# NE 591: Advanced Reactor Materials

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# SUPERCRITICAL WATER COOLED REACTORS

# Supercritical Water Reactor (SCWR)

- Similar to a traditional light water reactor, but operates at a supercritical pressure

- Water heated in the core becomes a supercritical fluid, which can directly be used in a steam turbine

- Removes the added step of a heat exchanger, increasing the efficiency of the reactor system
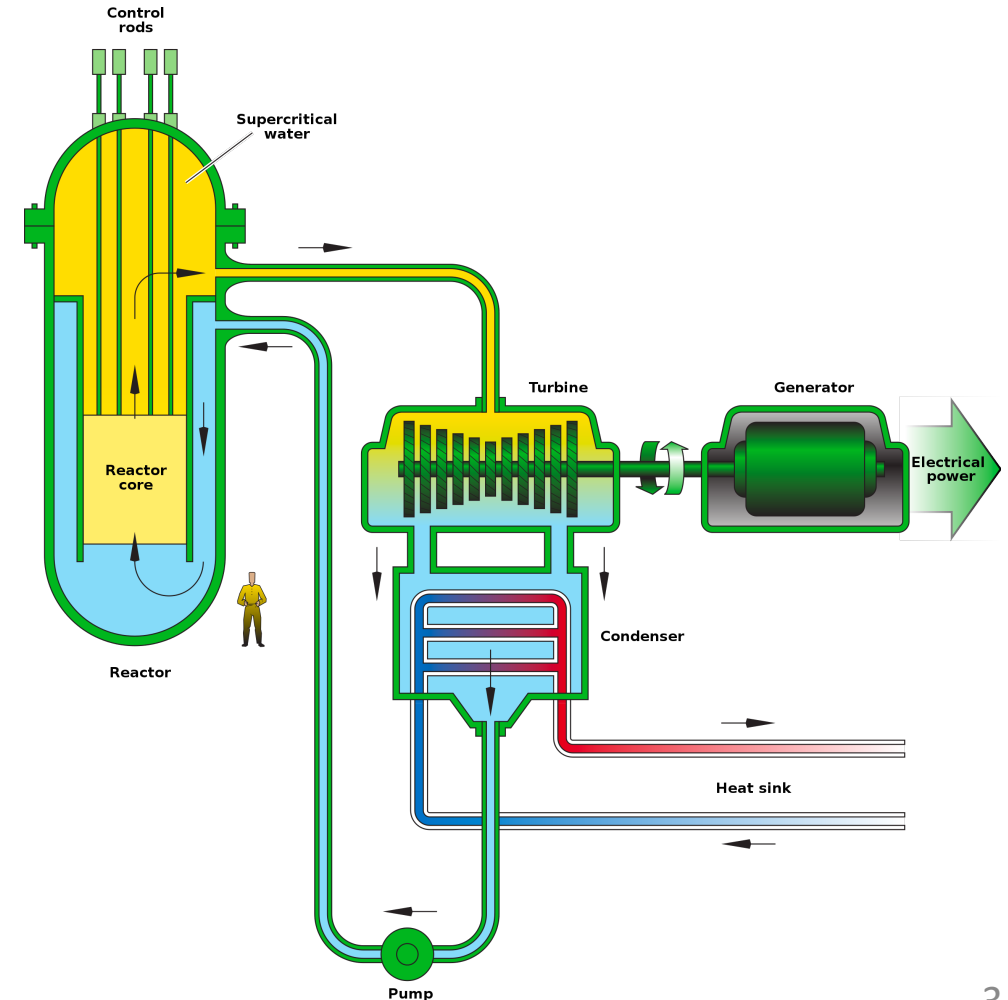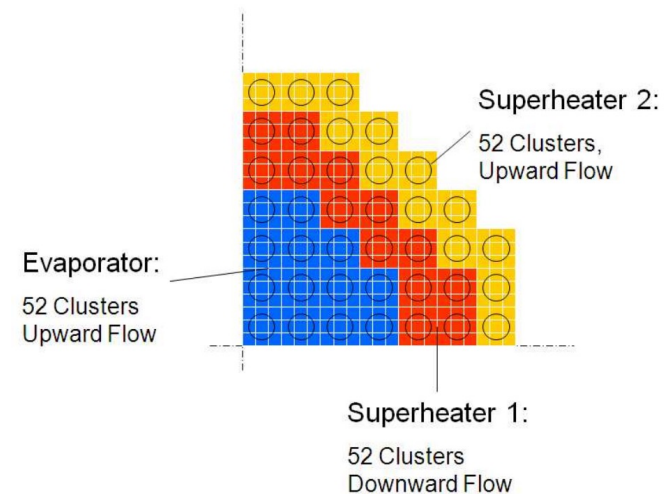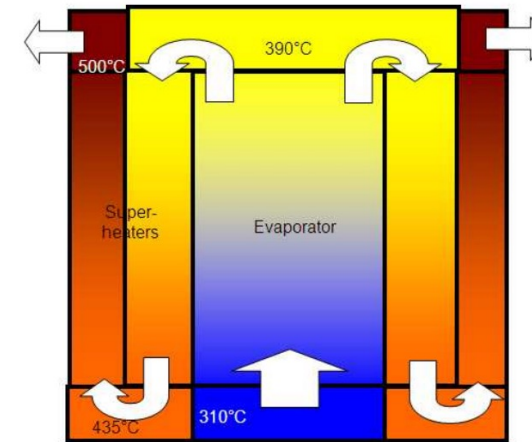
# Supercritical water

- A supercritical fluid is a substance with a temperature and pressure above its critical point
- At such a point, distinct solid and liquid phases do not exist
- Critical point of water is 22 MPa and 647 K
- Density is highly variable, based on temperature and pressure:
    - 0.78 g/cc @ 25 MPa and 280 C
    - 0.09 g/cc @ 25 MPa and 500 C
    - these are reasonable inlet/outlet temperatures for SCWR coolant



Phase Diagram for Water
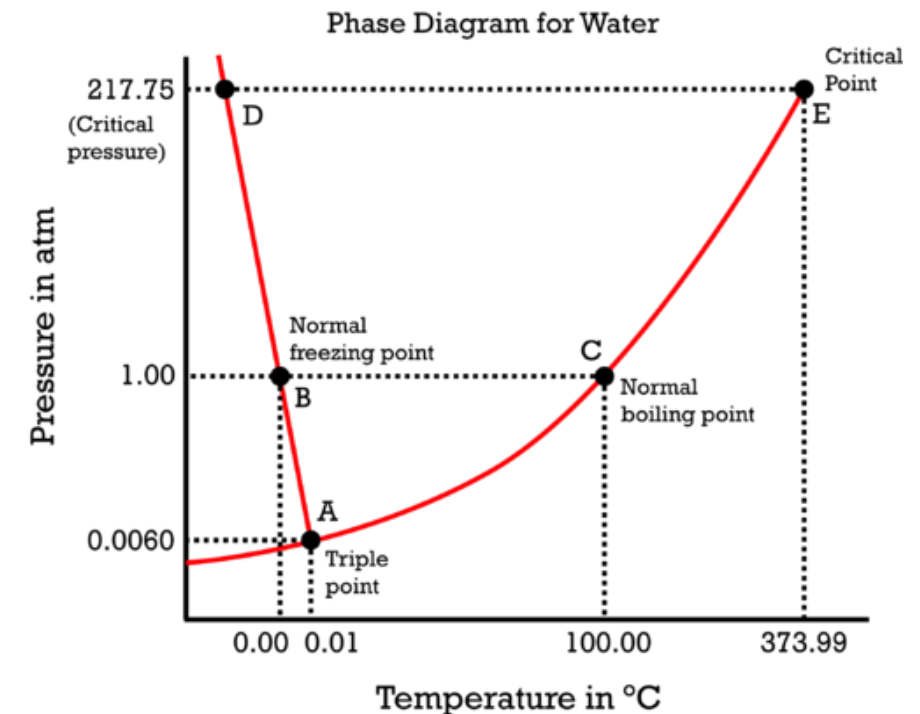
# Comparison to LWR

