NE 591: Advanced Reactor Materials

Fall 2021

Dr. Benjamin Beeler

Last Time

- 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

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, FFTF, and EBR-II reactors
- Nitride fuel is 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 also been proposed as a fuel for space reactors
- UN, PuN, and minor actinide mononitride (U,Pu,MA)N, has been proposed as one of the candidate fuels for Gen IV-type fast reactors
- U-free nitride fuel, such as (Pu,MA)N diluted by ZrN, has been studied for MA transmutation accelerator driven systems

Nitride Fuels

- 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

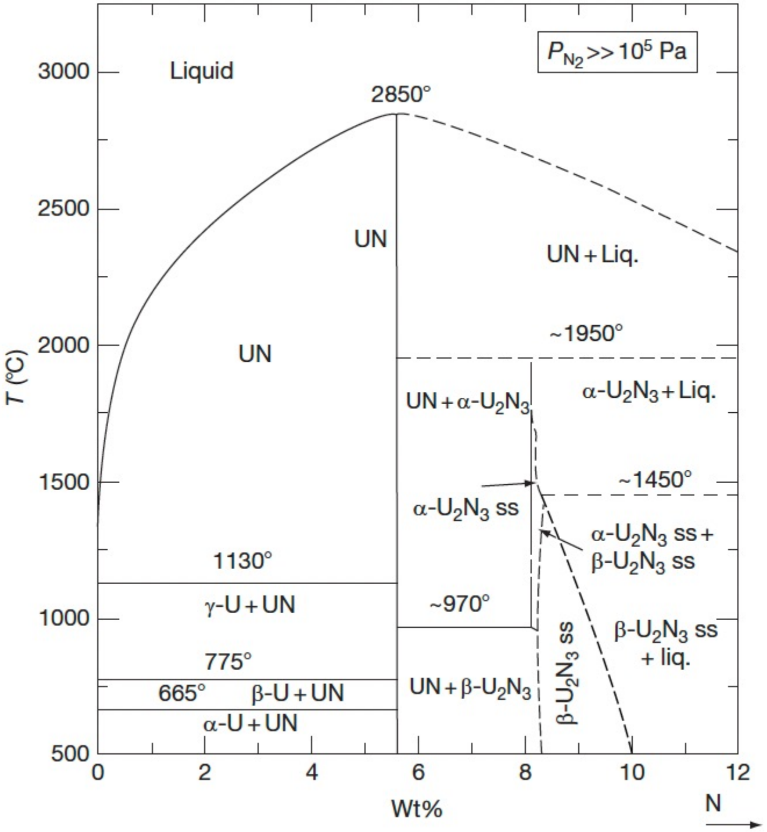
Drawbacks of Nitrides

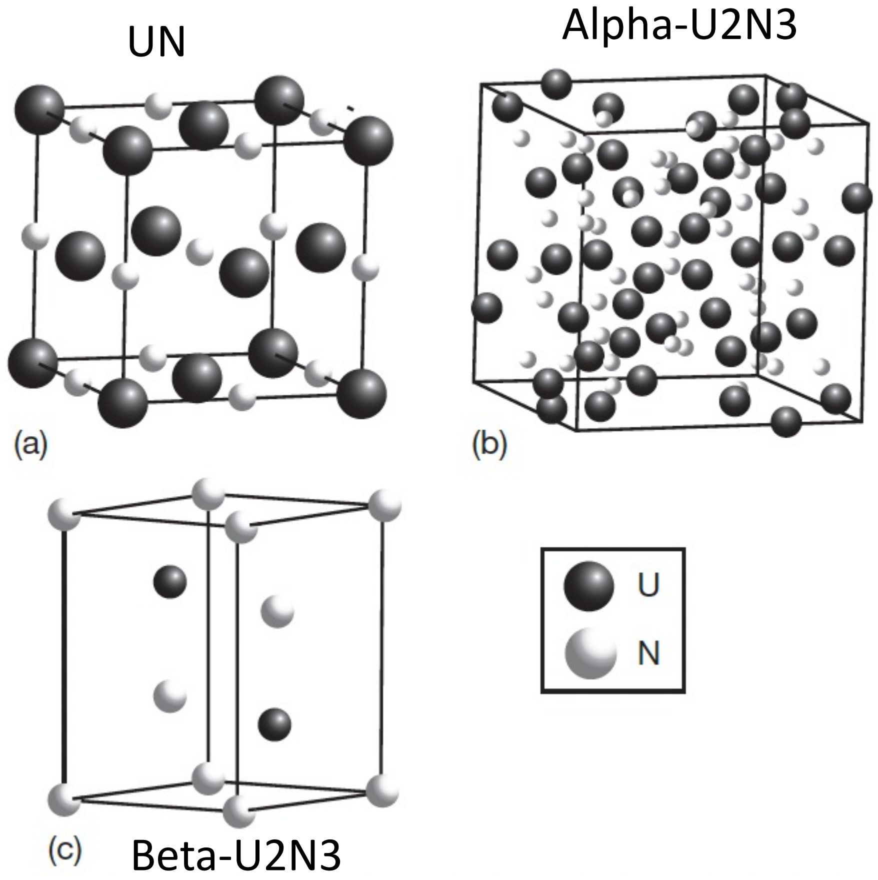
- Fabrication: the production of minor actinide (or even plutonium) containing nitride fuel is not straight forward and require some difficult production steps
- Oxidation resistance: the nitride pellets readily oxidizes in superheated steam
- Nitride powder is pyrophoric, requiring strict atmospheric 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

