

# **NE 795: Advanced Reactor Materials**

Fall 2023

Dr. Benjamin Beeler

# Last Time

- Wrapped up carbides
- FCCI, primary concern is carburization, formatting of Cr-C precipitates along grain boundaries and then crystallographic planes; governed by C diffusion into the cladding; FCCI is worse for Na-bonded pins, as C transport to cladding is faster
- Carbide fabrication: carbothermic reduction
- Started on nitrides
- Similar benefits to UC fuels, options for reprocessing, interest from a variety of reactor concepts
- UN and U<sub>2</sub>N<sub>3</sub> are main phases
- Same pin design types as carbides; similar fuel surface temperature evolution

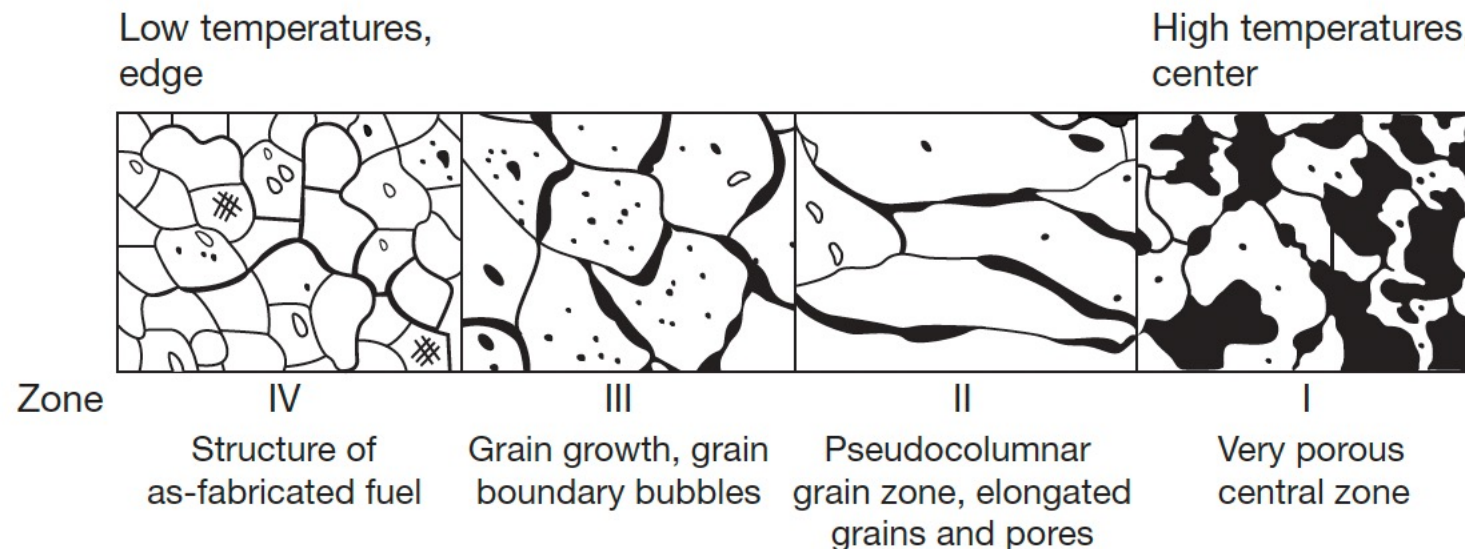
# Fission Products

- Fission products can form various nitride phases in the fuel matrix
- Noble gases will not react with N, and volatile species (Cs, I, Te) will form volatile compounds
- Pd, Rh, Ru, Mo, Tc form metallic precipitates
- Rare earths and transition metals 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%
- The increase in N can form U<sub>2</sub>N<sub>3</sub> phases

<i>Element<sup>a</sup></i>	<i>Chemical forms</i>	<i>Element</i>	<i>Chemical forms</i>
Ba	Ba <sub>3</sub> N <sub>2</sub>	Ce	CeN
Cs	Cs, CsI, CsTe	I	CsI
Kr	Kr	La	LaN
Mo	Mo	Nd	NdN
Pd	(U,Pu)(Pd,Ru,Rh) <sub>3</sub>	Pm	PmN
Pr	PrN	Rb	Rb, RbI
Rh	(U,Pu)(Pd,Ru,Rh) <sub>3</sub>	Ru	(U,Pu)(Pd,Ru,Rh) <sub>3</sub>
Sm	SmN	Sr	Sr <sub>3</sub> N <sub>2</sub>
Tc	Tc	Te	Te, CsTe
Xe	Xe	Y	YN
Zr	ZrN		