- SCWR
  - coolant in: 280 C
  - coolant out: 600 C
  - outlet specific enthalpy: 3150 kJ/kg
  - three pass coolant
  - coolant pressure: 25 MPa

- LWR
  - coolant in: 275 C
  - coolant out: 315 C
  - outlet specific enthalpy: 200 kJ/kg
  - one pass coolant
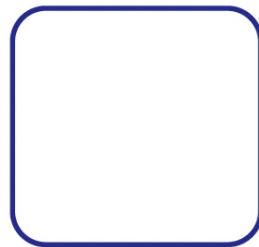  - coolant pressure: 15 MPa

# Features

- Supercritical water has excellent heat transfer properties allowing a high power density, a small core, and a small containment structure
- The use of a supercritical Rankine cycle with its typically higher temperatures improves efficiency (would be ~45 % versus ~33 % of current PWR/BWRs)
- This higher efficiency would lead to better fuel economy and a lighter fuel load, lessening residual (decay) heat
- SCWR is typically designed as a direct-cycle, whereby steam or hot supercritical water from the core is used directly in a steam turbine with no intermediate heat exchangers, etc
- SCWRs can operate as a fast breeder, or utilize heavy water and the thorium fuel cycle
- Disadvantages include operating at very high temperatures and pressures, increasing material challenges
- The economic advantage of a direct cycle is a downside with regard to safety, in that a cladding breach means your turbine and generators are directly exposed to radioactivity
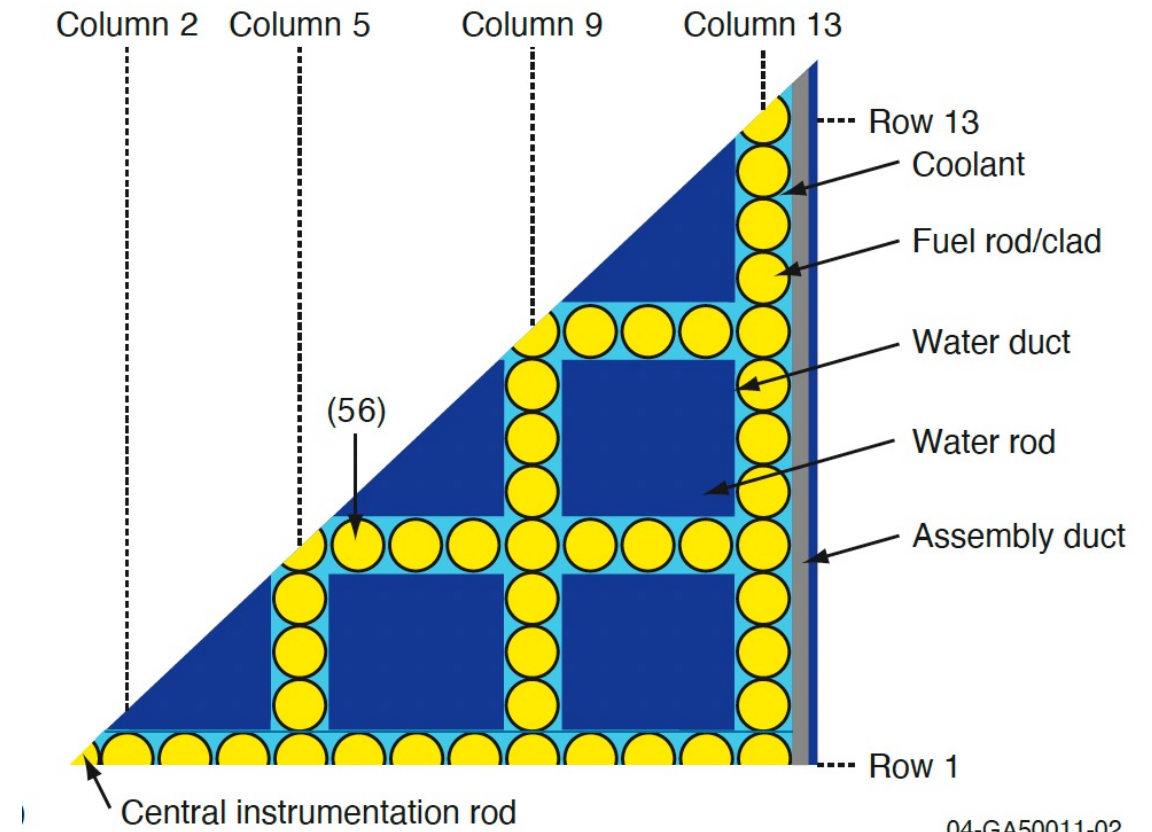- Corrosion in SCW is a challenge

# SCW geometry

- There is experience in SCW cycles in the fossil fuel industry, however they are able to use thick-walled geometries that are not feasible in nuclear designs

Fuel rod outer diameter = 12 mm
Clad wall thickness = 0.4 – 0.6 mm

Water rod outer diameter = 40 mm (square)
Water rod wall thickness = 0.4 mm

Column 2  Column 5    Column 9    Column 13

Row 13
Coolant
Fuel rod/clad
Water duct
(56)
Water rod
Assembly duct
Row 1

Central instrumentation rod

04-GA50011-02

1/8 assembly model SCWR core

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# Corrosion

- These very thin-walled components provide little margin for corrosion in an SCWR core, where the consequences of failure are significant

- Oxide films and deposition of corrosion products from out-of-core components can lead to overheating (and failure) and changes in reactivity

- SCW corrosion studies have included F/M steels, austenitic steels, Ni alloys, Zr alloys and Ti alloys

| Alloy class | Alloy | Temp. (°C) | Water chemistry | Exposure time (h) |
|---|---|---|---|---|
| Austenitic stainless steel | 304, 304L, 316, 316L, 316 + Zr, 310, 310S, 310 + Zr, 347H, Sanicro28, D9, 800H, AL6XN, Carpenter 20C B3, Nitronic-50, PNC1520, alloy 1.4970 | 290–650 | Deaerated ($<10$ ppb) to 8000 ppb dissolved oxygen | 100–3000 |
| Nickel-based | 600, 625, 690, 718, 825, C22, B2, C276, MAT21, MC | 290–600 | Deaerated ($<10$ ppb) to 8000 ppb dissolved oxygen, $<0.1$ mS cm$^{-1}$ | 100–3000 |
| Ferritic–martensitic | T91, T91a, T91b, HCM12A (T122), HCM12, HT-9 (12Cr–1Mo–1WVNb), NF616 (T92), MA956, 2.25Cr–1Mo (T11), P2 | 290–650 | Deaerated ($<10$ ppb) to 8000 ppb dissolved oxygen, $<0.1$ mS cm$^{-1}$ | 100–3000 |
| Oxide dispersion strengthened | 9Cr, 12Cr, F/M, 316, Inconel, Hastelloy G-30, 19Cr, 14Cr–4Al, 16Cr–4Al, 19Cr–4Al, 22Cr–4Al | 360–600 | 25 ppb | 200–3000 |
| Zirconium-based | Zr, Zr–Nb, Zr–Fe–Cr, Zr–Cr–Fe, Zr–Cu–Mo, Zr-2, Zr-4 | 400–500 | Deaerated ($<10$ ppb dissolved oxygen), $<0.1$ mS cm$^{-1}$ | $<2880$ |
| Titanium-based | Ti–3Al–2.5V, Ti–6Al–4V, Ti–15Mo–5Zr–3Al, Ti–15V–3Al–3Sn–3Cr | 290–550 | 8000 ppb dissolved oxygen, 0.1 mS cm$^{-1}$ | 500 |