Nitride Properties

	Oxide fuel	*Metallic fuel*	*Nitride fuel*
Chemical composition	$(U_{0.8}Pu_{0.2})O_2$	U–19Pu–10Zr (wt.%)	$(U_{0.8}Pu_{0.2})N$
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 ($W\,m^{-1}\,K^{-1}$)			
at 773 K	4.1	18	15
at 1273 K	2.9	31	18
Melting temperature (K)	3083	1330	3053[a]

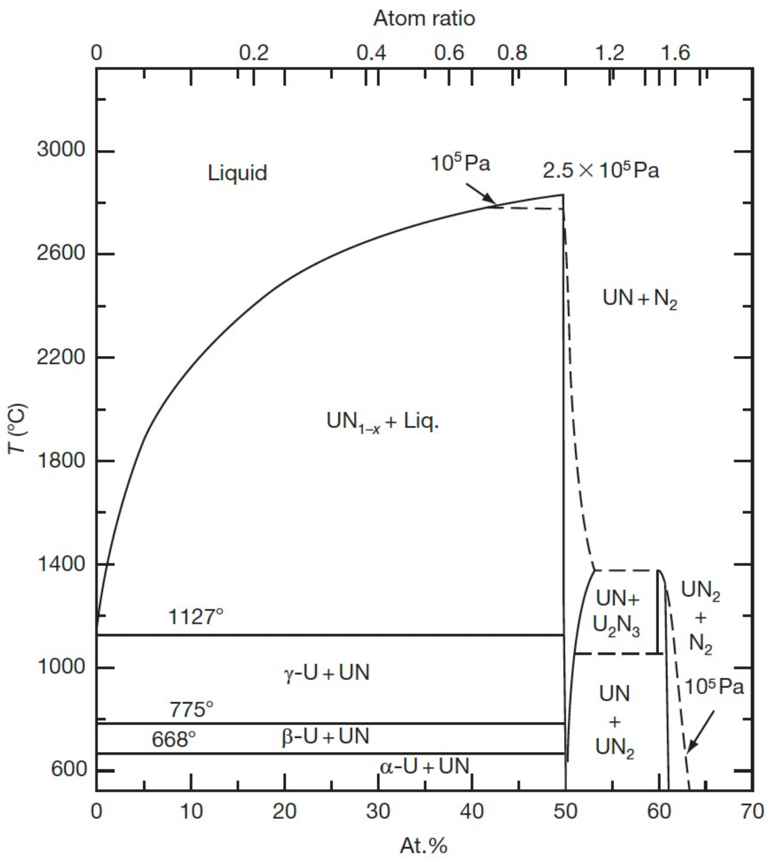
UN Phase Diagram





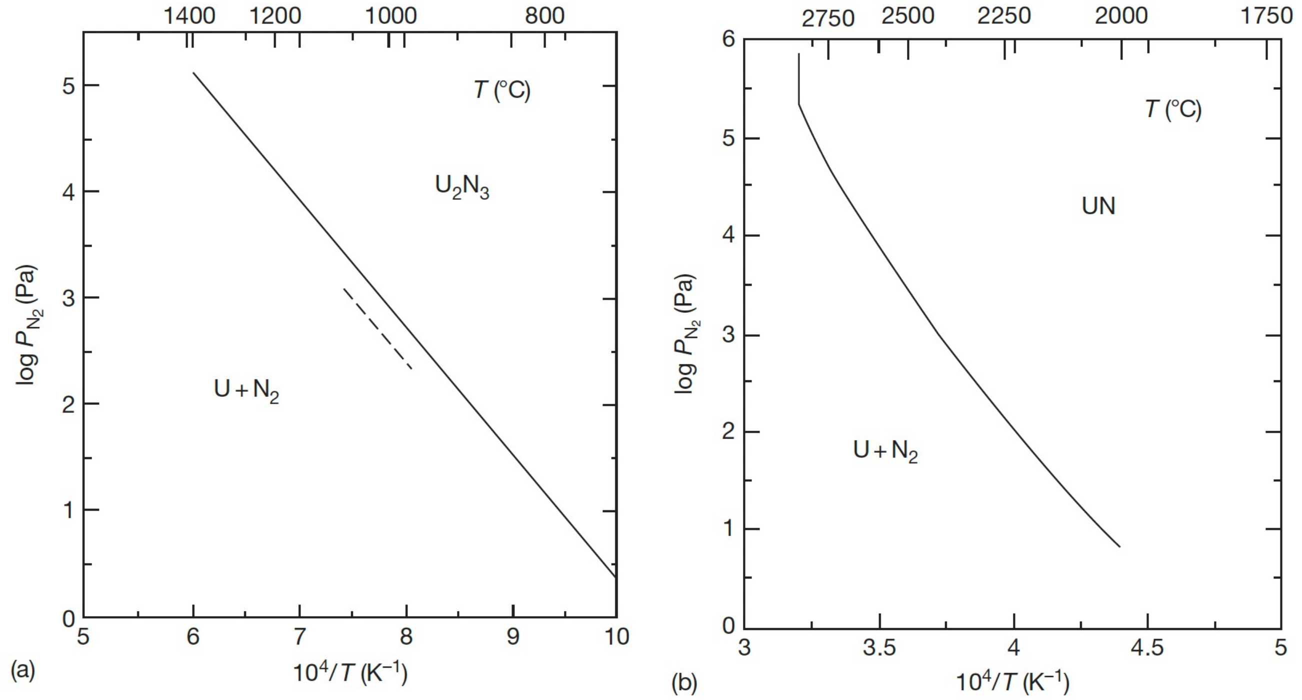
UN Phase Diagram

- 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

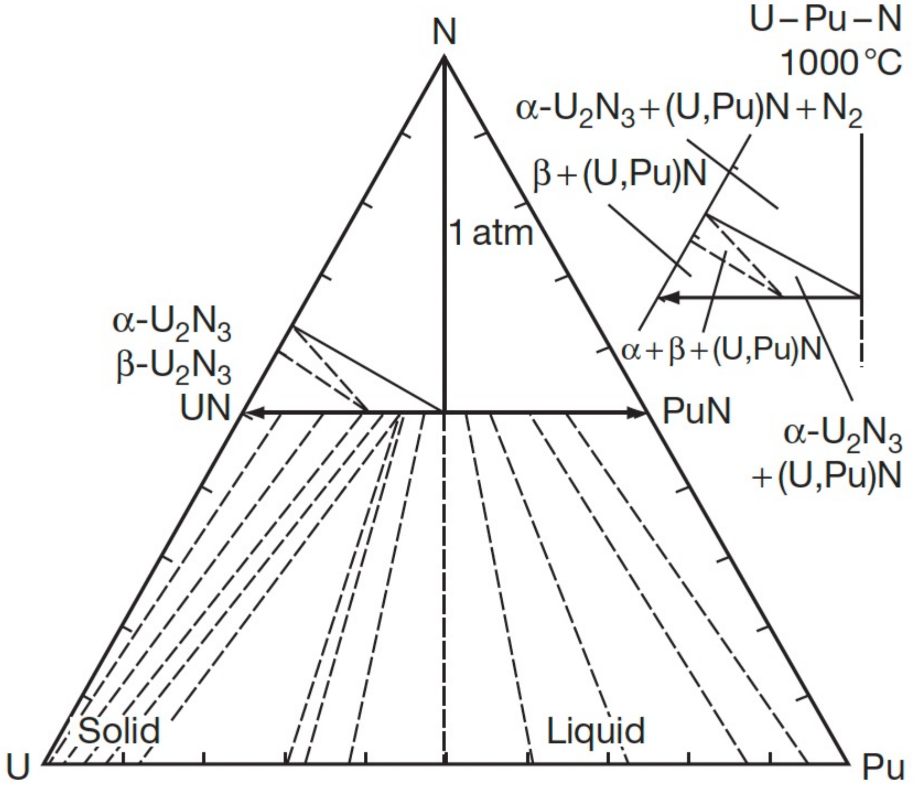


UN Decomposition

