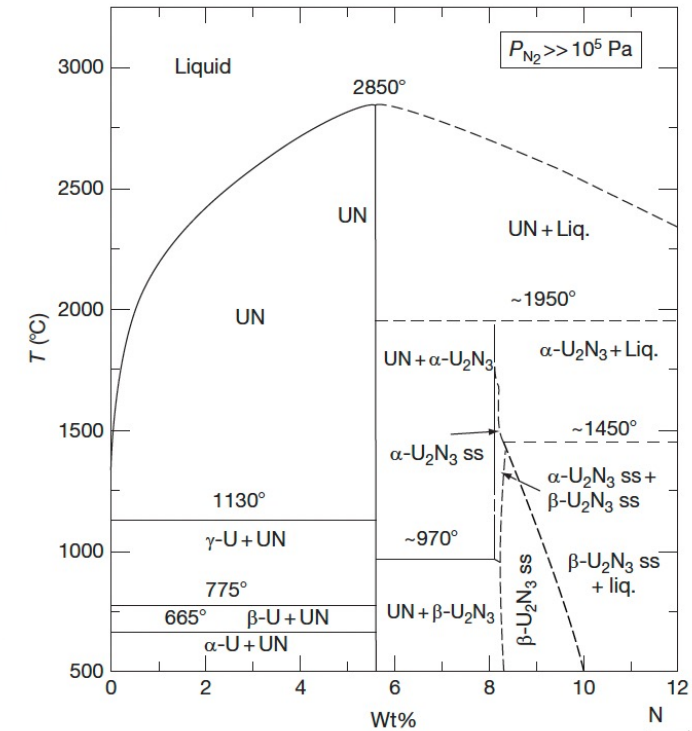
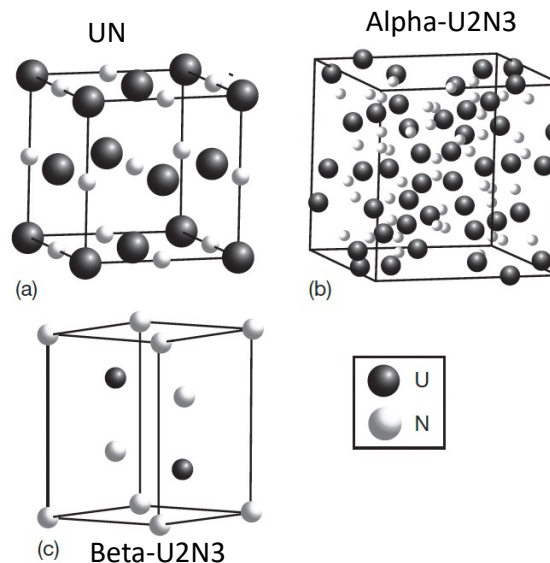
- The experience from irradiation of nitride fuels consists of about 1400 UN rods, 300 (U,Pu)N rods, and a few inert matrix and MA-bearing rodlets
- UN was used as a driver fuel for BR-10 for 18 years, and this is where the majority of the irradiation data comes from
- Similar to carbides, both Na-bonded and He-bonded pins have been studied, the majority being He

Table 1 Nitride fuel irradiation tests. Burn-up figures are given as fraction of actinides fissioned