# Alloy Classes

- Corrosion is strongly dependent upon the alloy class
- Oxidation is most rapid for F/M steels and slowest for Ni alloys
- Temperature has a very strong effect on corrosion
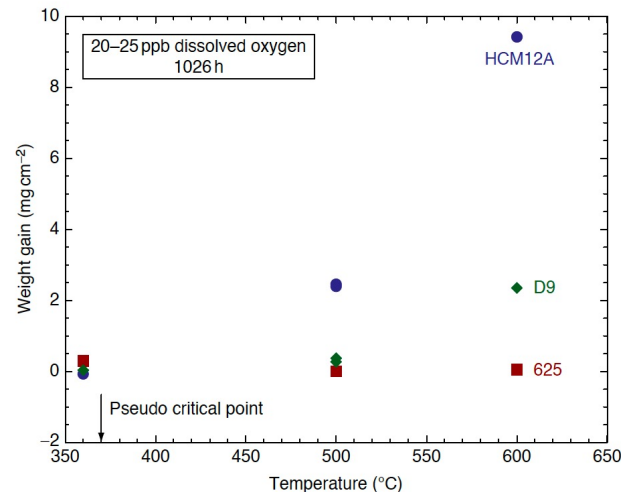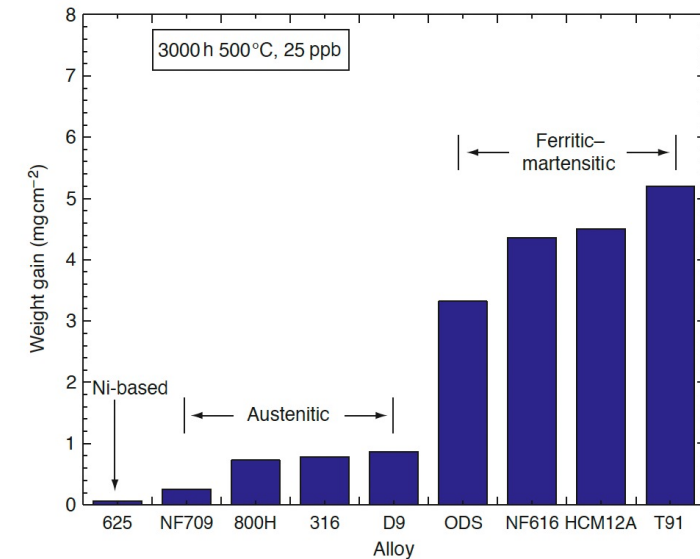


Dissolved O content 25 ppb



HCM12A = F/M
D9 = aust.
625 = Ni
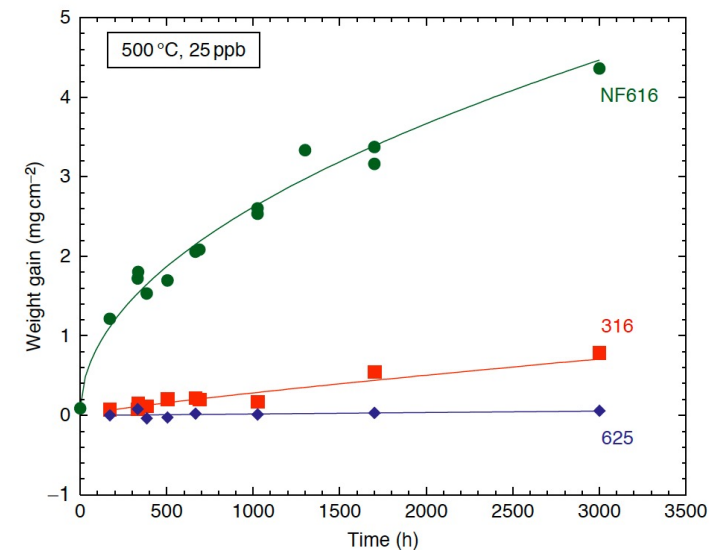
NF616 = F/M
316 = aust.
625 = Ni

# Stress Corrosion Cracking

- Austenitic stainless steels and nickel-based alloys exhibit susceptibility to IGSCC in pure SCW over the temperature range of 400–650C

- IGSCC decreases with temperature, but overall fracture increases with temperature

- Small additions of HCl or H2SO4 increase susceptibility to IGSCC in austenitic alloys

- Ni based alloys are more susceptible to SCC than austenitic steels

- Higher Cr content in Ni alloys seems to reduce the extent of SCC

- F/M alloys are generally resistant to SCC (HT-9 is an exception)

- Irradiation strongly exacerbates SCC, but the effect decreases with increasing temperature

# LEAD COOLED REACTORS

# ALFRED Reactor

- ALFRED, the advanced lead-cooled fast reactor European demonstrator
- ALFRED is today a 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
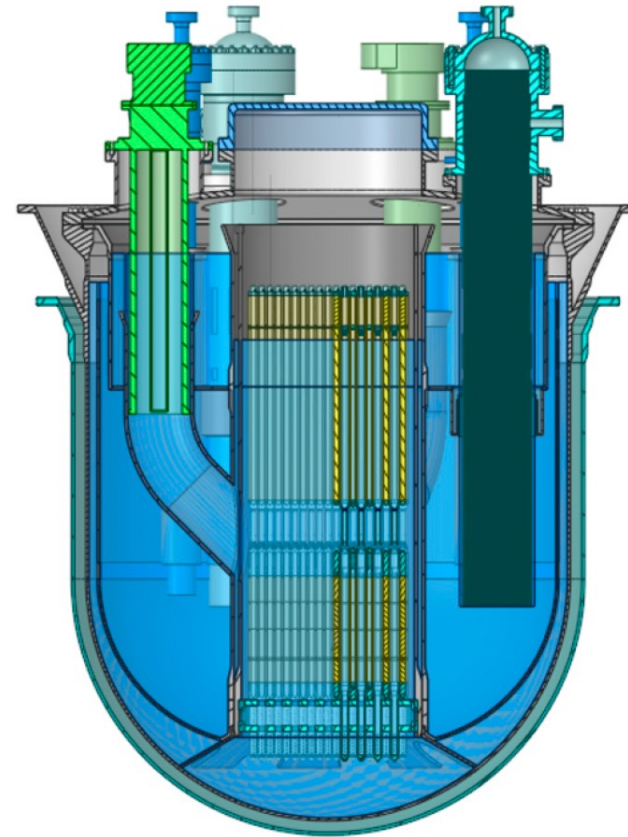
# ALFRED Reactor

- 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) | $\approx 0$ | 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 $Al_2O_3$ coating | 15–15Ti (AIM-1) + PLD $Al_2O_3$ coating |
| IV | AISI316L[a] + $Al_2O_3$ coating[b] | AISI316L[a] + $Al_2O_3$ coating[b] | AISI316L[a] + $Al_2O_3$ coating[b] |
| IS | AISI316L[a] + $Al_2O_3$ coating[b,c] | AISI316L[a] + $Al_2O_3$ coating[b,c] | AISI316L[a] + $Al_2O_3$ coating[b,c] |
| HEX | AISI316L[a] | AISI316L[a,d] | AISI316L or T91 + $Al_2O_3$ coating[b], or AFA steel[e] |
| RCP/shaft, impeller | AISI316L + $Al_2O_3$ coating[b] | AISI316L + $Al_2O_3$ coating[b] | AISI316L + $Al_2O_3$ coating[b] |
| RV | AISI316L[a] | AISI316L[a] | AISI316L[a] |