- The decomposition of U2N3 is the last stage in the formation of UN through carbothermic reduction, thus the equilibrium nitrogen pressure of UN and U2N3 is very important from the viewpoint of their use as nuclear fuels
- UN decomposes at 3073K and U2N3 decomposes 1620K at nitrogen pressure of 1 atm



MN Crystal Structure

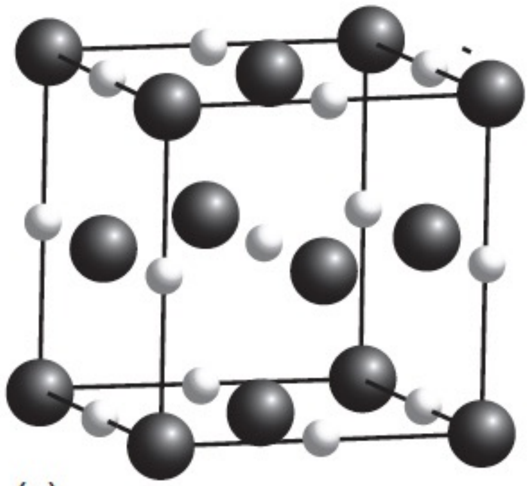


Compounds	*Structure*	*Lattice parameter (nm)*
ThN	NaCl-type fcc	0.5167
Th_3N_4	Th_3P_4-type hexagonal	$a = 0.3871$ $c = 2.7385$
UN	NaCl-type fcc	0.4889
α-U_2N_{3+x}	Mn_2O_3-type bcc	1.0685
β-U_2N_{3-x}	La_2O_3-type hexagonal	$a = 0.3696$ $c = 0.5840$
UN_{2-x}	CaF_2-type fcc	0.531
NpN	NaCl-type fcc	0.4899
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