Reactor	Fuel	Rods	Bond	χ [kW/m]	T_{fuel} [K]	Burn-up
BR-10	UN	1250	He	45	1175	9%
MTR	UN	13	He/NaK		390–1530	0.1%–3.8%
MTR	UN	48	He		1180–1800	0.2%–2.0%
MTR	UN	41	He		1210–1600	0.6%–4.6%
EBR-II	UN	4	He	30	1950–2050	0.8%
BR-2	(U,Pu)N	2	He/Na	160–330	800–2770	0%–1.6%
ETR/MTR	(U,Pu)N	55	He/Na	160	930–1900	3%–19%
JMTR	(U,Pu)N	4	He	65–73	1470–1770	3.4%–5.5%
HFR	(U,Pu)N	6	He	46–101	1500–2150	0.5%
EBR-II	(U,Pu)N	12	Na		1140	8.1%
EBR-II	(U,Pu)N	61	He			8.8%
EBR-II	(U,Pu)N	8	Na	85	1120	9.6%
Phénix	(U,Pu)N	14	He	41–73		4%–7%
JOYO	(U,Pu)N	2	He	75		4.3%
DFR	(U,Pu)N	6	He	130		1%–8%
Rapsodie	(U,Pu)N	1	Na	130		3.4%
BOR-60	(U,Pu)N	4	He	105	2270	4%
BOR-60	(U,Pu)N	2	He	20–55	930–1760	9%–12%
BN-600	(U,Pu)N	136	He	37–47		3%–5%
BOR-60	(Pu,Zr)N	2	He	20		19%
JMTR	(Pu,Zr)N	1	He	41	1270	15%
HFR	(Pu,Zr)N	2	He	43–47	1600	10%
JMTR	PuN-TiN	1	He	36	1080	17%
Phénix	(U,Pu,Am,Np)N	2	Na	37		1.6%
ATR	(U,Pu,Am,Np)N	2	Na	22–26		4.6%
Phénix	(Pu,Am,Zr)N	2	Na	28		4.1%
ATR	(Pu,Am,Zr)N	3	Na	11–17		3%–6%

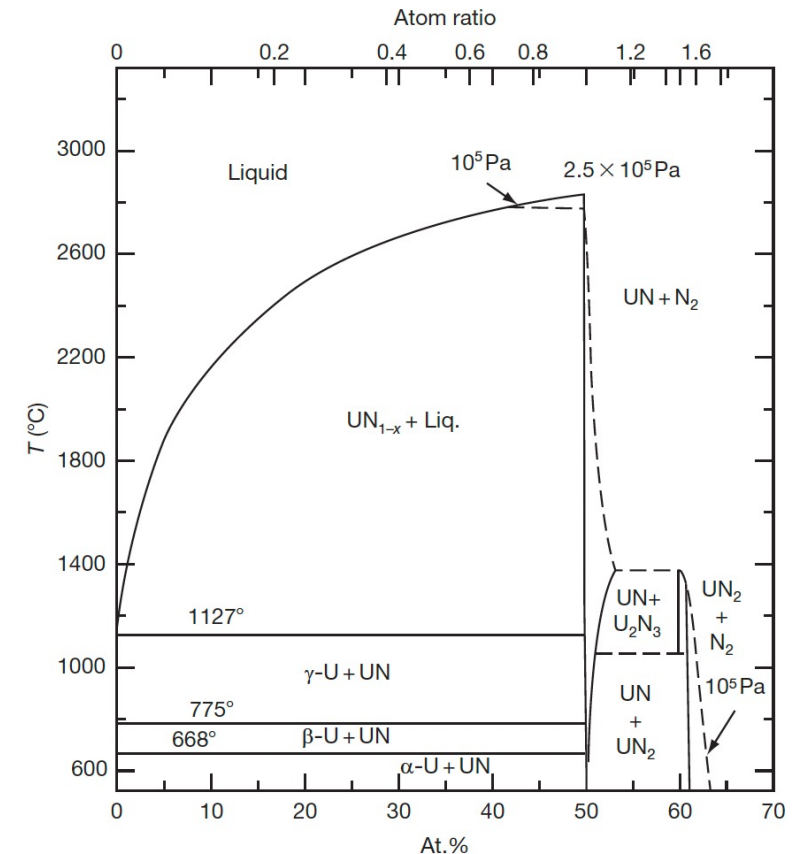
UN Phase Diagram

- There are two main uranium nitrides, UN and U₂N₃; the former has an NaCl-type cubic structure, and the latter has an M₂O₃-type cubic structure at low temperature (alpha-U₂N₃) and a hexagonal structure at higher temperature (beta-U₂N₃)
- The phase diagram of U–N is complicated since the diagram depends on nitrogen pressure
- There is still uncertainty regarding the phase diagram



