

NE 795: Advanced Reactor Materials

Fall 2023

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Housekeeping

- Sent out a google form for the presentation survey

Last Time

- Completed FCCI for metallic fuels
 - highlighted different compositions, and which species participate
 - Ce and Nd are primary FPs that diffuse into the cladding; Fe and Ni diffuse into the fuel
- Metal Fuel Fabrication
 - injection casting process
- Pyroprocessing
 - well established method relying on molten salt and anode deposition
- Metallic fuel performance modeling
 - BISON, ALFUS, LIFEMETAL
 - all still currently require extensive assumptions

MIXED OXIDE FUEL

MOX Introduction

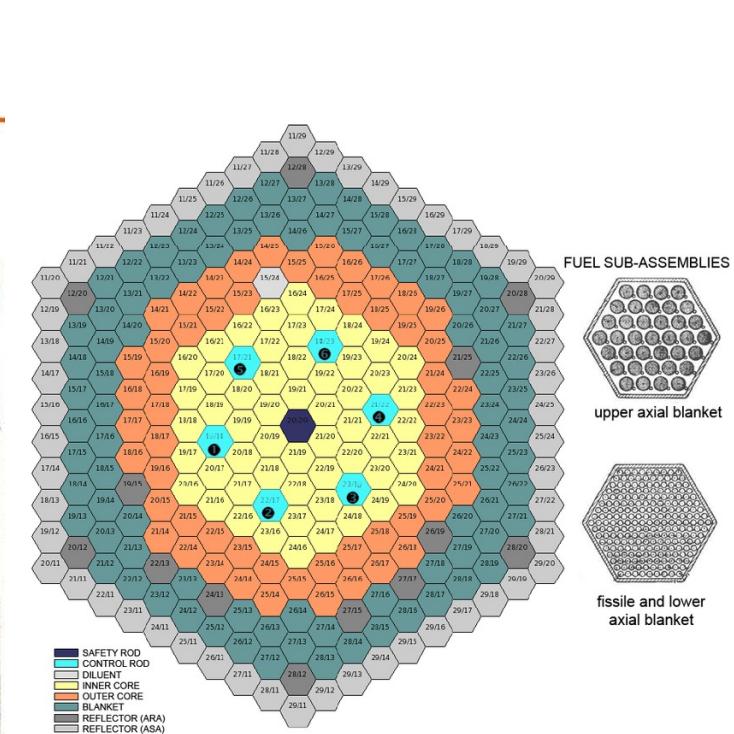
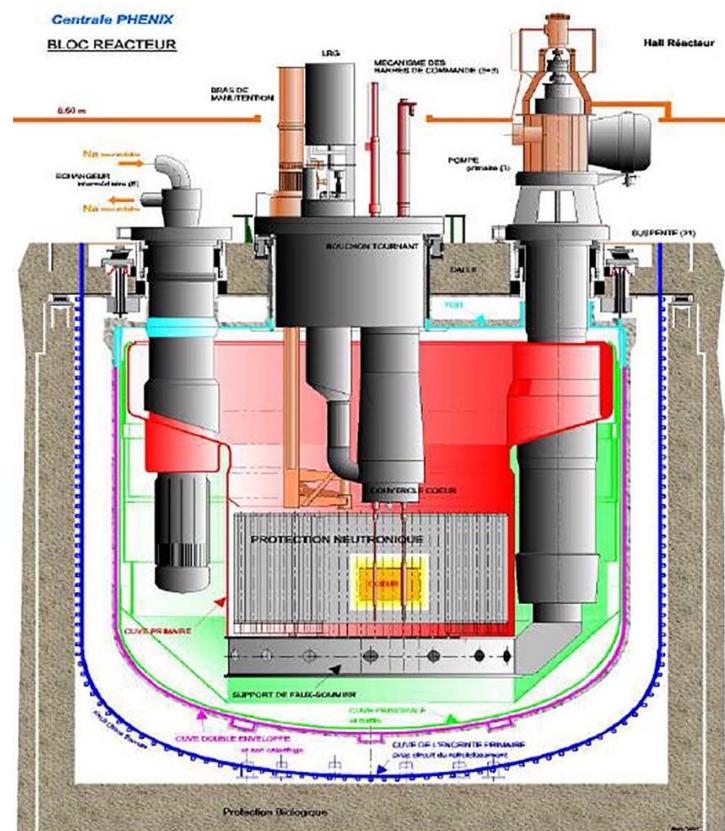
- Despite some disadvantages, such as its low U density, poor thermal conductivity, and its chemical reaction with sodium, MOX fuel ($\text{U},\text{Pu}\text{O}_2$) is the fuel that has been used most in fast reactors
- In order to avoid the dramatic swelling of metallic fuels, MOX fuels were explored in fast reactors
- Behavior was observed to be satisfactory and was relatively widely implemented in SFRs

