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Materials for Nuclear Energy
Nuclear Fuels, Uranium Oxide

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Outline

1. Radiation Damage Event
2. Atom Displacement
3. Damage Cascade
4. Point Defect Formation & Diffusion
5. Loss of, Sinks for Point Defects
6. Radiation Induced Segregation
7. Radiation Induced Dislocations
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9. Radiation Effects on Phase Stability
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11. Surrogates for Neutron Irradiation
12. Radiation Effects on Hardening, Deformation
13. Radiation Effects on Fracture Toughness, Embrittlement
14. Radiation Effects on Creep and Growth (Zr cladding alloys)
15. Radiation Effects on Corrosion: emphasis on Stress Corrosion Cracking (SCC)
16. **Nuclear Fuels, Uranium Oxide** (*not in Was*)
General aspects

• “For use as nuclear fuel, enriched UF$_6$ is converted into uranium dioxide (UO$_2$) powder that is then processed into pellet form. The pellets are then fired in a high-temperature, sintering furnace to create hard, ceramic pellets of enriched uranium. The cylindrical pellets then undergo a grinding process to achieve a uniform pellet size. The pellets are stacked, according to each nuclear core's design specifications, into tubes of corrosion-resistant metal alloy. The tubes are sealed to contain the fuel pellets: these tubes are called fuel rods. The finished fuel rods are grouped in special fuel assemblies that are then used to build up the nuclear fuel core of a power reactor.

• The metal used for the tubes depends on the design of the reactor - stainless steel was used in the past, but most reactors now use a zirconium alloy. For the most common types of reactors (BWRs and PWRs) the tubes are assembled into bundles with the tubes spaced precise distances apart. These bundles are then given a unique identification number, which enables them to be tracked from manufacture through use and into disposal.”

Centrifuge Enrichment

$^{238}\text{UF}_6$ is slightly heavier than $^{235}\text{UF}_6$ and collects on the outside walls (Depleted/Tails)

$^{235}\text{UF}_6$ is lighter and collects in the center (enriched)

Degree of enrichment depends on the rotational speed of the centrifuge

The gas centrifuge process has three characteristics that make it economically attractive for uranium enrichment:

**Proven technology:** Centrifuge is a proven enrichment process, currently used in several countries.

**Low operating costs:** Its energy requirements are less than 5% of the requirements of a comparably sized gaseous diffusion plant.

**Modular architecture:** The modularity of the centrifuge technology allows for flexible deployment, enabling capacity to be added in increments as demand increases.

Fuel Fabrication

- Reactor fuel is generally in the form of ceramic pellets.
- These are formed from pressed uranium oxide which is sintered (baked) at a high temperature (over 1400°C).
- The pellets are then encased in metal tubes to form fuel rods, which are arranged into a fuel assembly ready for introduction into a reactor.
$UF_6$ Gas to $UO_2$ Powder to Pellets

Fuel Pellets

UO$_2$ Pellet Manufacture

- Uranium dioxide fuel pellets, which are widely used in light water reactors, are manufactured by a conventional powder processing method [10].
- UO$_2$ powder is pressed into green pellets and then sintered at 1700-1780 °C in a hydrogen-containing gas.
- The UO$_2$ pellet properties - density, pore structure, and grain size - greatly influence the in-reactor performance of the UO$_2$ pellet. Typical grain size ~ 8 µm.
- In particular, the amount of fission gas released during an irradiation decreases as the grain size of the UO$_2$ pellets increases [11], and thus large-grain UO$_2$ pellets are desirable at a high burn-up. A large-grain UO$_2$ pellet meets the restraint of the fission gas release which is one of the most important requirements for a high burn-up fuel.
- The fabrication of large-grain UO$_2$ pellets has been investigated extensively, so many fabrication methods have been developed. The most common method is simply to add sintering agents to UO$_2$ powder. Many sintering agents are known such as niobia [12,13], titania [14], chromia [15], and magnesia [16].
References


Quoted from Nuclear Engineering And Technology, 40 No.1, Feb. 2008.
Phase Diagrams for UO$_2$

- These are the basic phase diagrams for the U-O system. However, the stoichiometry of the oxide phases can be controlled via the partial pressure of oxygen. Fuels are manufactured close to UO$_2$. 

[Wirth]
The O:U ratio can be controlled via the partial pressure of oxygen, which depends in turn on mass transfer, surface reaction and solid state diffusion rates. The relevant reaction is:

\[ xH_2O + UO_2 \rightarrow UO_{2+x} + xH_2 \]
Nuclear Fuel Assembly

Fuel Pellet

Fuel Rod

Fuel Assembly

Uranium Oxide

• The materials characteristics of the $\text{UO}_2$ pellets are important to the optimal functioning of the fuel.

• A certain amount of porosity is required in the fuel because it serves to trap fission gases. This is in contrast to the metallic components.

• A gap is deliberately introduced between the fuel pellets and the cladding to allow for subsequent swelling.
Irradiation Effects in Oxide Fuels

- Pellet re-distribution
- Swelling, Porosity evolution
- Grain growth, Recrystallization
- Extensive cracking
- RIM structure (Pu rich)
- Swelling, precipitation & release of fission products
- Degraded thermal conductivity
- Mechanical & Chemical interaction with the cladding due to swelling & fission product transport

From: K. Edsinger, EPRI
Temperature, RIM effects

• The low thermal diffusivity of the fuel means that a significant thermal gradient exists during operation. This T profile induces enough (thermoelastic) stress to cause cracking. The cracking further influences the transport of fission products. The horizontal axis is relative radius, such that “zero” is the center of the pellet.