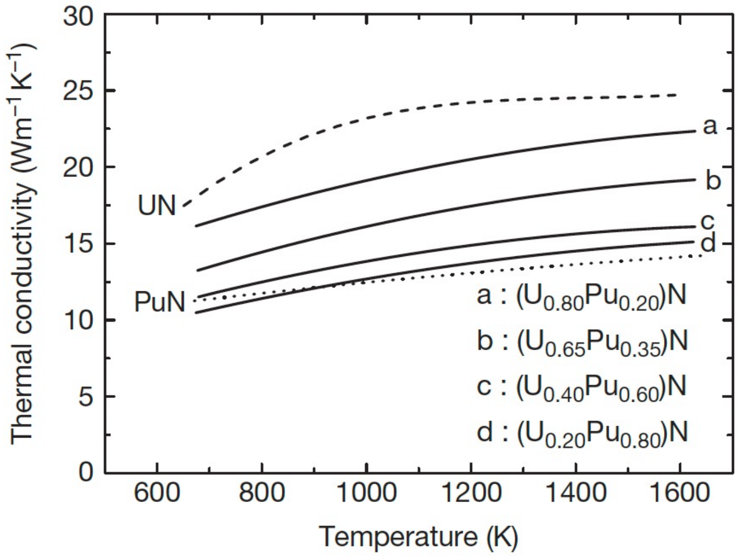
- In a mononitride lattice with NaCl-type structure, small nitrogen atoms are incorporated into a dense face-centered cubic packing of metal atoms

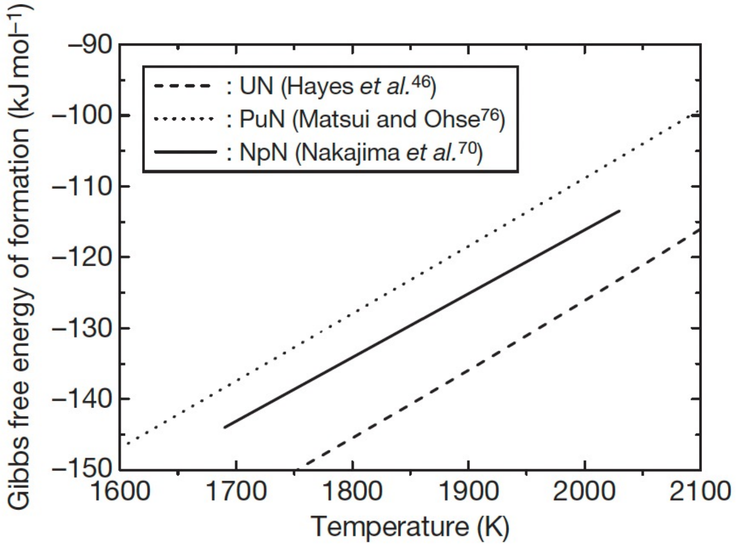


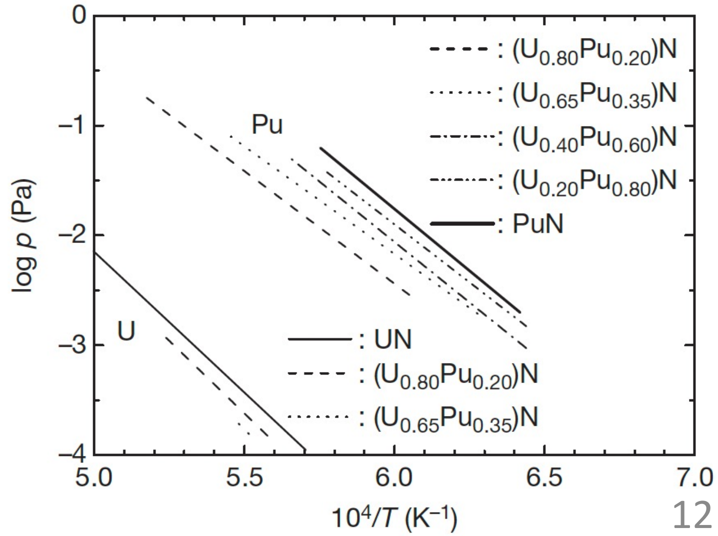
(a)

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







Nitride Fabrication

- Similar to carbide fuels, preparation of nitrides from either metallic sources or from the hydriding-dehydriding process were explored in the 1960s and remain an option for laboratory implementation
- These reactions are exothermic and should be carried out slowly by temperature cycling for better control of the products
- It is difficult to apply the metal or hydride route to a technological fuel production line
- These processes include the nitridation of U or Pu metal in N2 or NH3 at 1073–1173 K, arc-melting of U or Pu metal under N2 pressure, nitridation of fine-grained U or Pu powder formed by the decomposition of hydrides with N2 or NH3 and direct reaction of UH3 or $PuH_{2.7}$ with N2 or NH3