# 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 corrosion 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
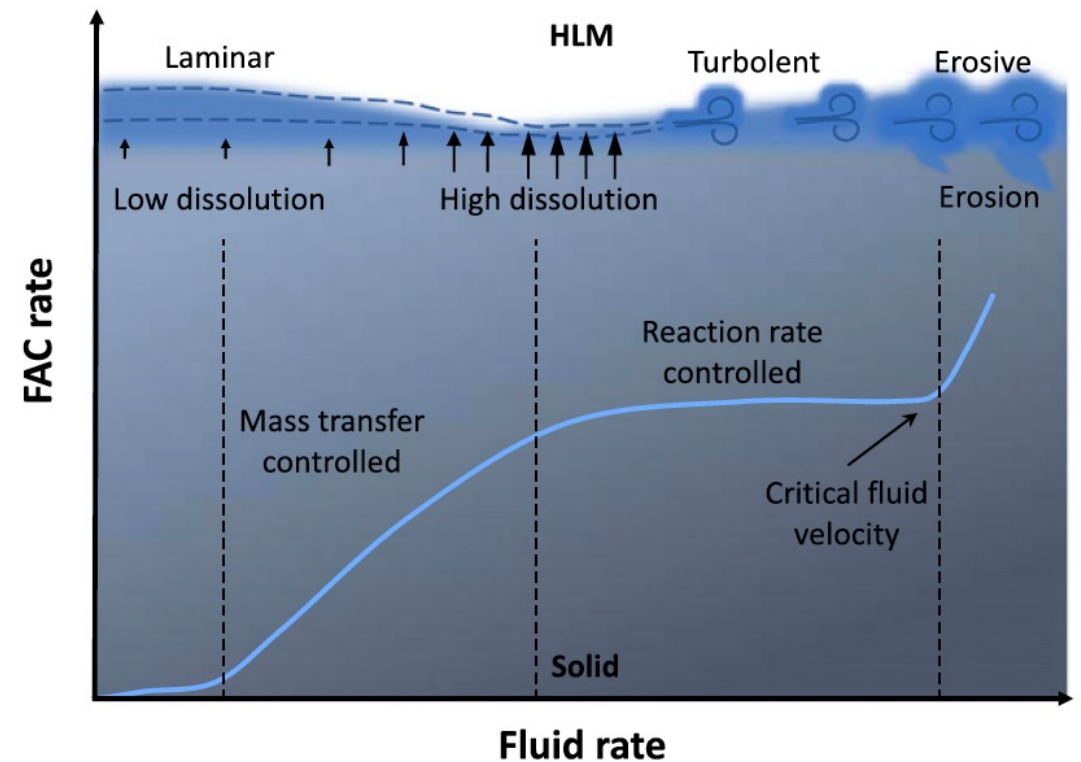
# Flow Accelerated Corrosion

- 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



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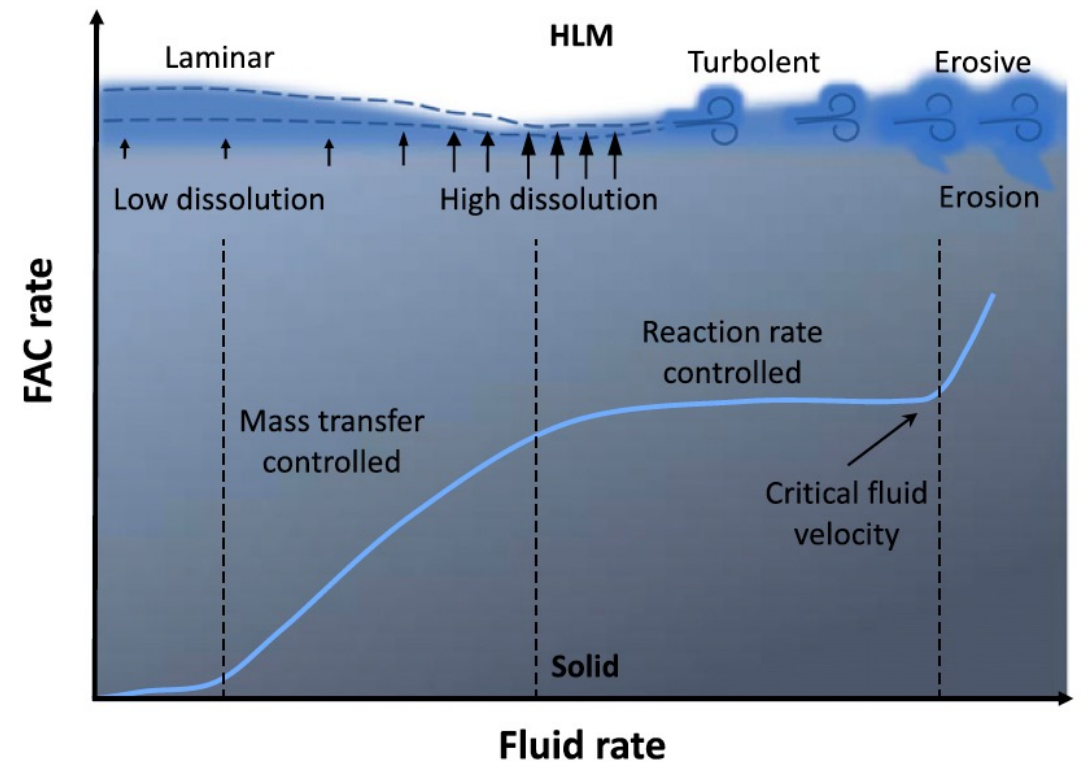
# Impurities

- 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
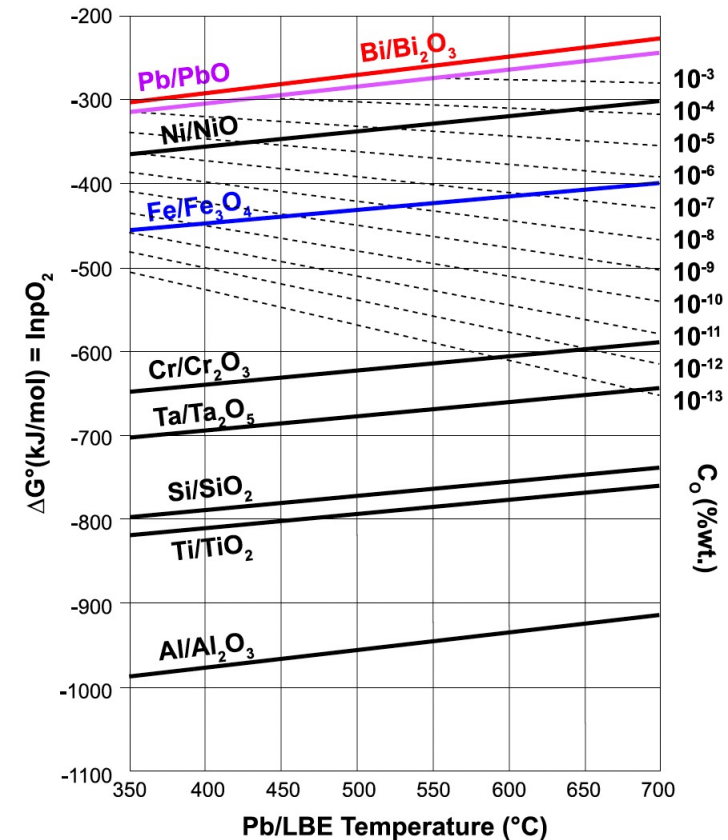
# Oxide Passivation