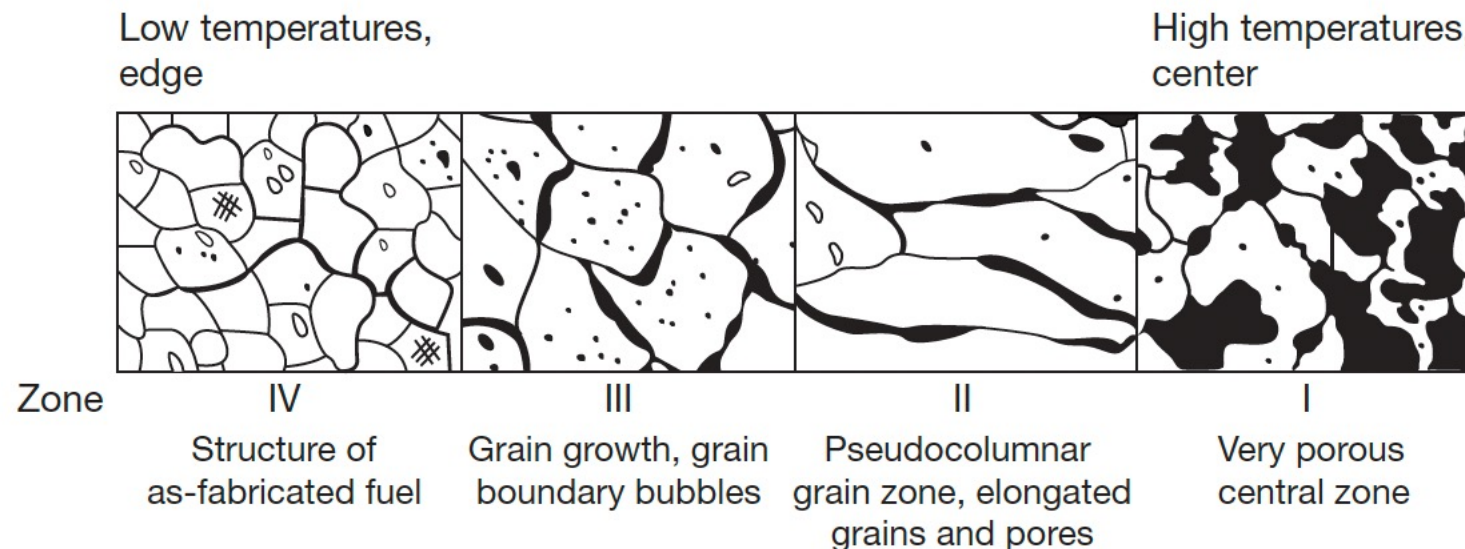
# Nitride Restructuring

- Because of relatively low fuel temperature and temperature gradient, the restructuring of (U,Pu)N fuel is mild in comparison to 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 (not due to pore migration)



# Nitride Restructuring

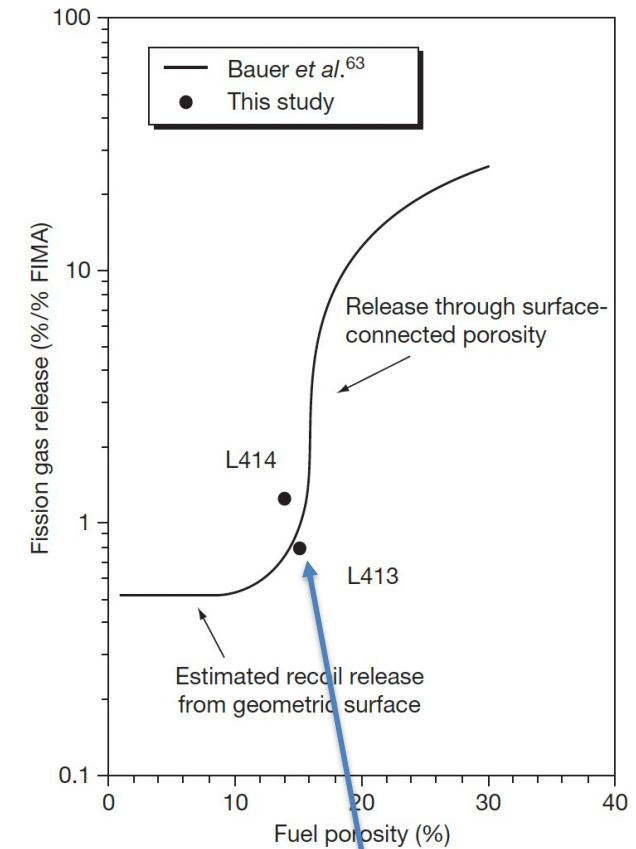
- Zone 2 is found in MOX fuels and sometimes in carbide fuels, but NOT in UN fuels
- Zone 3 displays grain growth, grain boundary bubbles, and healing of cracks
- Zone 4 has the as-fabricated structure, low swelling, small bubbles
- Fission gas release is prevalent in zone 1 and zone 3, with large amount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



# Fission Gas Release

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

$$R = \left[ \text{Exp} \left( 0.0025 \left( 90 \frac{(\rho/\rho_{TD})^{0.77}}{B^{0.09}} - T \right) + 1 \right) \right]^{-1}$$



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 UO<sub>2</sub> 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)

# Swelling and FCMI

- High power He-bonded pins with high TD caused a number of cladding failures, leading to suggested conditions of <80 kW/m and TD ~ 75%
- Thus, FG swelling is highly temperature dependent
- Solid swelling is estimated at 0.5% per % FIMA
- This is significantly lower than metallic fuels
- Swelling correlations have been developed taking temperature, burnup, and as-fabricated density into account

$$\Delta V/V(\%) = 4.7 \times 10^{-11} T_{\text{av}}^{3.12} \text{Bu}^{0.83} D^{0.5}$$