Table 1 Main characteristics of standard fuel pins irradiated in the prototype and commercial fast reactors ($\rho > 200 \text{ MWth}$)

	<i>BN350</i>	<i>Phénix</i>	<i>PFR</i>	<i>BN600</i>	<i>FFTF^a</i>	<i>Super-Phénix</i>	<i>MONJU</i>
First criticality	1972	1973	1974	1979	1980	1985	1994
Thermal power (MWth)	750	563	600	1470	400	3000	714
Electric power (MWe)	350 ^b	250	250	600	—	1200	280
Type of fuel	UO_2	$(\text{U},\text{Pu})\text{O}_2$	$(\text{U},\text{Pu})\text{O}_2$	UO_2	$(\text{U},\text{Pu})\text{O}_2$	$(\text{U},\text{Pu})\text{O}_2$	$(\text{U},\text{Pu})\text{O}_2$
No. of subassemblies (inner/outer core)	109/117	55/48	28/44	209/160	28/45	193/171	108/90
No. of pins per assembly	127	217	325	127	217	271	169
Type of spacer	Wire	Wire	Grids	Wire	Wire	Wire	Wire
Length of pin (m)	1.8	1.793	2.25	2.445	2.38	2.7	2.813
Height of fissile column (m)	1.06	0.85	0.914	1.0	0.914	1.0	0.93
Lower fertile column length (m)	0.4	0.3	0.45	0.4	—	0.3	0.35
Upper fertile column length (m)	0.57	0.31	0.45	0.4	—	0.3	0.3
Clad outer diameter (mm)	6.9	6.55	5.8	6.9	5.84	8.5	6.5
Clad thickness (mm)	0.4	0.45	0.38	0.4	0.38	0.565	0.47
Helical wire diameter (mm)		1.15			1.42	1.2	1.32
Pellet diameter (mm)		5.42				7.14	5.4
Fuel clad diametral gap (mm)		0.23			0.14	0.23	0.16
Central hole diameter (mm)	0	0	1.5	0		2.0	0
Fissile atoms/(U + Pu) (%) (inner core/outer core)	17/26	18/23	22/28	17/26	20/25	15/22	16/21
Fuel density (% TD)	95	95.5	97	95	91	95.5	85
Smeared density (%)	75	88	78	77	86	83	80
Plenum volume (cm ³)	8	13	14	21	19	43	28
Maximum linear power (W cm ⁻¹)	400	450	420	472	413	470	360
Peak cladding temperature (°C)	570	650	670	700	660	620	675
Maximum neutron flux ($10^{15} \text{ n cm}^{-2} \text{ s}^{-1}$)	7	7.1	7.6	7.7	7	6	6.0
Maximum burnup (at.%) (GWd t ⁻¹)	9.0	16.9	23.5	11.8	24.5	Not relevant	Not relevant
Maximum dose (dpa)	60	156	155	90	—	—	—