Carbothermic Reduction

- Carbothermic reduction is the most widely used process for preparing nitride fuel
- The starting material is a dioxide and carbon, and the general reaction is

$$MO_2 + 2C + 0.5N_2 = MN + 2CO$$

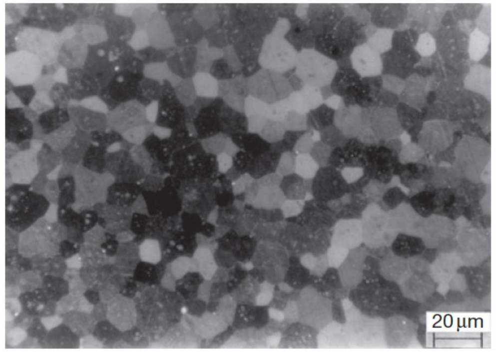
- The mixture of dioxide and carbon is heated in N2 gas stream, usually at 1773–1973 K
- An excess amount of carbon is usually added to the mixture to reduce the oxygen content
- The residual carbon is removed from the products by heating in a N2-H2 stream
- The initial C/MO2 mixing ratio was historically chosen at 2.2–2.5 for the preparation of UN and (U,Pu)N
- For the preparation of UN and (U,Pu)N, the atmosphere is changed to Ar or He from N2 or N2–H2 to prevent the formation of higher nitrides

Carbothermic Reduction

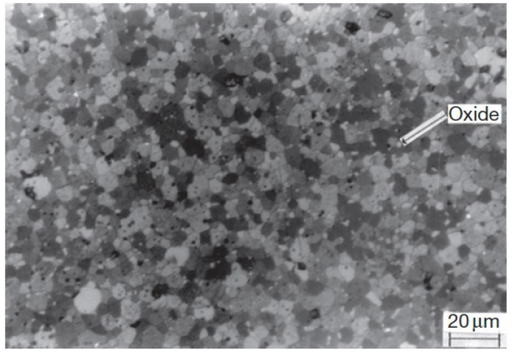
- Typical impurities in nitride fuel prepared by carbothermic reduction are oxygen and carbon
- The level of impurities can be kept lower than 1000–2000 ppm for both oxygen and carbon by adjusting the initial C/MO2 mixing ratio
- Carbonitrides (U/Pu-C-N) have complete solubility in the MN systems, while oxides have solubility around 10%
- MA-N can be manufactured in the same way, but has different C, N, and O potentials, requiring slightly different mixtures of streams
- Am also has a high vapor pressure and it is a challenge to keep it from vaporizing during fabrication
- This requires operating at lower temperatures for the N2 stream
- Unlike carbides, Pu volatilization is not an issue

Nitride Pellets

- Nitride fuel pellets are usually prepared by a classical powder metallurgical manner; the product of carbothermic reduction is ground to powder by use of a ball mill, pressed into green pellets and sintered in a furnace at 1923–2023 K
- Actinide nitride powder has a low sinter-ability in comparison with that of oxide or carbide powder, which is derived from a low diffusion rate of metal atoms in mononitrides
- A high sintering temperature (i.e., T>1973 K) is necessary for preparing dense UN or (U,Pu)N pellets higher than 90% TD
- Oxygen impurities tend to promote the sintering of UN, but greater than 1 wt% decreases the density and results in an overly fine grain structure



(U,Pu)N pellet containing 0.21 wt% oxygen



(U,Pu)N pellet containing 0.99 wt% oxygen

UN Irradiation

- 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

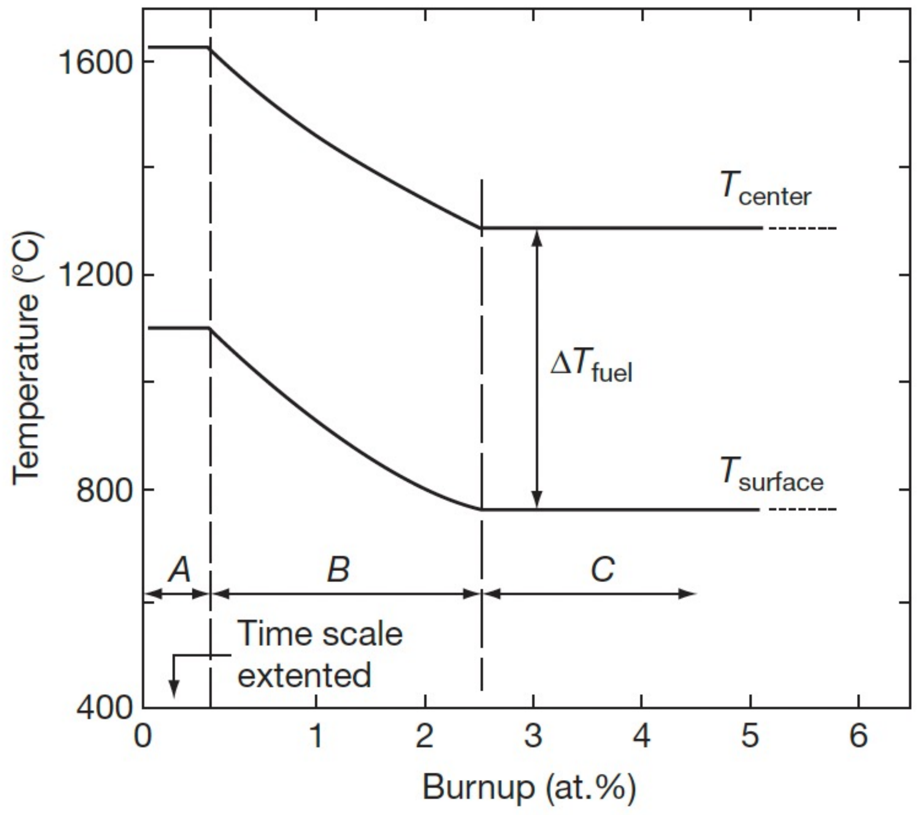
Reactor	*Bonding*	*Max. linear power* ($kW\,m^{-1}$)	*Max. burnup (% FIMA)*	*References*
EBR-II	He and Na	110	9.3	Bauer *et al.*[58]
DFR	He	130	7.6	Blank[59]
RAPSODIE	Na	130	3.4	Blank[59]
PHENIX	He	73	6.9	Fromont *et al.*[60]
JOYO	He	75	4.3	Inoue *et al.*[61]