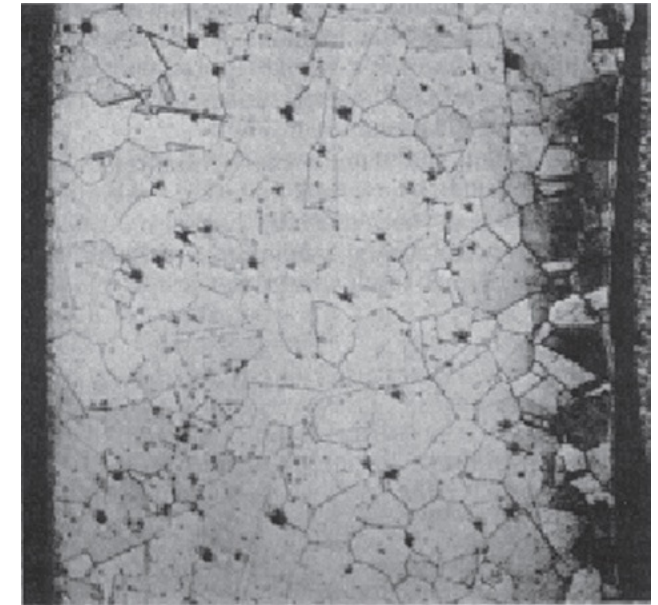
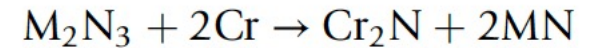


# FCCI

- Similar to carbide fuels, but without the problems of carburization
- Pure UN and PuN are stable with respect to most major cladding constituents
- Hypostoichiometric MN containing free U or Pu should be avoided as a eutectic melting reaction with the cladding can occur
- Formation of (U,Pu)Fe<sub>2</sub> and (U,Pu)Ni<sub>5</sub>-type intermetallic compounds – same as carbides
- In systems with excess N, U<sub>2</sub>N<sub>3</sub> can be stripped of N to form Fe, Ni, and Mo nitrides
- Thus, hyperstoichiometric UN is less compatible with cladding

# Cladding Nitriding

- Hyperstoichiometric MN containing sesquinitride can cause nitrogen penetration and form a reaction layer at the cladding inner surface
- Since N/U increases with burnup, more N becomes available with time
- Oxygen impurities present can convert the fuel into oxide form, freeing nitrogen and allowing for nitriding
- Excessive nitriding of cladding materials has not been reported



Appearance of clad nitriding of Type 304 stainless steel cladding

# Reprocessing

- Both hydrochemical and pyrochemical processes were proposed for the reprocessing techniques
- The disposal of long-lived  $^{14}\text{C}$  and the recovery of expensive  $^{15}\text{N}$  are key topics in reprocessing
- Hydrochemical processes include the direct dissolution of spent nitride fuel in  $\text{HNO}_3$  and the voloxidation of spent nitride fuel followed by the dissolution in  $\text{HNO}_3$
- 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 similar to that for metallic fuel can also be applied for nitrides
- Conversion to an oxide may be performed for the purpose of N-15 recovering via exposure to air

# 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 N<sub>2</sub> or NH<sub>3</sub> at 1073–1173 K, arc-melting of U or Pu metal under N<sub>2</sub> pressure, nitridation of fine-grained U or Pu powder formed by the decomposition of hydrides with N<sub>2</sub> or NH<sub>3</sub> and direct reaction of UH<sub>3</sub> or PuH<sub>2.7</sub> with N<sub>2</sub> or NH<sub>3</sub>

# Carbothermic Reduction

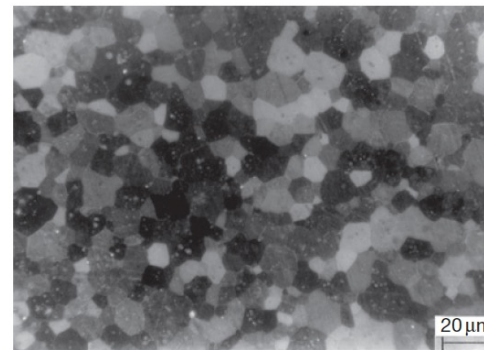
- Carbothermic reduction is the most widely used process for preparing nitride fuel
- The starting material is a dioxide and carbon, and the general reaction is
$$\text{MO}_2 + 2\text{C} + 0.5\text{N}_2 = \text{MN} + 2\text{CO}$$
- The mixture of dioxide and carbon is heated in N<sub>2</sub> gas stream, 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 N<sub>2</sub>-H<sub>2</sub> stream
- The initial C/MO<sub>2</sub> 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 N<sub>2</sub> or N<sub>2</sub>-H<sub>2</sub> to prevent the formation of higher nitrides

# Carbothermic Reduction

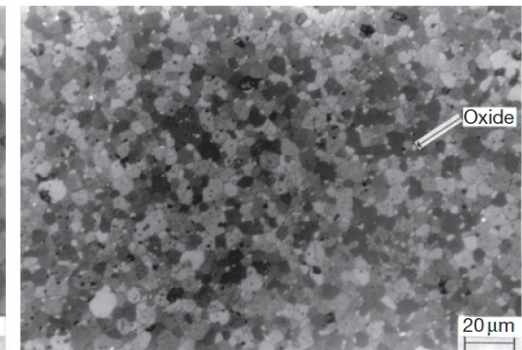
- Typical impurities in nitride fuel prepared by carbothermic reduction are oxygen and carbon
- The level of impurities can be kept lower than 1000 ppm for both oxygen and carbon by adjusting the initial C/MO<sub>2</sub> mixing ratio
- Carbonitrides (U/Pu-C-N) have complete solubility in the MN systems, 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 N<sub>2</sub> 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 sinterability 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