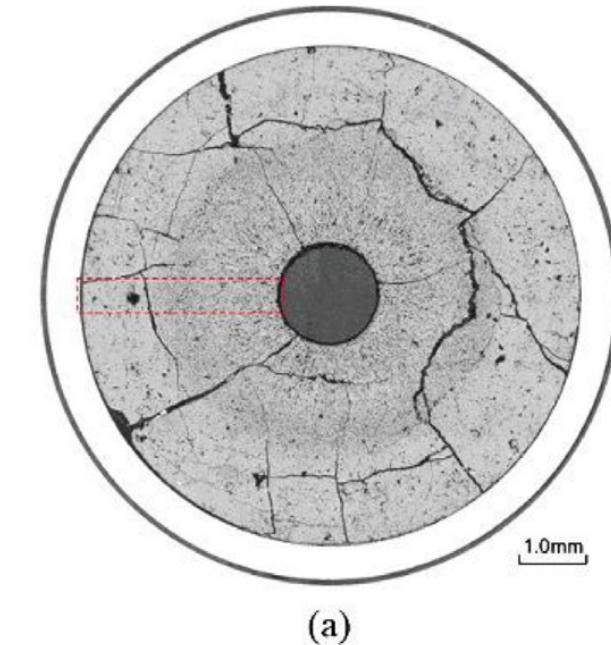
MOX Fuel Design

- Typical fuel pin is 2-3 m long, with MOX pellets stacked 1 m with a plenum above and below the fueled zone
- He bond, steel cladding
- Hexagonal core and hexagonal assemblies
- Each assembly contains 100-200 fuel pins
- Schematics are from Phenix reactor

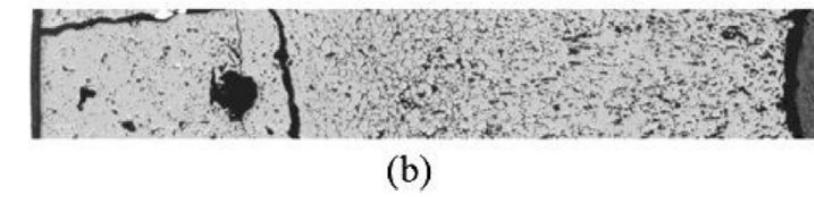


MOX Fuels in SFRs

- MOX fuel operates at linear heating rates that are 2X higher than LWR fuels (450 W/cm)
- MOX will run at higher temperatures than LWR fuel, and thus with different properties
- Fission product phases and evolving microstructures create highly localized properties that can differ significantly from the bulk fuel
- Stoichiometry and Pu content are important factors that dictate thermal properties



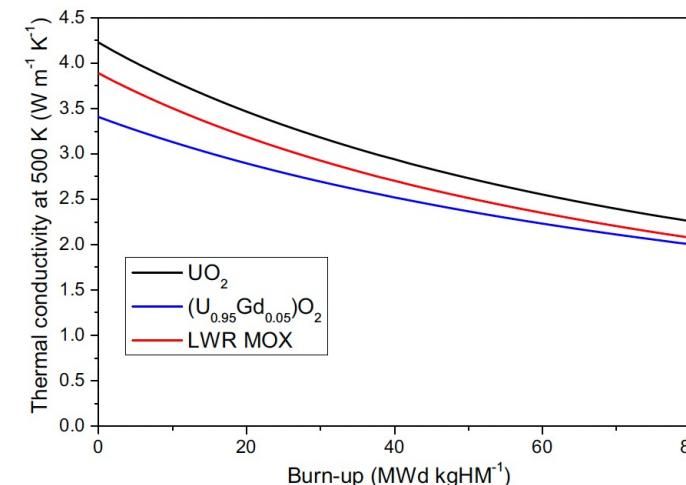
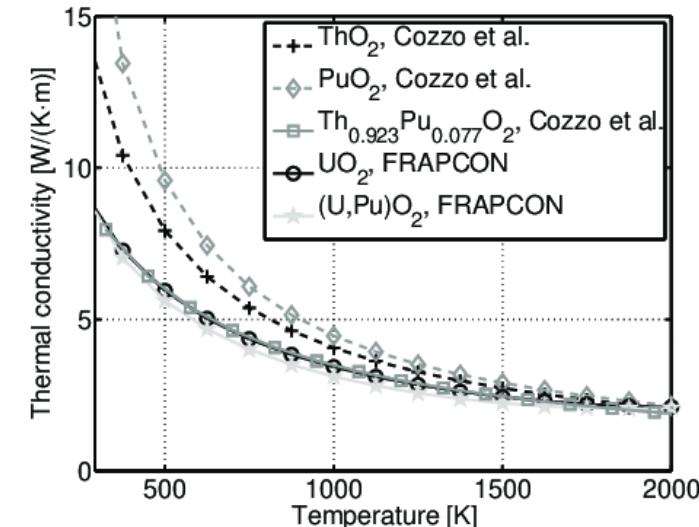
(a)