- 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 Fe3O4 and FeCrO2 phases
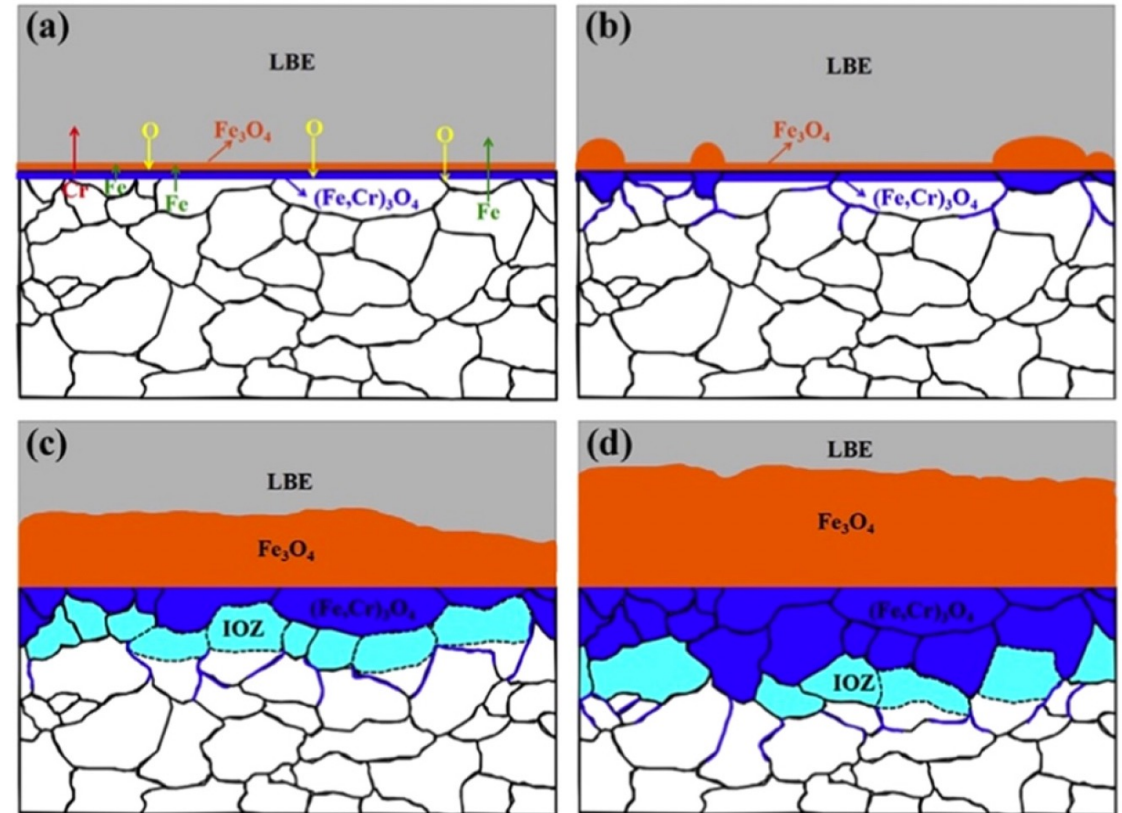
# Mechanical Property Effects

- 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
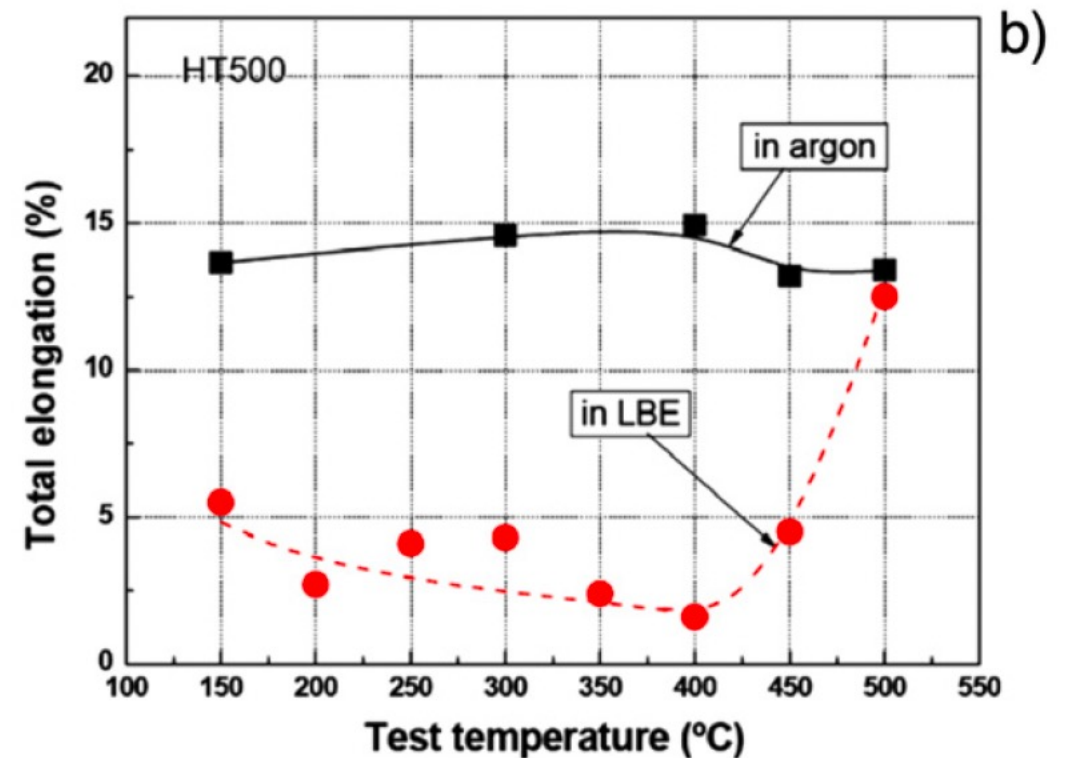
# LME

- 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
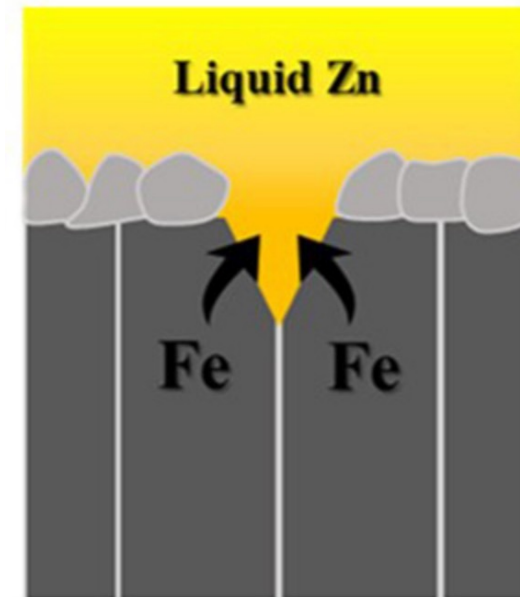
# COMPOSITE FUELS

# Composite Fuels

- Composite fuels consist of a fissile phase dispersed in an inert, nonfuel matrix
- These types of fuels have been used since the 1950s in high-temperature and high-power density applications
- Composite fuels are typically distinguished into two types: Cermet and Cercer