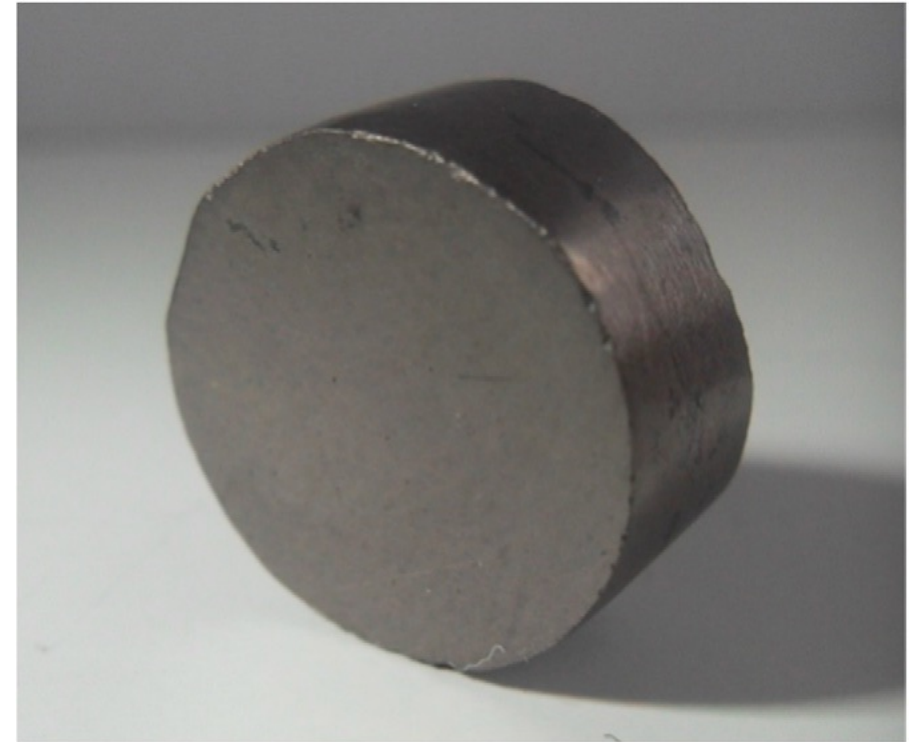
(U,Pu)N pellet containing  
0.21 wt% oxygen



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

# Nitrogen enrichment

- Nitrogen enrichment is critical for utilization in thermal reactors, and provides significant benefits for fast reactors
- The cost of nitrogen enrichment is currently about 10x that which is needed to economical fuel development



UN pellet produced by spark plasma sintering



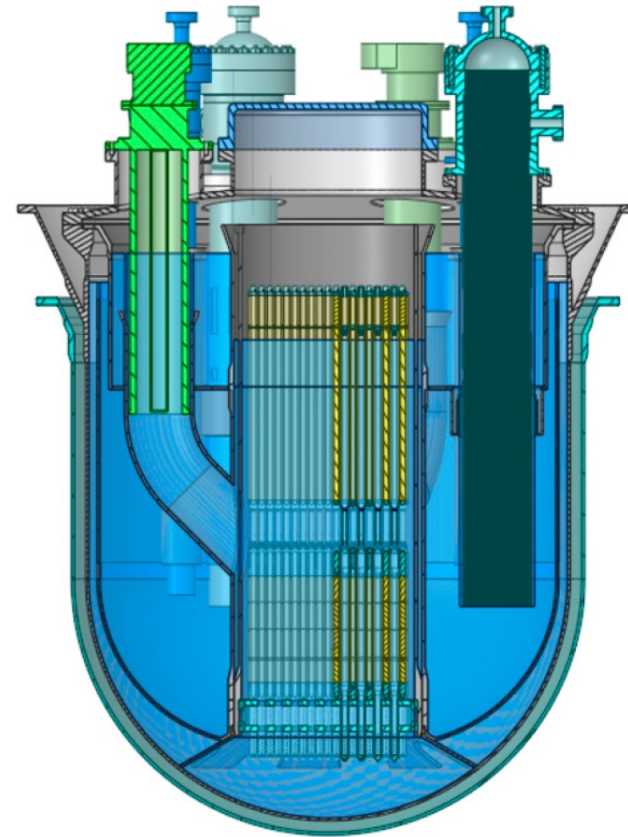
# Summary

- 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

# LEAD COOLED REACTORS

# ALFRED Reactor

- ALFRED, the advanced lead-cooled fast reactor European demonstrator
- ALFRED is a planned demonstrator reactor designed with the specific purpose to test and qualify innovative components and procedures to be used in commercial reactors
- Pool type, MOX hollowed fuel pellets, natural and forced circulation
- Planned commercial operation in 2035-2040



# ALFRED Reactor

- ALFRED plans to operate in a staged manner for licensing purposes, ramping up activities
- Currently planned materials are listed for the different stages, relying heavily on coatings and austenitic steels
- An example 15-15Ti steel in the US is D9
- Different reactor concepts with different candidate materials