(b)

Thermal Properties

- Because we have higher temperatures, knowledge of the thermal field is critical
- Thermal conductivity is similar to UO₂, transport via phonons
- Porosity, off-stoichiometry, fission products, etc., cause scattering and degrade k , metallic precipitates increase k
- The mixed oxide typically has worse conductivity than either pure oxide
- Degrades with burnup
- Various models have been developed to describe the degradation

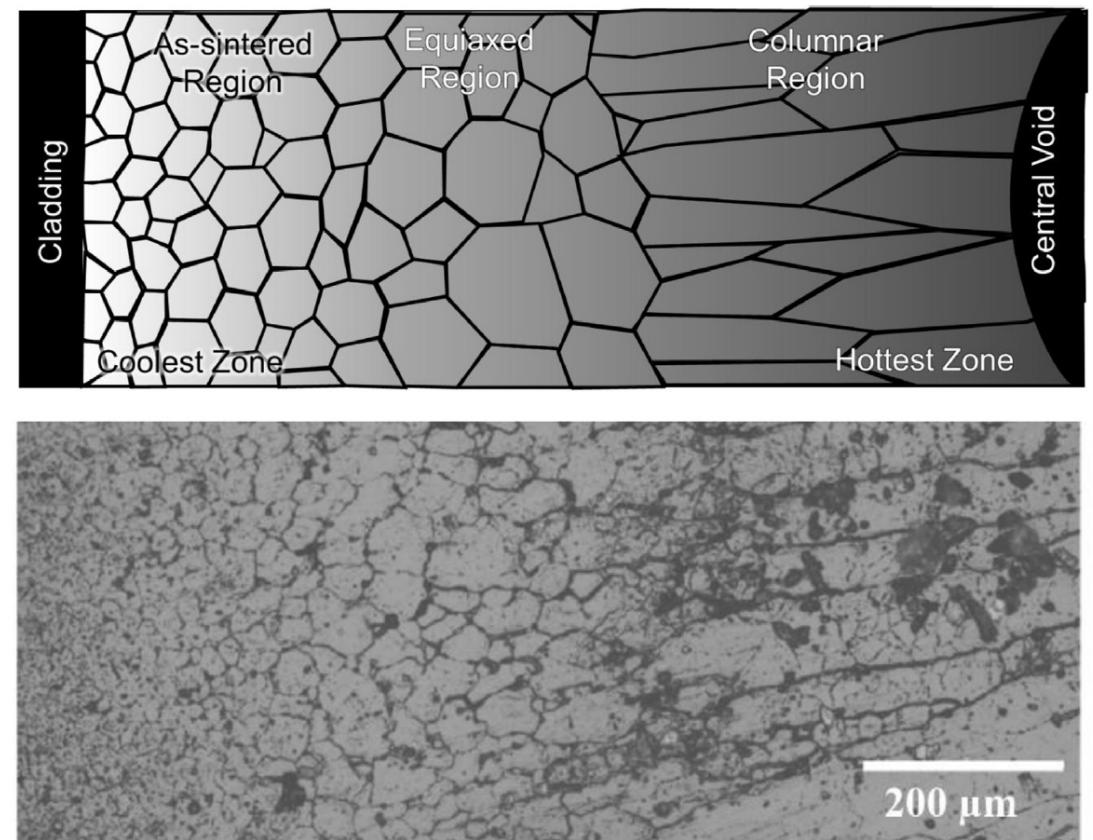


MOX Restructuring

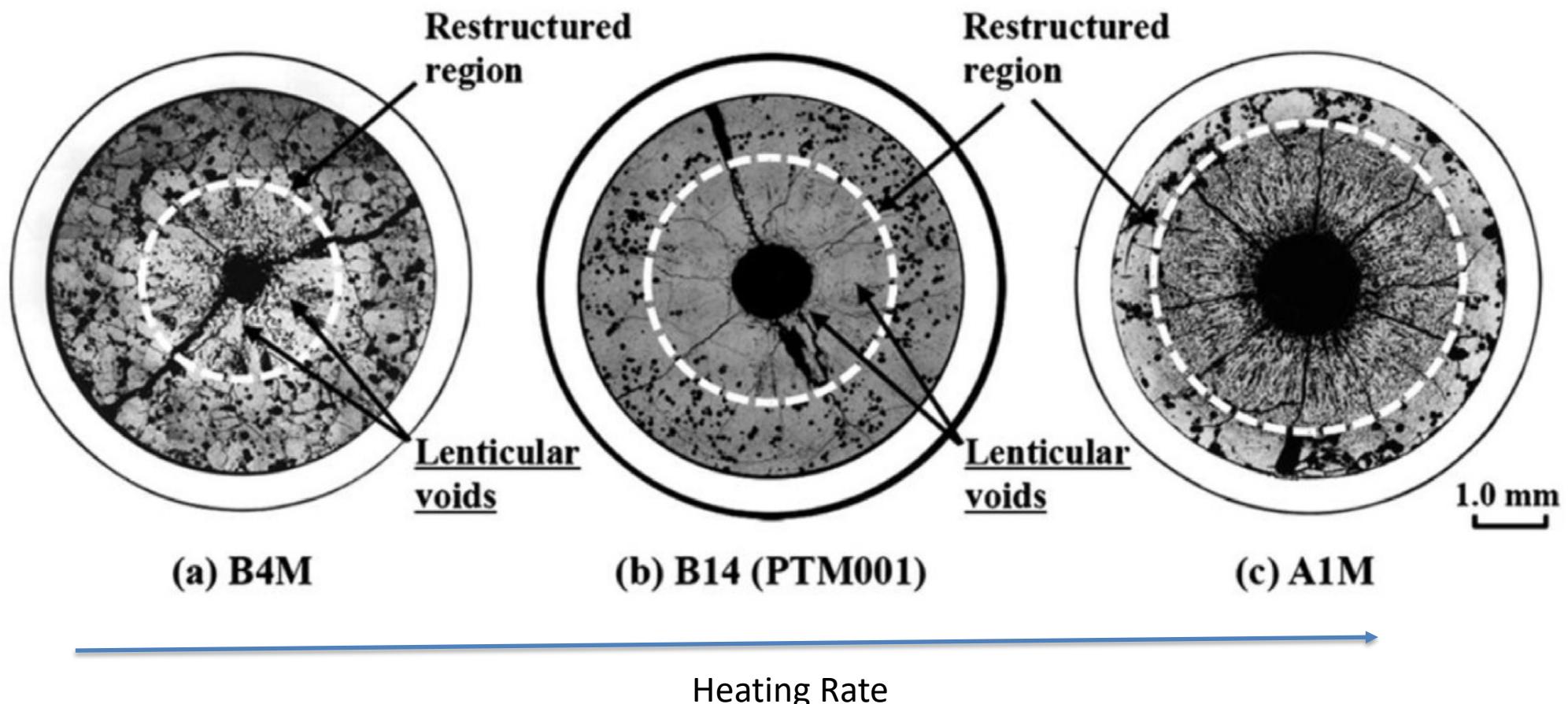
- Oxide nuclear fuels are commonly touted for their outstanding high temperature capabilities under irradiation, but this stability comes with the tradeoff of low thermal conductivity
- Due to the low thermal transport, a steep temperature gradient is formed along the radius of the fuel pellet, with the hottest region at the center of the pellet and coolest near the cladding
- This leads to grain growth and restructuring
- Pu bearing fast reactor oxide fuels display four defining regions of a restructured pellet:
 - the central void, the columnar grain growth region, the equiaxed grain growth region, and the as-sintered region
- The higher temperatures and heating rates form coarse, elongated grains that grow radially toward the outer rim of the fuel