- Cermet: ceramic fuel particles dispersed in a metallic matrix
- Cercer: ceramic fuel particles in a ceramic matrix
- 47 different fuel matrix combinations have been experimentally explored
- Composite fuels have potential as high burnup fuels to either transmute transuranic elements, or to replace conventional UO2 fuel pellets

# Composite Fuels

- The most complete experimental work focused on UO2 particles dispersed in stainless steel

- The primary feature that distinguishes composite fuels from the pellet-in-cladding fuel types is the localization of fuel material within an inert matrix

- Fuel particles can be individually clad within the matrix material by an individual coating

Fuel kernels — Matrix

Cladding

Coating

Outer 'pressure vessel'

Porous 'buffer'
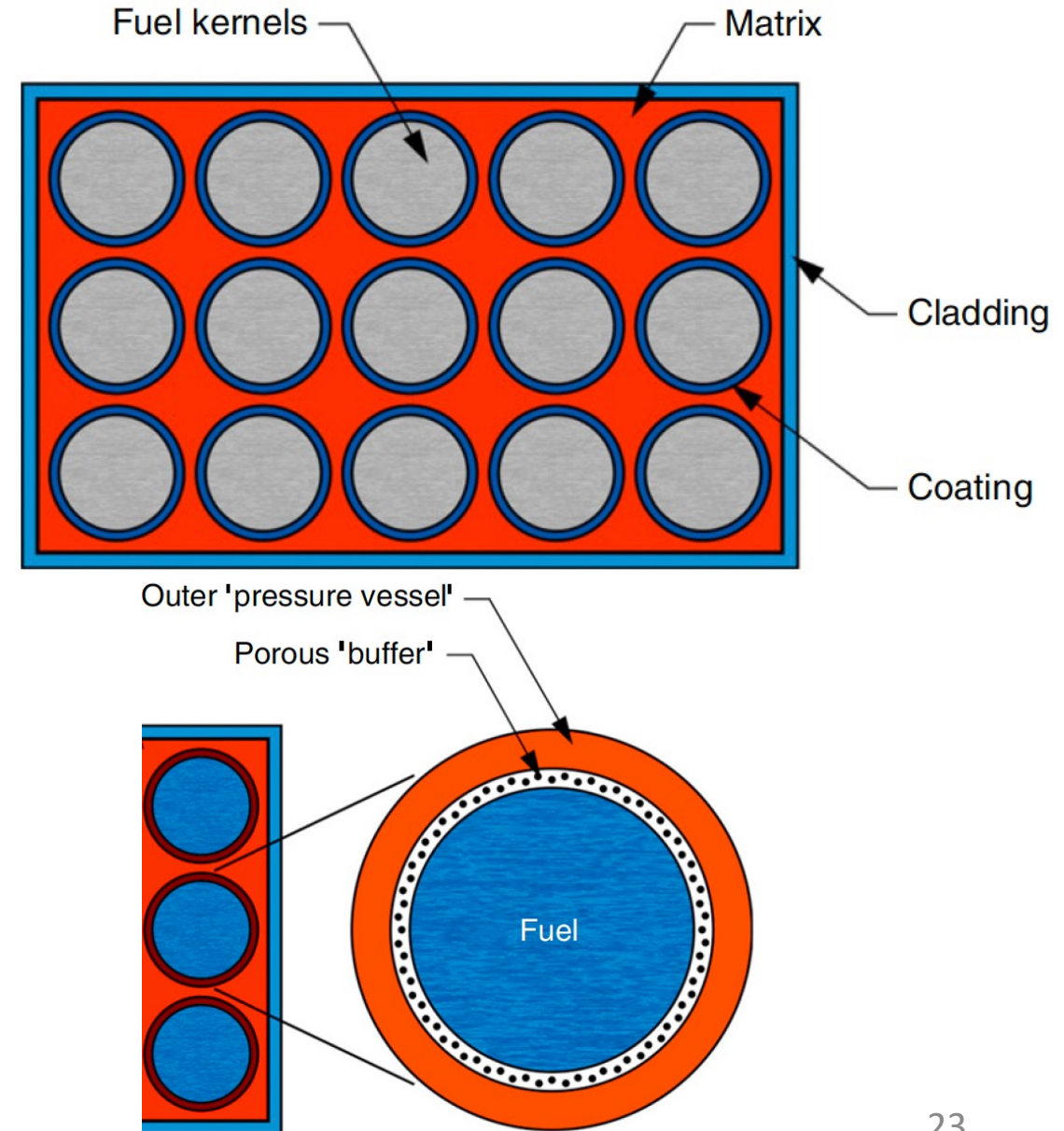
Fuel

# Cermet Fuel

- The performance of the Cermet fuel depends on the ability of the matrix to retain strength and ductility during irradiation
- The strength of the matrix must be sufficient to resist cracking from stresses due to solid fission products and fission gas swelling
- The major source of matrix degradation is the fission fragments ejected from the fuel

- The distance between (or density) of fuel particles must be sufficient such that the damage region around a given particle does not overlap with an adjacent particle
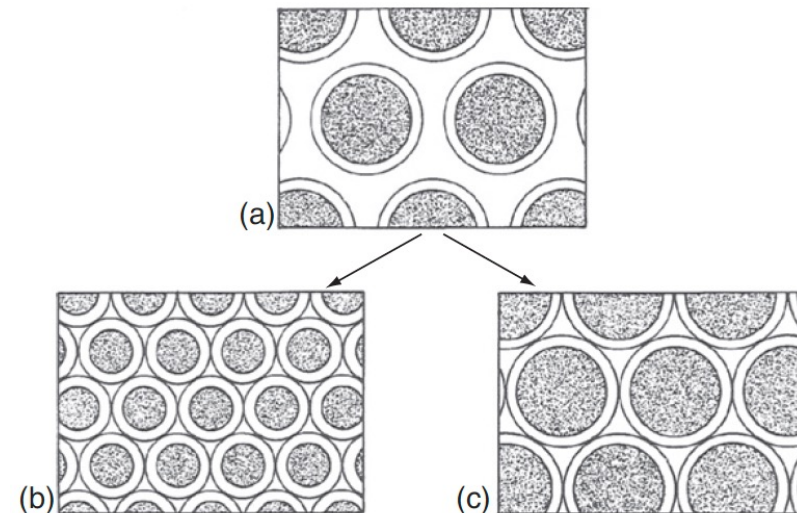
# Cercer Fuel

- The typical failure mode in cercer fuels is fuel particle swelling that leads to a tensile stress in the matrix, followed by matrix cracking

- Models have been constructed to predict failure taken from thermal expansion in duplex ceramics

- Increasing the interparticle distance, decreasing the particle size, decreasing fuel swelling and thermal expansion, etc., reduce the probability of fracture of the matrix

$$\left[\frac{\beta R_{\mathrm{p}}(\beta+2)}{\pi(\beta+1)}\right]^{1/2}\left[\left(\frac{1}{(\beta+1)^2}+6\frac{\sqrt{2}}{\pi}V_{\mathrm{p}}\right)c_4\right] > K_{\mathrm{IC}}$$

# Composite Thermal Conductivity

- The behavior of composite fuels can be heavily influenced by fuel operating temperature, and thermal conductivity is of primary importance in the irradiation behavior of these fuels