**Table 2** ALFRED main parameters in the stages of operation

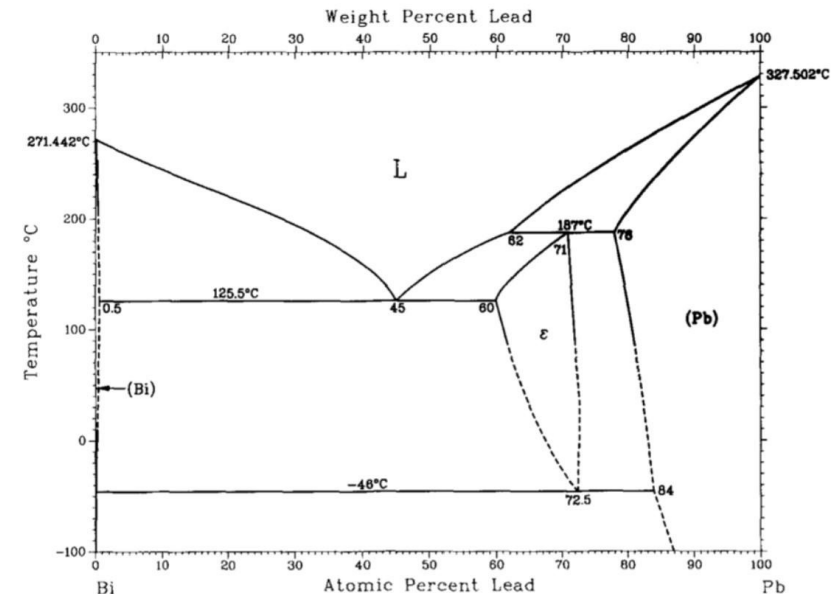
	Stage 0 (Commissioning)	Stage 1 (Low temp.)	Stage 2 (Medium temp.)	Stage 3 (High temp.)
Core inlet temperature (°C)	390	390	400	400
Core outlet temperature (°C)	390	430	480	520
Core thermal power (MW)	≈ 0	100	200	300

**Table 3** ALFRED RCS SSCs candidate materials and protective measures

Component/Part	Stage 1	Stage 2	Stage 3
FA/cladding	15-15Ti (AIM-1)	15-15Ti (AIM-1) + PLD Al <sub>2</sub> O <sub>3</sub> coating	15-15Ti (AIM-1) + PLD Al <sub>2</sub> O <sub>3</sub> coating
IV	AISI316L <sup>a</sup> + Al <sub>2</sub> O <sub>3</sub> coating <sup>b</sup>	AISI316L <sup>a</sup> + Al <sub>2</sub> O <sub>3</sub> coating <sup>b</sup>	AISI316L <sup>a</sup> + Al <sub>2</sub> O <sub>3</sub> coating <sup>b</sup>
IS	AISI316L <sup>a</sup> + Al <sub>2</sub> O <sub>3</sub> coating <sup>b,c</sup>	AISI316L <sup>a</sup> + Al <sub>2</sub> O <sub>3</sub> coating <sup>b,c</sup>	AISI316L <sup>a</sup> + Al <sub>2</sub> O <sub>3</sub> coating <sup>b,c</sup>
HEX	AISI316L <sup>a</sup>	AISI316L <sup>a,d</sup>	AISI316L or T91 + Al <sub>2</sub> O <sub>3</sub> coating <sup>b</sup> , or AFA steel <sup>e</sup>
RCP/shaft, impeller	AISI316L + Al <sub>2</sub> O <sub>3</sub> coating <sup>b</sup>	AISI316L + Al <sub>2</sub> O <sub>3</sub> coating <sup>b</sup>	AISI316L + Al <sub>2</sub> O <sub>3</sub> coating <sup>b</sup>
RV	AISI316L <sup>a</sup>	AISI316L <sup>a</sup>	AISI316L <sup>a</sup>