MOX Restructuring

- The equiaxed region consists of grains that have undergone significant growth when compared to the un-irradiated samples
- Central voids have been shown to appear in irradiation times as short as 10 min, demonstrating that the appearance of the central void is a result of fuel temperature and linear heating rate, not high burnup
- The central void forms from the accumulation of voids and pores present in the fuel along a thermal gradient

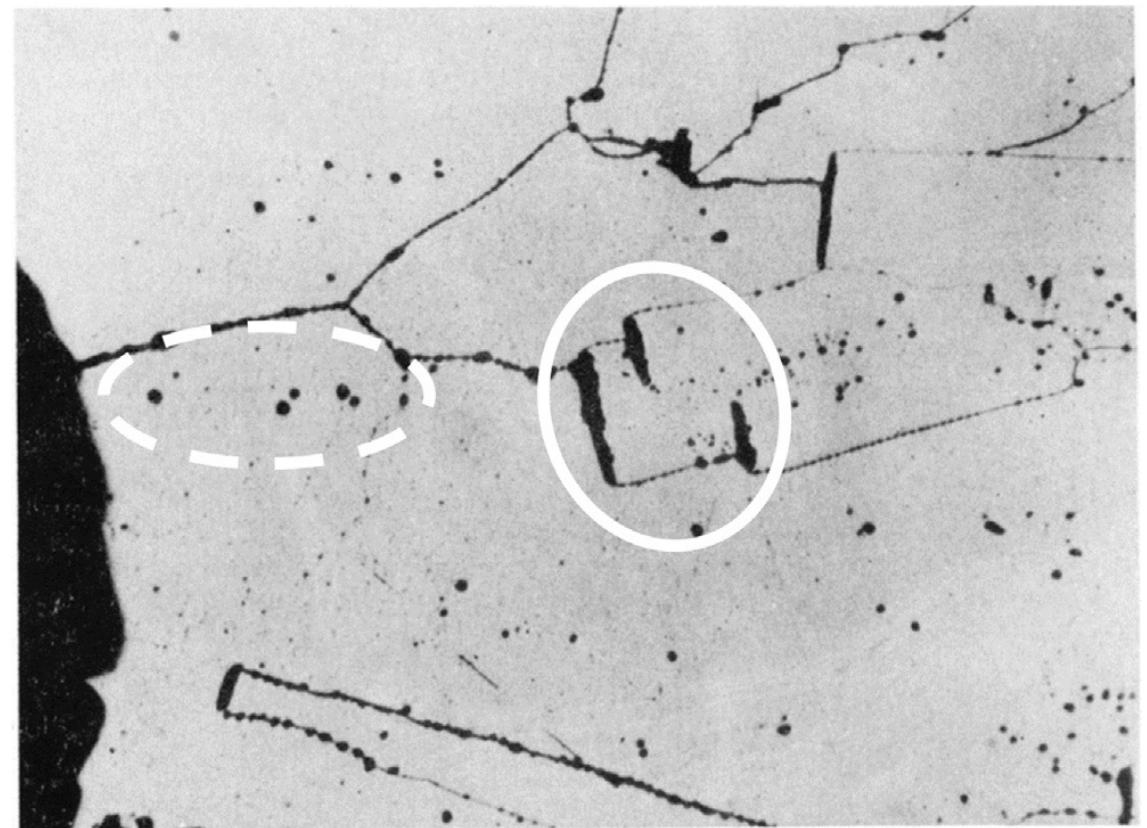


MOX Pore Formation



MOX Pore Formation

- The smallest spherical pores are highly mobile, being able to quickly and easily move through the restructured region
- Intermediate sized pores become flat and elongated as they travel towards the fuel centers, leaving streaks at the tips of the voids as they travel
- These “lenticular” voids are the most readily identifiable porosity feature in the irradiated MOX fuels due to their distinct shape