- Fuel particle size, shape, orientation, and distribution, and matrix porosity and the thermal conductivities of the fuel and matrix species are the key properties of interest
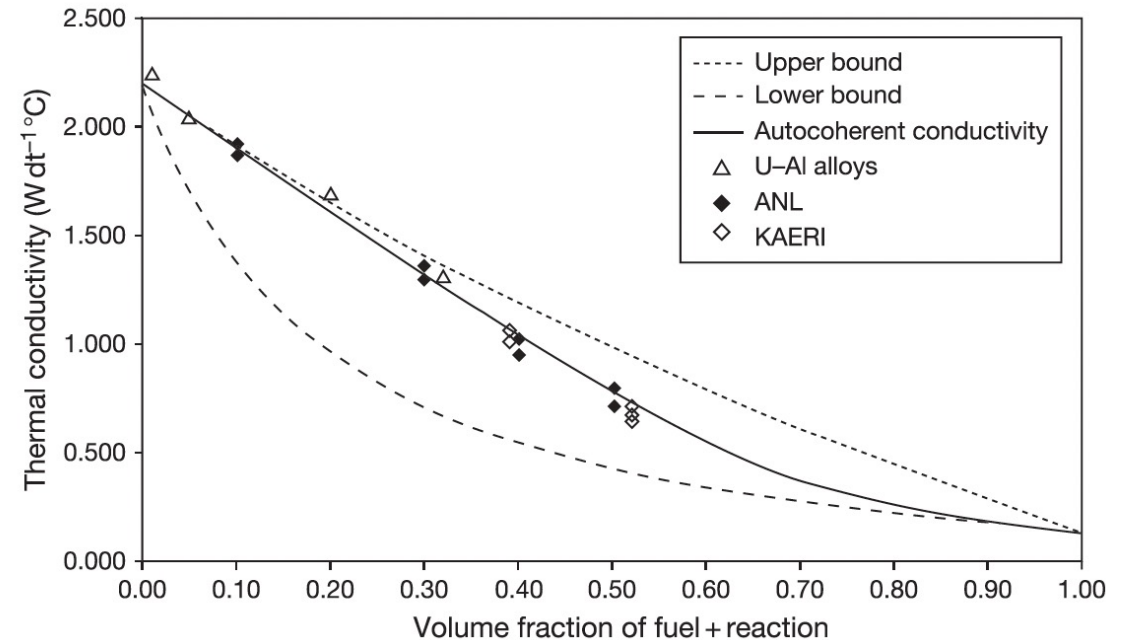
# Irradiation Behavior

- Most irradiation information is on UO2 dispersed in stainless steel
- Full-size 20vol% plate-type elements reached 65 at% burnup at surface temperatures of 315–427C with no blistering or cracking
- There are bounding limits on fission density (+ loading) and surface temperature
- Higher matrix loadings are possible, but are restricted to low (<15%) burnups
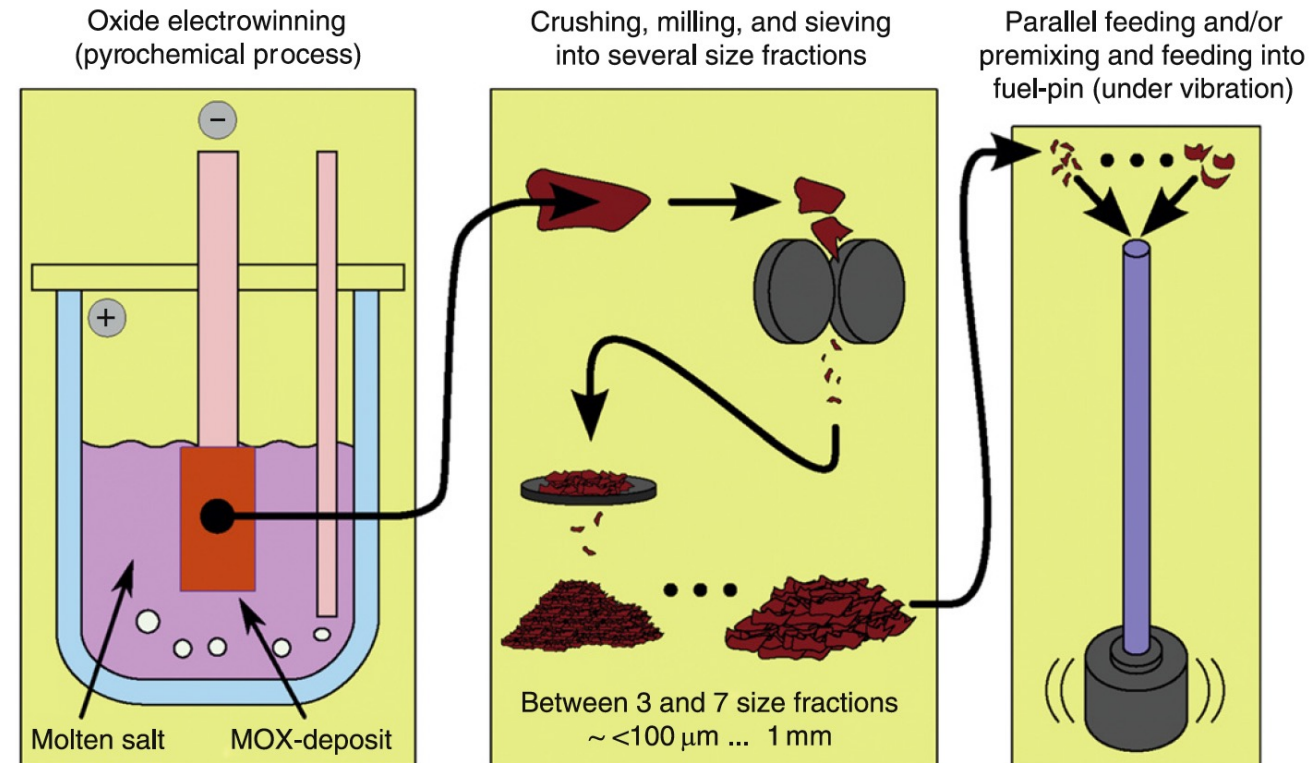