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

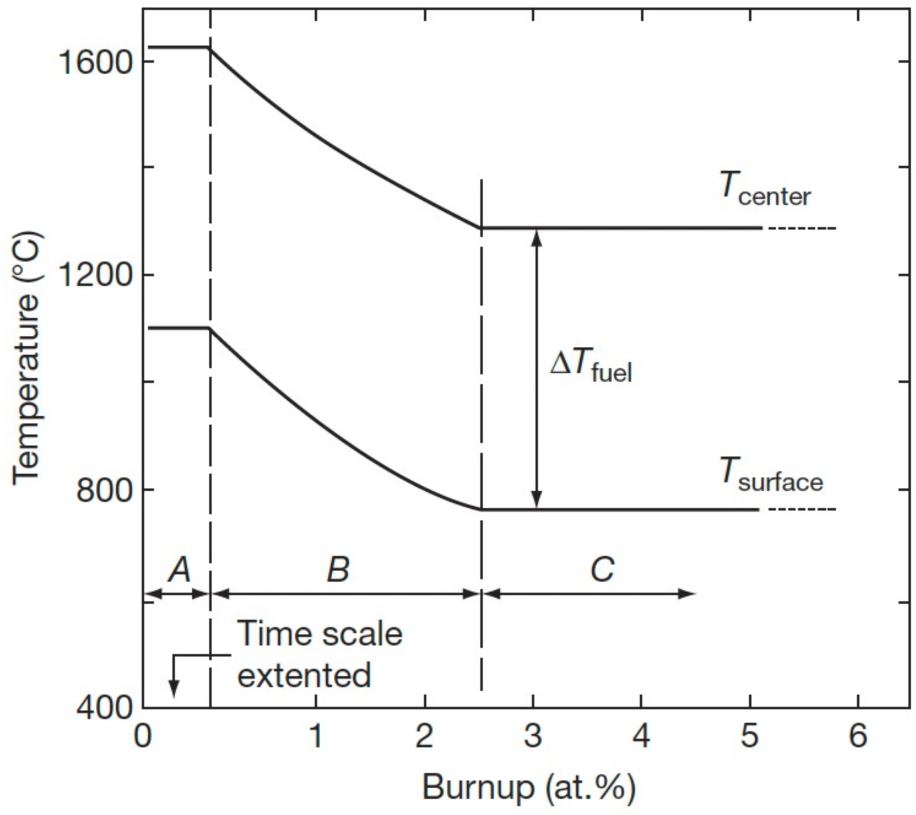
UN Pins

- 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



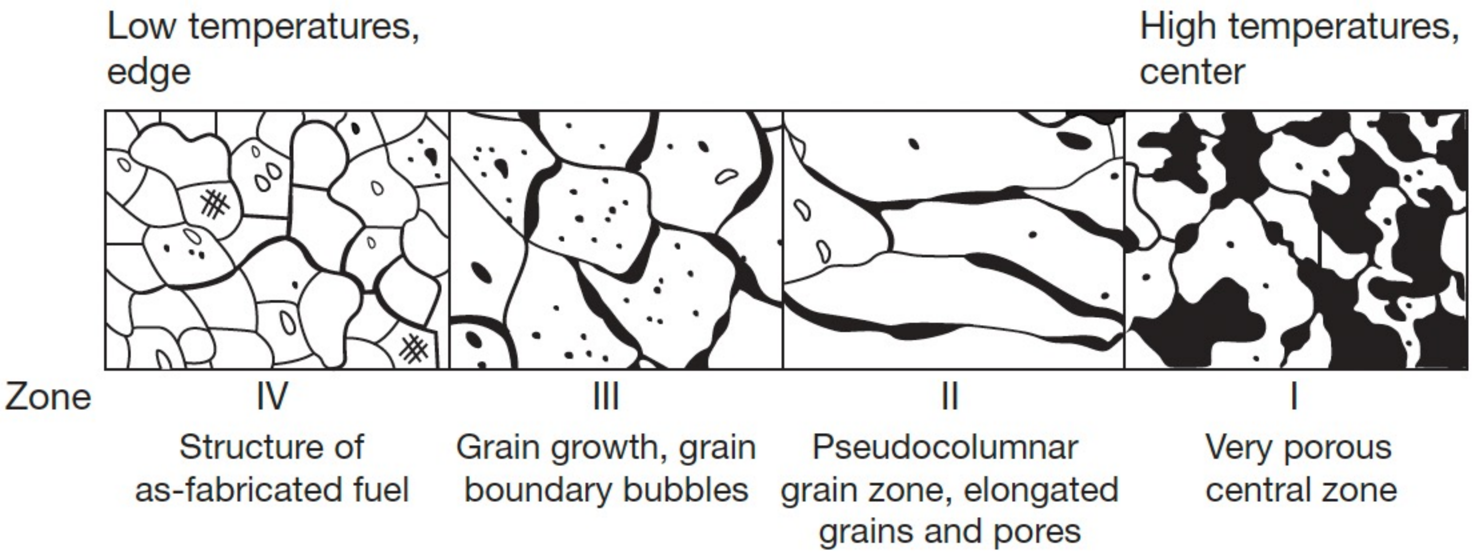
Fission Products

- Fission products can form various nitride phases in the fuel matrix
- Noble gases will of course not react with N, and volatile species (Cs, I, Te) will form volatile compounds
- Pd, Rh, and Ru form metallic precipitates
- Rare earths are dissolved in the U/Pu-N matrix
- The N/U ratio was evaluated and reported to increase by 2% at a burnup of 10%

Element[a]	*Chemical forms*	*Element*	*Chemical forms*
Ba	Ba_3N_2	Ce	CeN