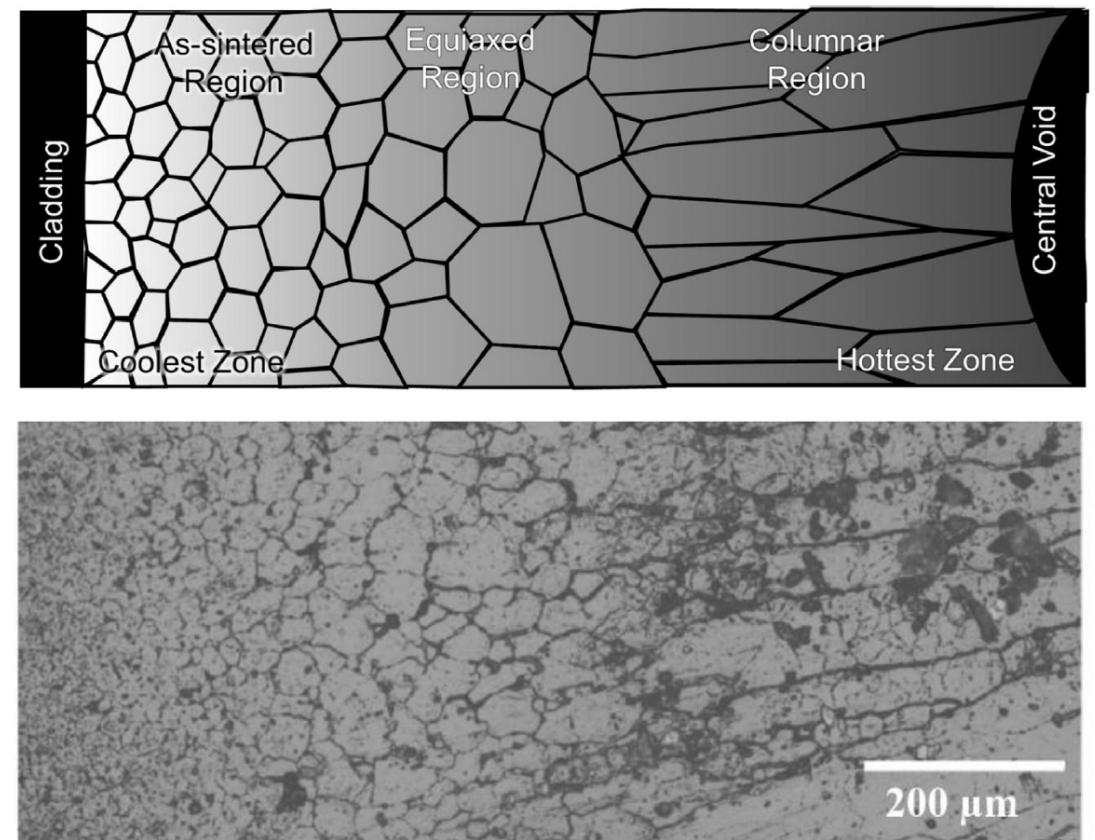
Pore Migration

- Hot to cold side of the pores has a steeper temperature gradient than in the fuel
- The pressure of the fuel vapor is higher on the hot side of the lenticular pore, which induces an evaporation–condensation mechanism
- Matter evaporates from the hot face and condenses on the cold face
- Induces an inverse displacement of the lenticular pores that climb the thermal gradient toward the center of the pellet
- The oxide vapor condenses on the cold side in a nearly single crystal way
- The lenticular pores destroy the initial fuel microstructure and leave behind very elongated ‘columnar grains’ that appear clearly in micrographs