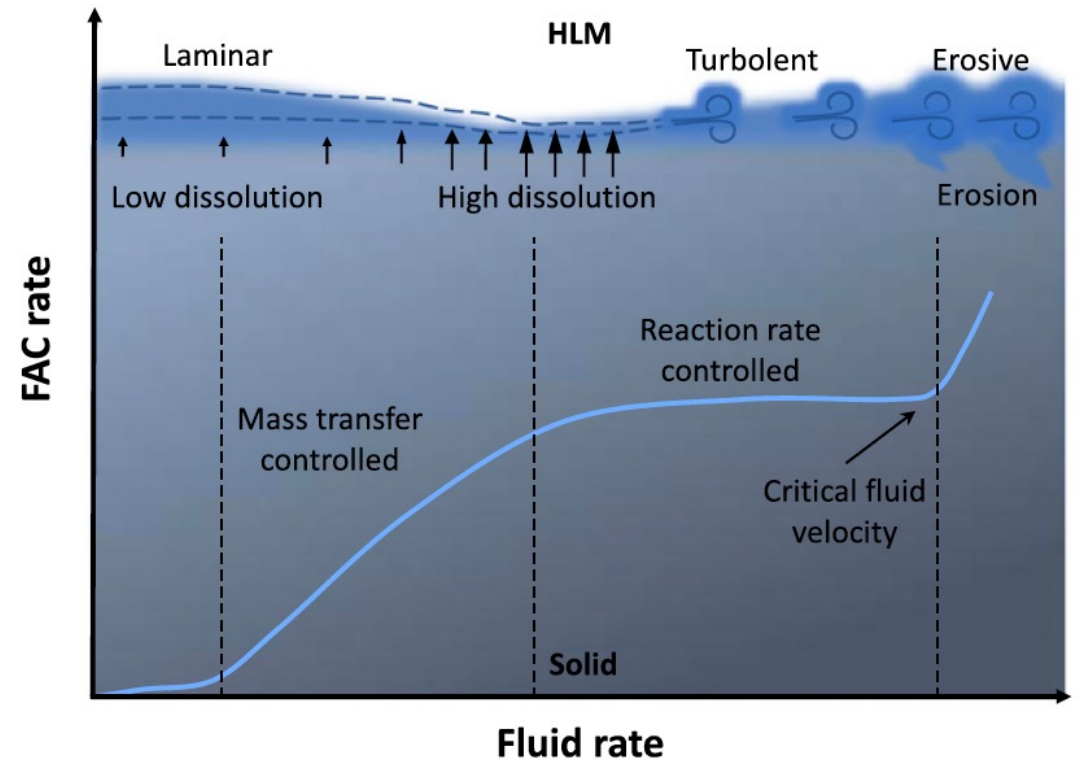
# Lead Corrosion

- The challenge of using heavy liquid metal coolant (lead and lead-bismuth) is the compatibility with structural materials at high temperature
- Pb and lead-bismuth eutectic (LBE) provide highly corrosive conditions for most structural and cladding materials
- This is most problematic for thin-walled components such as cladding tubes or heat exchangers
- Corrosion in Pb and LBE is due to the dissolution of different constituent elements, their transport, and their chemical reactions with oxygen and nitrogen



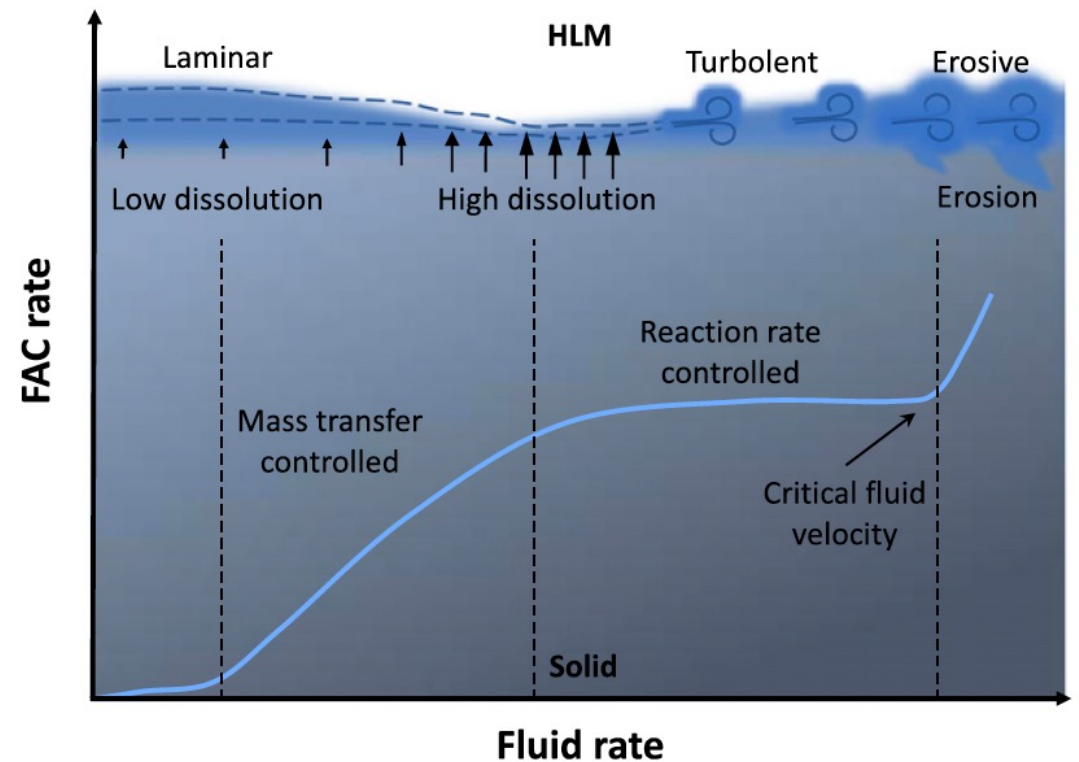
# Flow Accelerated Corrosion

- At low flow velocity, the corrosion is controlled by mass transfer, that is by diffusion of dissolved elements in the boundary layer
- When the flow velocity increases, the thickness of the laminar boundary layer decreases, leading to an increase of the corrosion rate; the enhanced flow velocity locally reduces the corrosion product concentration at the interface, further promoting the diffusion process in the boundary layer