Cs	Cs, CsI, CsTe	I	CsI
Kr	Kr	La	LaN
Mo	Mo	Nd	NdN
Pd	$(U,Pu)(Pd,Ru,Rh)_3$	Pm	PmN
Pr	PrN	Rb	Rb, RbI
Rh	$(U,Pu)(Pd,Ru,Rh)_3$	Ru	$(U,Pu)(Pd,Ru,Rh)_3$
Sm	SmN	Sr	Sr_3N_2
Tc	Tc	Te	Te, CsTe
Xe	Xe	Y	YN
Zr	ZrN		

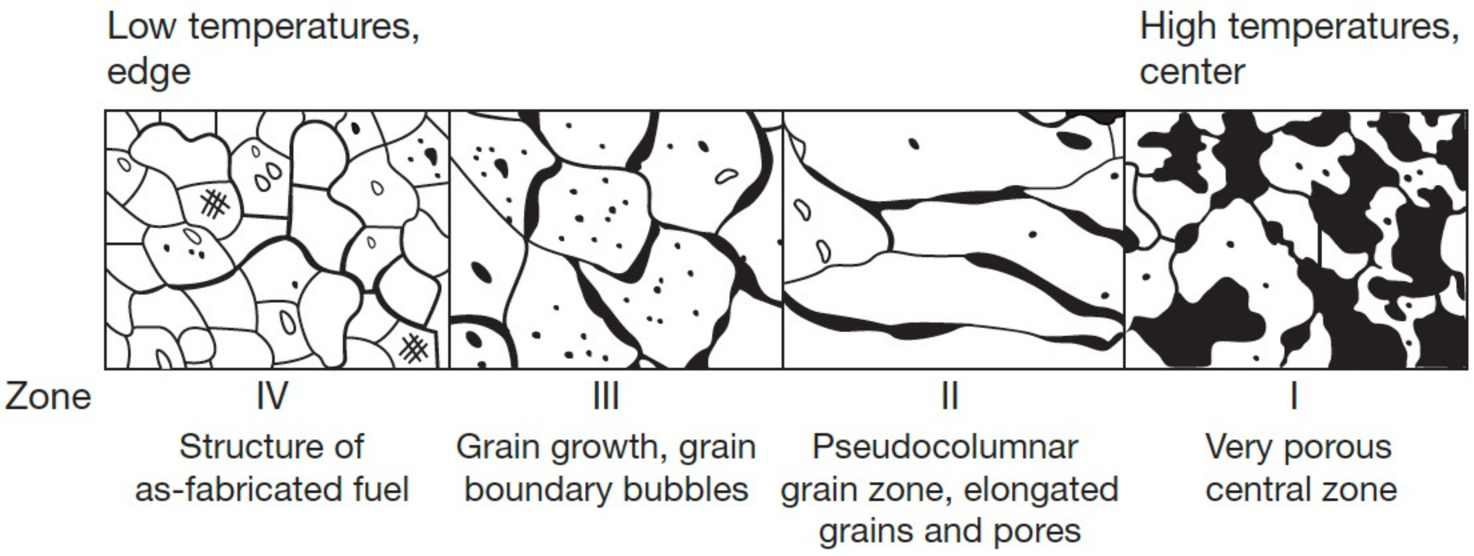
Nitride Restructuring

- Because of relatively low fuel temperature and temperature gradient, the restructuring of (U,Pu)N fuel is mild in comparison with MOX fuel for fast reactors
- For He bonded pins at high power, restructuring does occur with three distinct zones
- Zone 1 is found in the central of the fuel pellet was characterized by very porous structure; a small central hole was sometimes observed