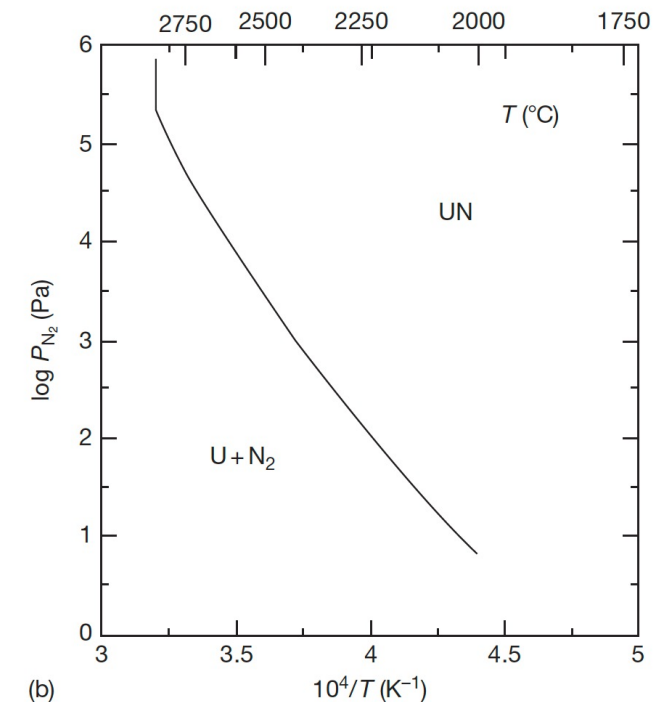
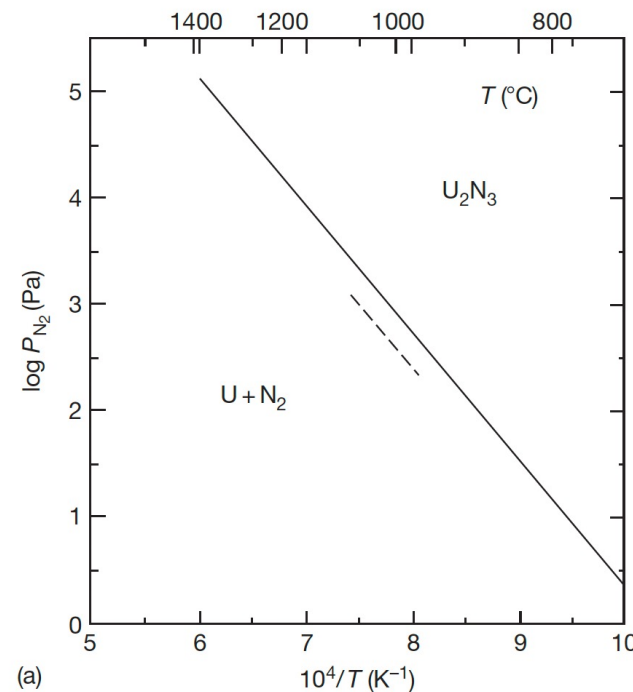
UN Phase Diagram

- Where nitrogen pressure is greater than 10^5 Pa, UN melts at 3123K and that UN and U₂N₃ have a wide range of nonstoichiometry
- At lower nitrogen pressure (<2E5 Pa) UN decomposes such that UN and U₂N₃ have little nonstoichiometry
- At low P_N , the beta-U₂N₃ phase changes to UN₂
- U₂N₃ decomposes to UN, and UN decomposes to U and nitrogen at nitrogen pressure below 2.5 atm