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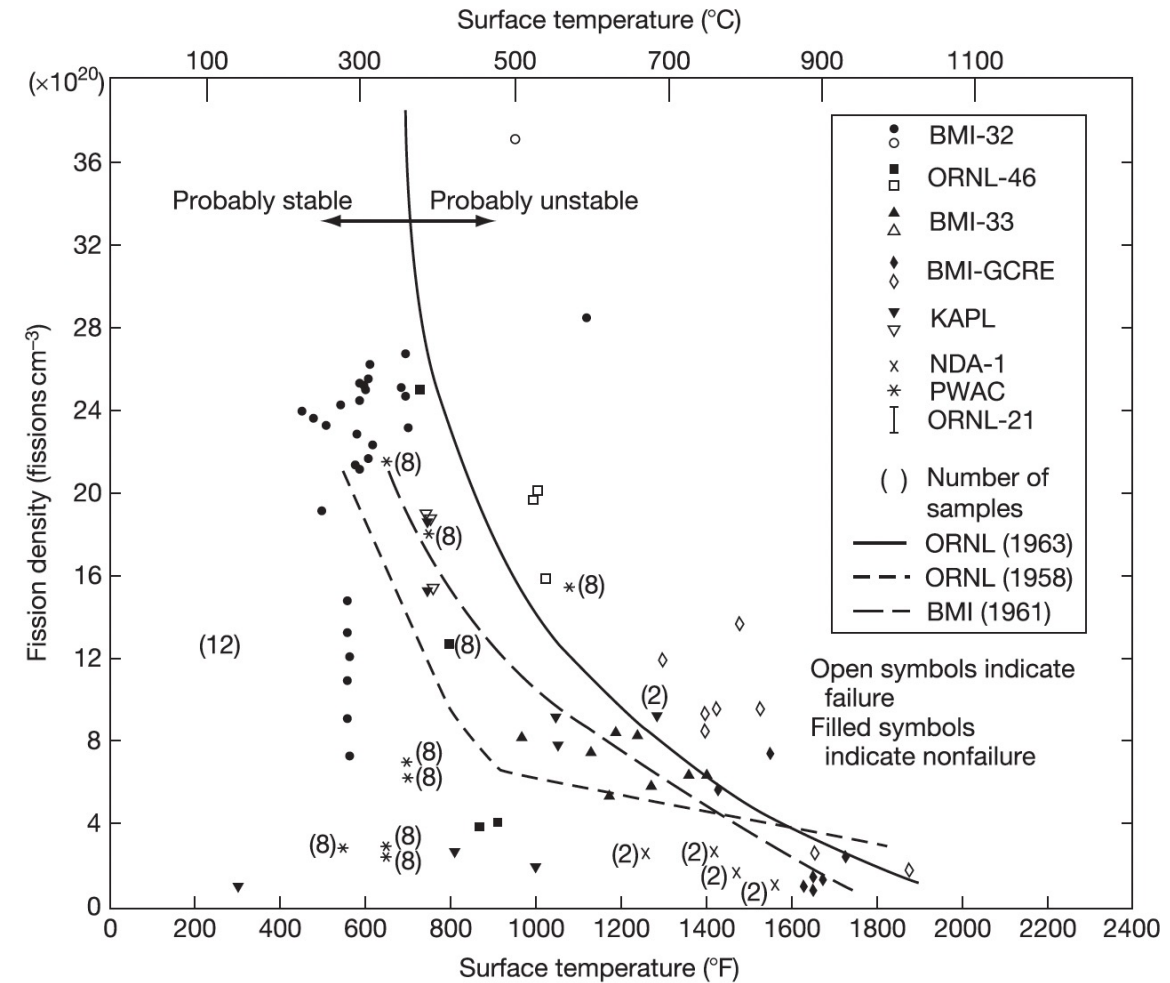
# PARTICLE FUELS

# Particle Fuels

- When the fissile isotopes are coming from spent fuel that is chemically separated (reprocessed), particle fuel with its direct filling of fuel particles into the fuel pin offers several advantages
- Two major types of particle fuel are sphere-pac and Vipac

Vipac

sphere-pac
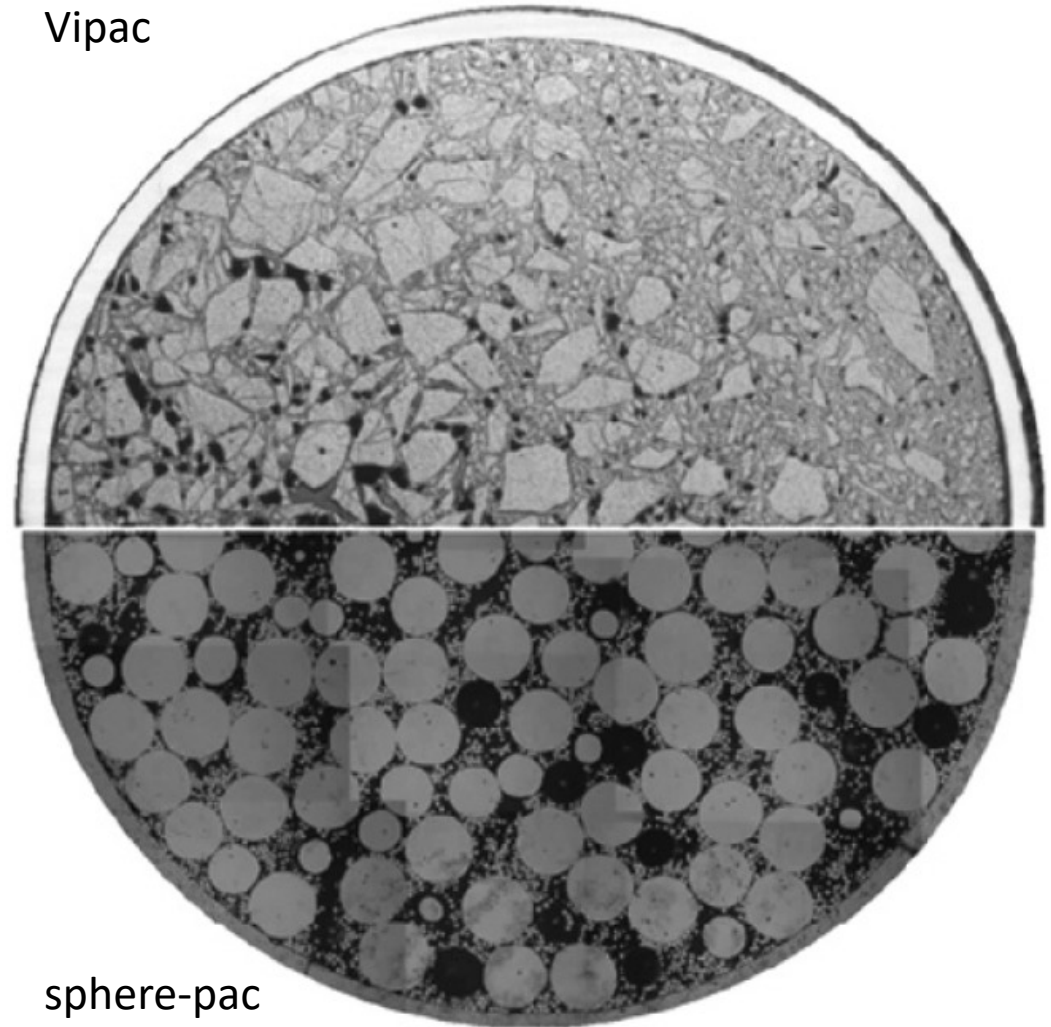
# Vipac

- The usage of randomly shaped (angular shards) particles as nuclear fuel component filled in a cladding goes back to the 1950s
- Reprocessing of fuel from the BOR-60 reactor was pursued to developed fuel for the BN-600 reactor – MOX fueled fast reactors
- These particles are fed into the cladding under vibration
- Vibration packing = Vipac



Oxide electrowinning (pyrochemical process)

Molten salt    MOX-deposit

Crushing, milling, and sieving into several size fractions

Between 3 and 7 size fractions ~ <100 μm ... 1 mm

Parallel feeding and/or premixing and feeding into fuel-pin (under vibration)

# Sphere-Pac

- Sphere-pac fuel is also composed of particles which are directly filled into a fuel pin
- However, particles are shaped into spheres to generate a more predictable arrangement of particles in the fuel pin
- Sphere-pac is used in conjunction with the PUREX process, combined with follow-up processes such as actinide extraction

- A fully aqueous method offers excellent distribution of the fissile material in the matrix and the formation of solid solution in the ceramic
- This also eliminates the need for mechanical devices, reduces powder generation, and thus minimizes contamination

# Particle Fuels

- This modified geometry of fuel will present important changes in the fuel properties as a unit

- The thermal conductivity is reduced, which increases the centerline temperature, and can lead to restructuring

- The fuel is softer because of the void space, reducing FCMI

- Significantly higher fission gas release, due to the prevalence of free surfaces

- In the case of a cladding breach, this increased fuel surface area provides greater opportunity for coolant reaction with the fuel

- At fuel startup, fuel particles are not bonded, and in case of early life cladding breach, potential loss of fuel particles