Nitride Restructuring

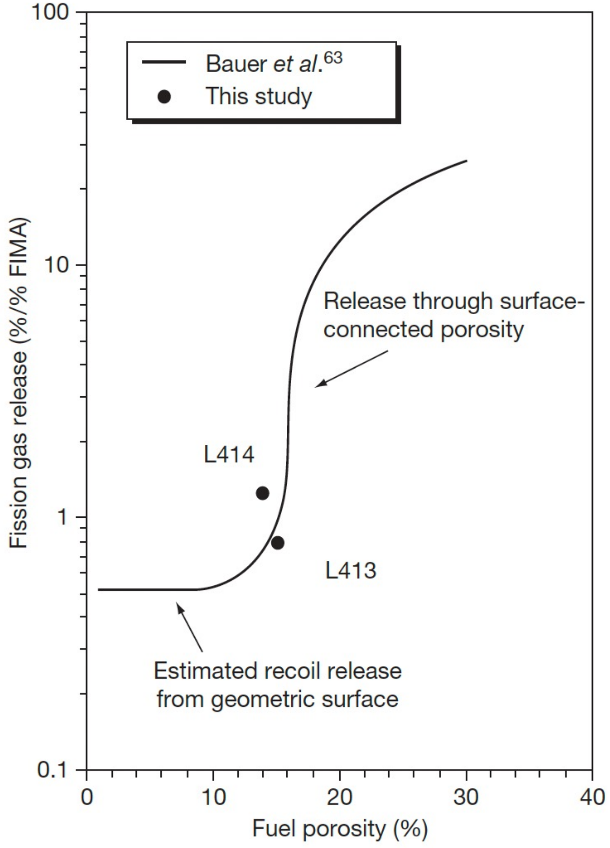
- Zone 2 is found in MOX fuels and sometimes in carbide fuels, but not in UN fuels
- Zone 3 displays grain growth, grain boundary bubbles, and healing of cracks
- Zone 4 has the as-fabricated structure
- Fission gas release is prevalent in zone 1 and zone 3, with large amount of UN swelling



Fission Gas Release

- There have been no systematic results dealing with fission gas release of nitride fuel, due to limited irradiations
- It is generally known that FP gas release of nitride fuel is much lower than that of MOX fuel
- Gas release will be influenced by burnup, pellet density, grain size, the characteristics of porosities, and temperature

$$R = 100/\left\{\exp\left[0.0025\left(90\mathrm{D}^{0.77}/\mathrm{Bu}^{0.09} - \mathrm{T}\right)\right] + 1\right\}$$



Fuel at 4.3% FIMA

Swelling and FCMI

- Since FG release is low, its possible that swelling is large
- Volumetric swelling is caused by the accumulation of solid FP and crack formation in the pellets
- The volumetric swelling rate of (U,Pu)N fuel irradiated to 9.3% FIMA was evaluated at 1.83% per FIMA% without the constraint of the cladding tube
- This is considerably higher than UO2 fuels, and lower than metallic fuels
- The creep rate of (U,Pu)N fuel is low in comparison with MOX or metallic fuel at operating temperatures due to a slow diffusion rate of metal atoms in nitride fuel
- Thus, focus has been placed upon the degree of FCMI in UN fuels
- FCMI in a general sense can be mitigated by the reduced TD and operating at a reasonable linear power (<100kW/m)

Reprocessing

- Both hydrochemical and pyrochemical processes were proposed for the reprocessing techniques
- The disposal of long-lived ^{14}C and the recovery of expensive ^{15}N are key topics in reprocessing
- Hydrochemical processes include the direct dissolution of spent nitride fuel in HNO3 and the voloxidation of spent nitride fuel followed by the dissolution in HNO3
- The product of hydrochemical reprocessing is the nitric solution of U+Pu to be converted to oxide, and then to nitride by carbothermic reduction
- Pyrochemical processing is very similar to that for metallic fuel

Summary

- Nitrides have a higher U density and higher thermal conductivity than oxides, with a higher melting point than carbides
- Difficult fabrication, requiring atmospheric controls and enrichment of N, especially in thermal or transmutation applications
- Carbothermic reduction is the primary fabrication route
- Very few irradiations have been performed, none to especially high burnups
- Three stages in temperature, with gap closure leading to steady state behavior
- Nitride fuel undergoes restructuring, with central porous region, large grained region, and as-fabricated microstructure
- FCMI is a key life limiting phenomenon due to little creep in UN fuels

Exam 3

- This concludes our module 3
- Exam will take place next Tuesday (11/2)
- Will cover molten salts, carbides and nitrides
- DFT lecture and QE not covered, as that is project related