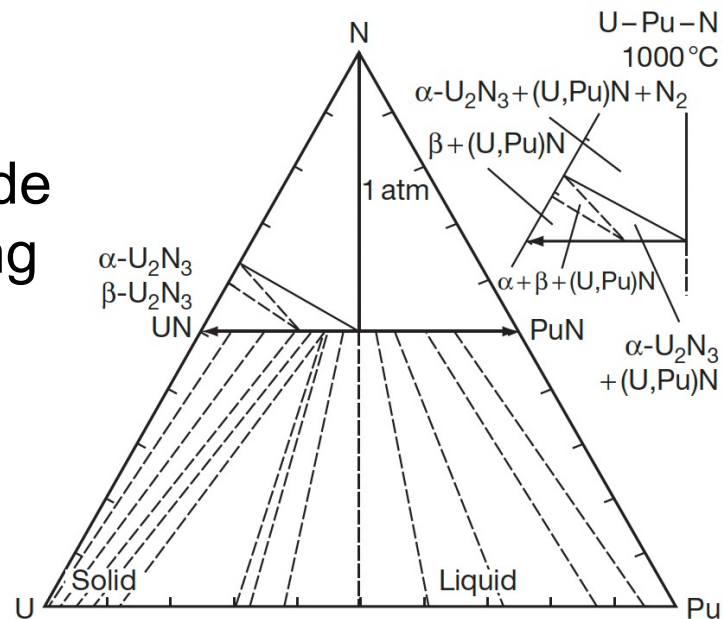
UN Decomposition

- The decomposition of U_2N_3 is the last stage in the formation of UN through carbothermic reduction, thus the equilibrium nitrogen pressure of UN and U_2N_3 is very important from the viewpoint of their use as nuclear fuels
- UN decomposes at 3073K and U_2N_3 decomposes 1620K at nitrogen pressure of 1 atm



MN Crystal Structure

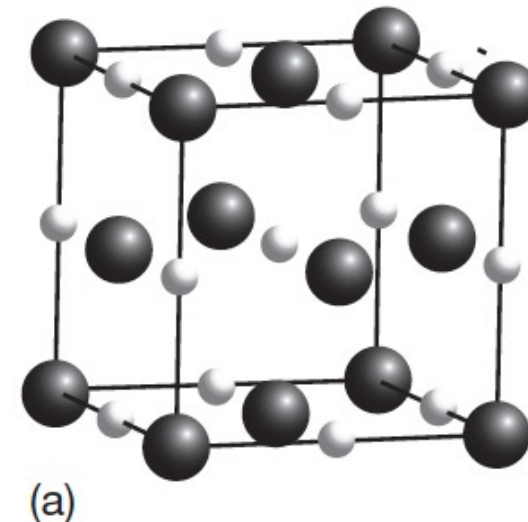
- UN has same NaCl-type close-packed structure as UC
- Several actinides also share this NaCl-type structure, and thus can exist as substitutional species in UN/PuN
- Allows for fabrication of homogeneous mixed nitride fuels, including MA-bearing fuels



Compounds	Structure	Lattice parameter (nm)
ThN	NaCl-type fcc	0.5167
Th ₃ N ₄	Th ₃ P ₄ -type hexagonal	$a = 0.3871$ $c = 2.7385$
UN	NaCl-type fcc	0.4889
α -U ₂ N _{3+x}	Mn ₂ O ₃ -type bcc	1.0685
β -U ₂ N _{3-x}	La ₂ O ₃ -type hexagonal	$a = 0.3696$ $c = 0.5840$
UN _{2-x}	CaF ₂ -type fcc	0.531
NpN	NaCl-type fcc	0.4899
PuN	NaCl-type fcc	0.4905
AmN	NaCl-type fcc	0.4995
CmN	NaCl-type fcc	0.5027