• Also Pu accumulates at the periphery of the pellets from resonance capture of U-238. The burn-up is significantly higher in the rim by a factor of about 2.

**Xe Conc., Porosity, RIM μstructure**

- The Xe concentration (unfortunately!) is highest at the periphery, as is the porosity.
- The grain size at the edge (above) is much finer than in the bulk (below); mechanisms not yet clear but almost certainly must involve recrystallization.

Competing Effects

- Swelling of the fuel expands the oxide pellets against the (Zircaloy) cladding. This is good in the sense that it closes or minimizes the gap thereby promoting heat transfer. However, it also induces hoop stress in the cladding, which accelerates failure (of the cladding).
- The dominant driver for swelling is fission gas release of Xe and Kr. These (high Z) noble gases reduce heat transfer in the fuel-cladding gap.
Fission Products in Fuel

- Dissolved in UO$_2$: Rare Earths + (Mo) + (Zr)
- Metallic inclusions: Noble Metals + (Mo)
- Second oxide phase: Ba + (Zr) as BaZrO$_3$
- Alkali metals: Cs (as Cs$_2$O or Cs$_2$UO$_4$)
- Rare gases: Xe + Kr
- Zr in the fuel present in second oxide
- Mo present either dissolved in oxide, or as metallic inclusions
- Xe both in solution and in gas bubbles
- Rare earths form tri-valent oxides (oxygen released from fissioning of U); Zr & Mo form tetra-valent oxides; Ba, Sr di-valent.
Estimate Xe bubble size

(a) Given a flux of $10^{19}$ neutrons/m$^2$/s, estimate the rate (per m$^3$ per s) at which Xe atoms are produced, assuming that 1% of the fission products are Xe. Assume that the macroscopic cross-section for fission is 0.1 m$^{-1}$.

- Given the stated flux and assumption that the fraction is 1% that results in Xe, the number of Xe atoms generated is the flux, times the macroscopic fission cross-section, 0.1 cm$^{-1}$, times the fraction:

$$\text{Atoms}(\text{Xe}) = 10^{19}.\text{m}^{-2}\text{s}^{-1} * 0.1 \text{ m}^{-1} * 0.01 = 10^{16} \text{ Xe atoms m}^{-3}\text{s}^{-1}$$

(b) Convert this quantity to a volume generated (per m$^3$ per s) using standard conversions to arrive at liters at STP [standard temperature, pressure]. Note that this volume will be an underestimate since the fuel temperature is substantially higher than STP, although the pressures are somewhat higher also.

- Liters(\text{Xe}) = 10^{16} \text{ Xe atoms m}^{-3}\text{s}^{-1} * (\text{Avogadro} = 0.602 10^{24})^{-1} * 22.4 \text{ liters/mole} = 0.372 \times 10^{-6} \text{ liters / m}^3 / \text{s}.

(c) Assuming that gas bubbles are nucleated at a number density of $10^{23}$ /m$^3$, how big will the bubbles be (sphere equivalent diameter, in meters) if they contain all the gas generated over 1 day? Comment on the magnitude of your result.

- $0.000000372 \text{ liters / m}^3 / \text{s} * 3600 * 24 = 0.03215 \text{ liters /m}^3/\text{day} = 3.215 \times 10^{-5} \text{ m}^3 /\text{m}^3/\text{day}$. Divide up this volume over $10^{23}$ bubbles per m$^3$, gives $3.215 \times 10^{-28} \text{ m}^3/\text{bubble}$ – taking the sphere equivalent diameter gives $8.5 \times 10^{-10} \text{ m}$, or nearly 1 nm. This may not seem to be a large value, given that the bubble spacing is approximately 20 nm, but this is the size after only 1 day, and fuel remains in a reactor for about 4 years!
**Xe Diffusion & Fission Gas Release**

- Fission gas release may be linked to diffusion along grain boundaries and out of the oxide fuel.
- Occurs only in the central portion of the fuel pellets where the temperatures are >1000°C and the Xe diffusion coefficient in the UO$_2$ lattice is sufficiently high. 
  \[ D_g(\text{Xe}) = 3.5 \times 10^{-9} \exp\left(-\frac{Q}{RT}\right) \text{ m}^2\text{s}^{-1}, \quad Q = 250,000 \text{ kJ/mole} \]
- The characteristic time for diffusing species to move a distance x is \(\frac{x^2}{D_g}\). The shortest distance fission products can move to reach an escape path is the radius of the grains in the fuel. For \(\sim 10 \mu\text{m}\) grain sizes, \(x = a \sim 5 \times 10^{-6} \text{ m}\). At 1000°C, the diffusivity of Xe is \(D_g = 2 \times 10^{-19} \text{ m}^2\text{s}^{-1}\). Thus, the time required to reach a grain boundary from the center of the grain is:

\[
 t \approx \frac{x^2}{D_g} = \frac{(5 \times 10^{-6})^2}{2 \times 10^{-19}} = 1.25 \times 10^8 \text{ s} \approx 4 \text{ years}
\]
- This is about equal to the time that a fuel rod spends in the reactor (~ 4 years). If reaching the grain boundaries in the fuel is sufficient to deliver the gas to the rod interior, then fission gas release will be observed in high burn-up fuel.
- Note the significance of larger grain sizes in the fuel!
Summary

• Standard nuclear fuel is uranium oxide.
• $\text{UO}_2$ is only the approximate form although nuclear fuel is manufactured to be close to stoichiometric.
• Fission products include noble gases such as Kr and Xe. During service, the fuel is subject to significant thermal gradients and therefore stresses. Cracking and gas bubble formation occur.
• It is important to avoid mechanical failure of the cladding and, in particular, to avoid release of radioactive fission products.
Supplemental Slides

• (none)