# Flow Accelerated Corrosion

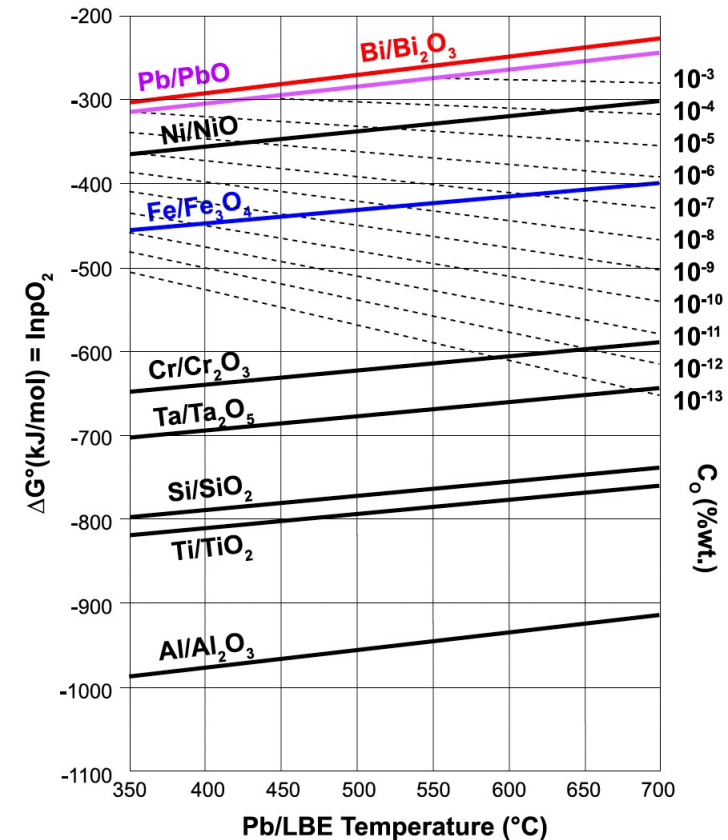
- When the velocity is high enough to “clean” the surface of the solid metal from the corrosion products, the corrosion becomes flow-independent and therefore it is considered reaction rate controlled
- At higher flow velocities, above a critical value, erosion-corrosion and also cavitation-corrosion may occur, leading to a significant increase of the corrosion rate





# Impurities

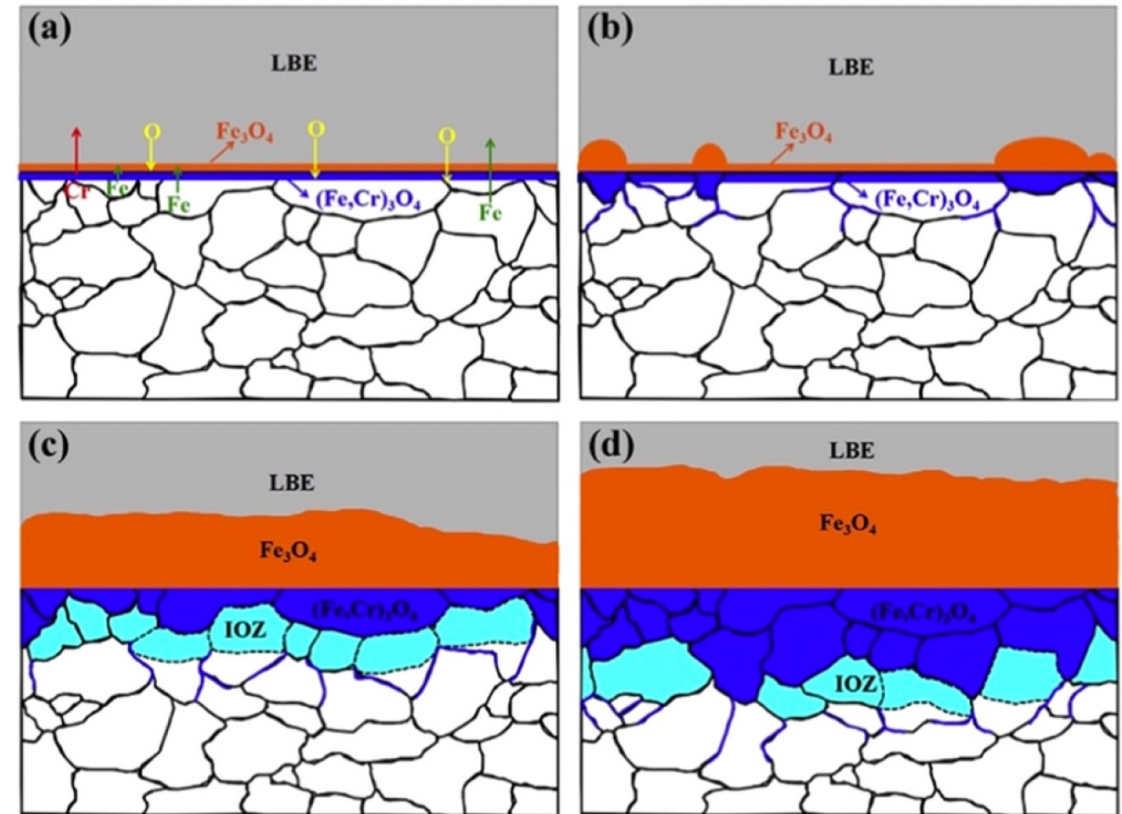
- A factor that has a considerable effect on the corrosion rate processes is the presence of nonmetallic impurities such as carbon, nitrogen, and oxygen
- Impurity elements can take part in corrosion reactions and can form compounds with dissolved species
- Oxides of the steel components are more stable than the LBE, and thus a Fe-Cr oxide layer on steel surfaces can protect the structural materials