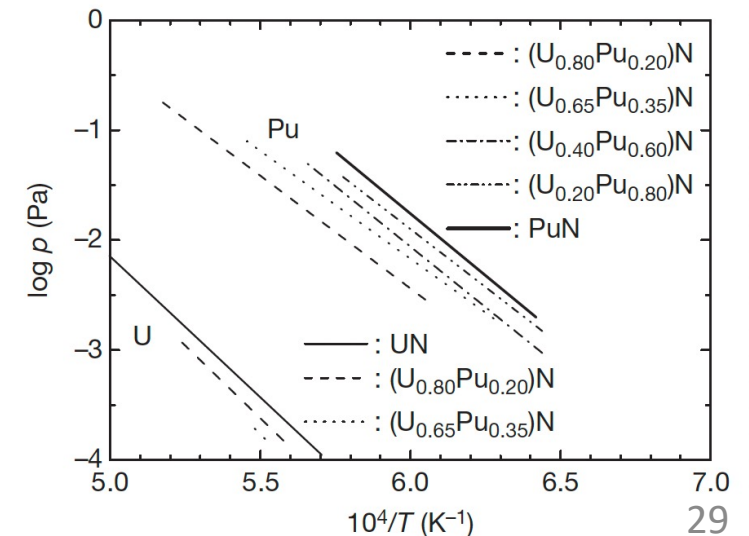
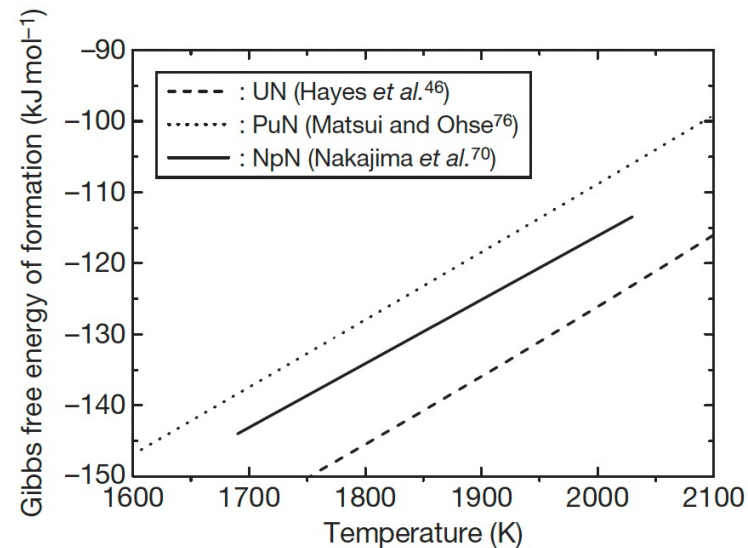
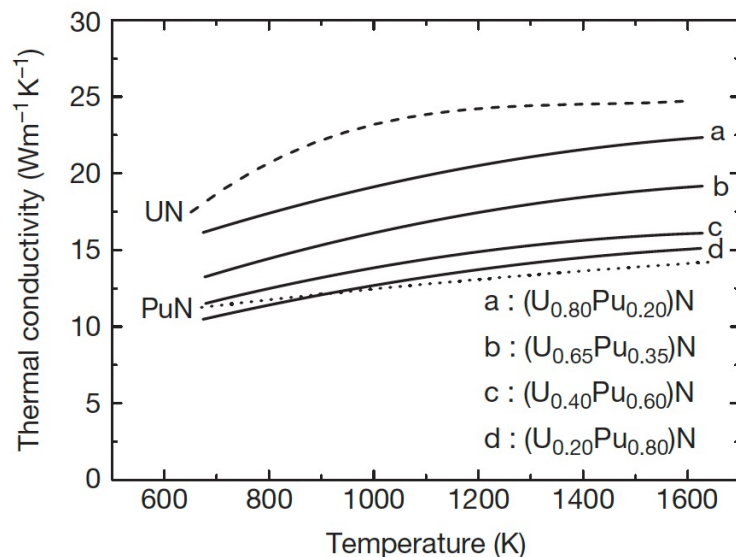
Ternary U/Pu-N

- The ternary system is characterized by a complete solubility of UN and PuN
- The (U,Pu)N phase has a narrow composition range of the N/(U+Pu) molar ratio
- Although Pu₂N₃ does not exist in the Pu–N system, a sesquinitride phase was identified in the U–Pu–N system at a Pu/(U+Pu) molar ratio of 0.15
- In a mononitride lattice with NaCl-type structure, small nitrogen atoms are incorporated into a dense face-centered cubic packing of metal atoms



Effect of Pu on U/Pu N Properties

- The addition of Pu can dramatically affect thermophysical properties
- Pu is more volatile than U, and has a higher vapor pressure
- Pu degrades the thermal conductivity by as much as 2X
- PuN is less stable than UN, and could be susceptible to radiolysis



UN Irradiation Performance

- The irradiation experience of nitride fuel is rather limited in comparison with the other fuels for fast reactors, such as oxide, metallic, and carbide fuels
- The number of (U,Pu)N fuel pins irradiated in fast reactors so far is smaller than 200
- UN pins have reached 10% FIMA in fast reactors, and greater than 15% FIMA in thermal reactors