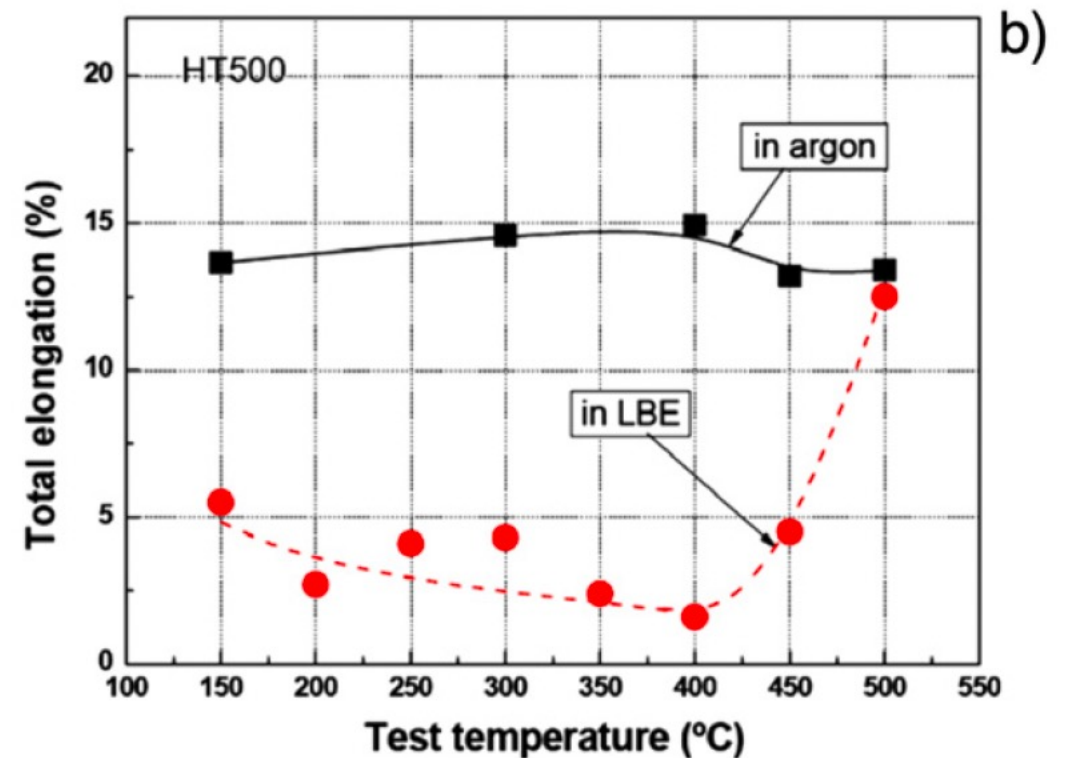
# Oxide Passivation

- Adequate control of the oxygen concentration allows one to maintain the Fe-Cr oxide film, without oxidizing the LBE
- If insufficient oxygen is present, the steel will suffer dissolution corrosion
- The oxide layer can form as a multi-layered structure dependent upon O content, temperature, and flow, with  $\text{Fe}_3\text{O}_4$  and  $\text{FeCrO}_2$  phases



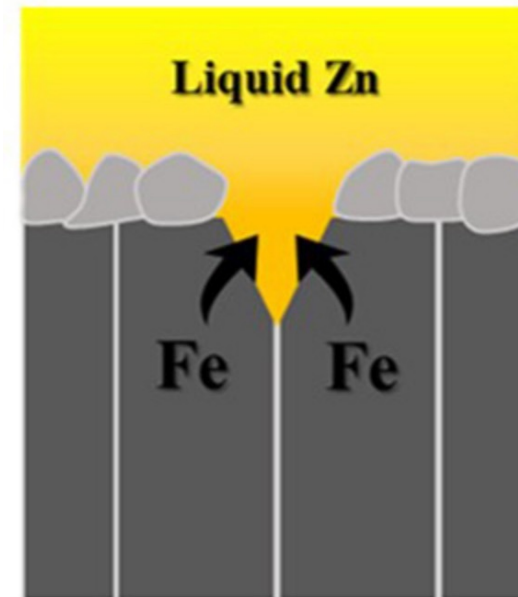
# Mechanical Property Effects

- Liquid metal embrittlement (LME) is a known phenomenon, but its mechanism is not fully understood
- Contact with LM causes a decrease in ductility, resulting in a premature brittle failure in an otherwise ductile material
- LME occurs by nucleation of a crack at the wetted surface of a solid and the subsequent propagation into the bulk until ultimate failure



# LME

- The loss of ductility of solid metals when in contact with liquid metal appears to be limited to a particular temperature range known as the ductility trough
- For the F/M T91 steel in liquid lead, a ductility trough between 160C and 425C was found
- The ductility trough is detected by following the evolution of the ultimate tensile stress or energy to rupture with temperature
- The working theory on LME is based on a reduction of the surface energy by absorption of liquid metal atoms at the crack tip of the solid



# End of Module 3

- This concludes our module 3
- Exam will take place next Thursday (11/2)
- Will cover molten salts, carbides and nitrides, and Pb-cooled reactors