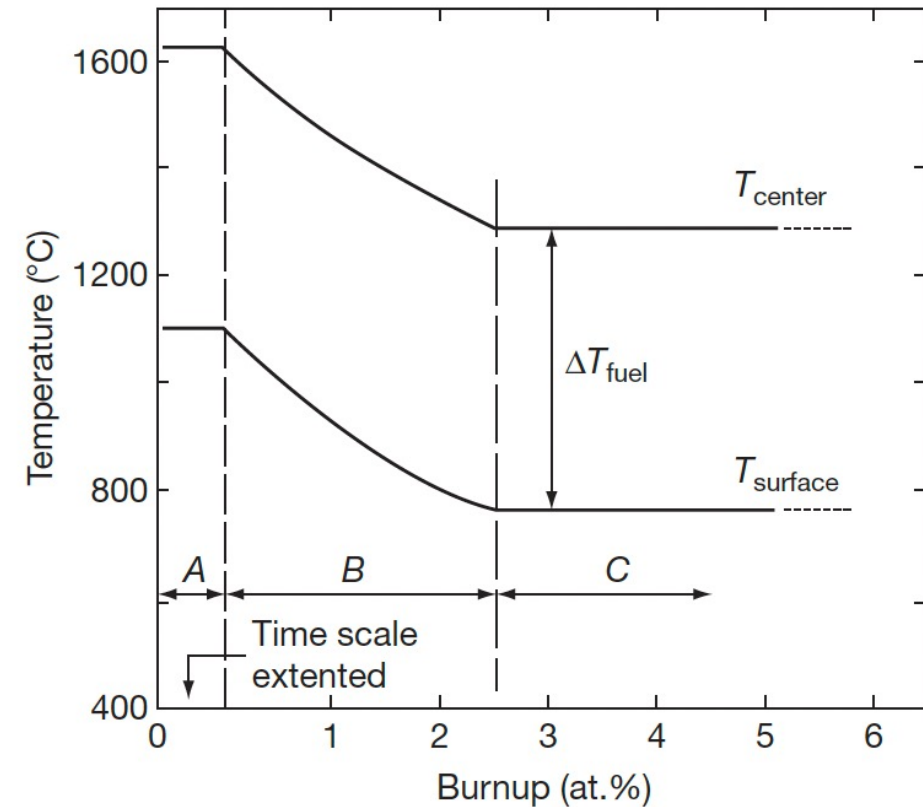
<i>Reactor</i>	<i>Bonding</i>	<i>Max. linear power (kW m⁻¹)</i>	<i>Max. burnup (% FIMA)</i>	<i>References</i>
EBR-II	He and Na	110	9.3	Bauer <i>et al.</i> ⁵⁸
DFR	He	130	7.6	Blank ⁵⁹
RAPSODIE	Na	130	3.4	Blank ⁵⁹
PHENIX	He	73	6.9	Fromont <i>et al.</i> ⁶⁰
JOYO	He	75	4.3	Inoue <i>et al.</i> ⁶¹

UN Pins

- Similar to carbides, pin designs are either He-bonded or Na-bonded
- He-bonded fuel pin is characterized by low-density pellets (80–85% of theoretical density (TD)) and a small gap
- Na-bonded fuel pin is characterized by high-density pellets (>90% TD) and a large gap
- Na-bonded concept has the advantage of keeping the fuel temperature relatively low due to good thermal conductivity of liquid Na
- Difficulties with Na are the reactivity in air, and additional hurdles in fabrication and reprocessing

UN Pins

- The He-bonding concept is considered as the reference for (U,Pu)N fuel
- The temperature of fuel pellets becomes high in comparison with the fuel with Na bonding, especially at an early stage of irradiation
- The small gap is closed by free swelling of fuel pellets at a burnup of 2–3% FIMA



Temperature with Burnup

- Similar to carbides, have three stages in temperature
- Stage A is the first rise of power and lasts for one to several days
- Stage B has the resintering of pellets center and closure of He gap
- Stage C is the quasi steady state irradiation period in which FCMI begins
- The TD of the fuel is reduced to ~80% to avoid excessive strain on the cladding