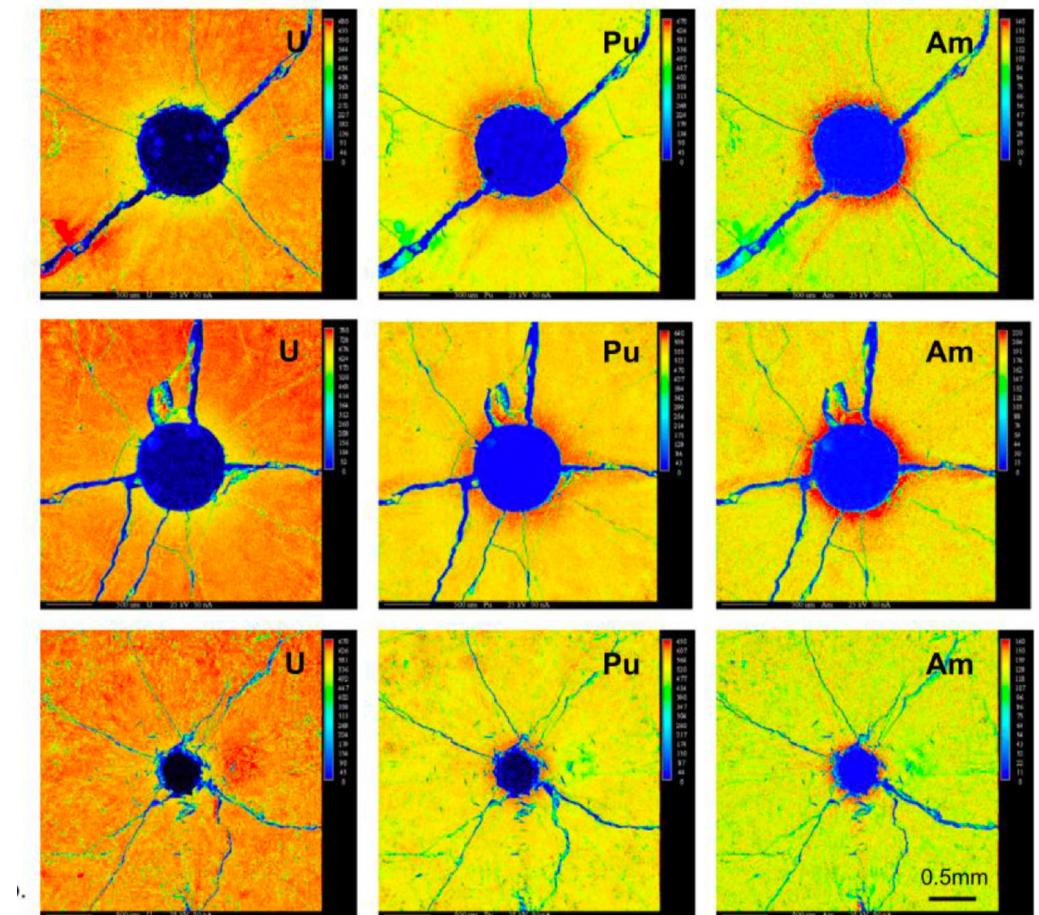
MOX Restructuring

- The velocity of the pores varies rapidly with temperature, and the columnar grains only form at temperatures above ~1800C
- Below 1800C, an equiaxed region consists of grains that have undergone significant growth when compared to the un-irradiated samples
- At the periphery of the fuel pellet, temperatures are sufficiently low to limit grain growth, and thus the microstructure doesn't undergo rapid changes



Redistribution of Pu

- The movement of pores leads to a redistribution of plutonium, resulting in a spike in Pu concentration surrounding the central void
- Similar behavior has been observed for americium
- This transuranic concentration increase is accompanied with a decrease in U concentration
- This redistribution increases the local fission rate and centerline temperature, while generating lower melting point phases

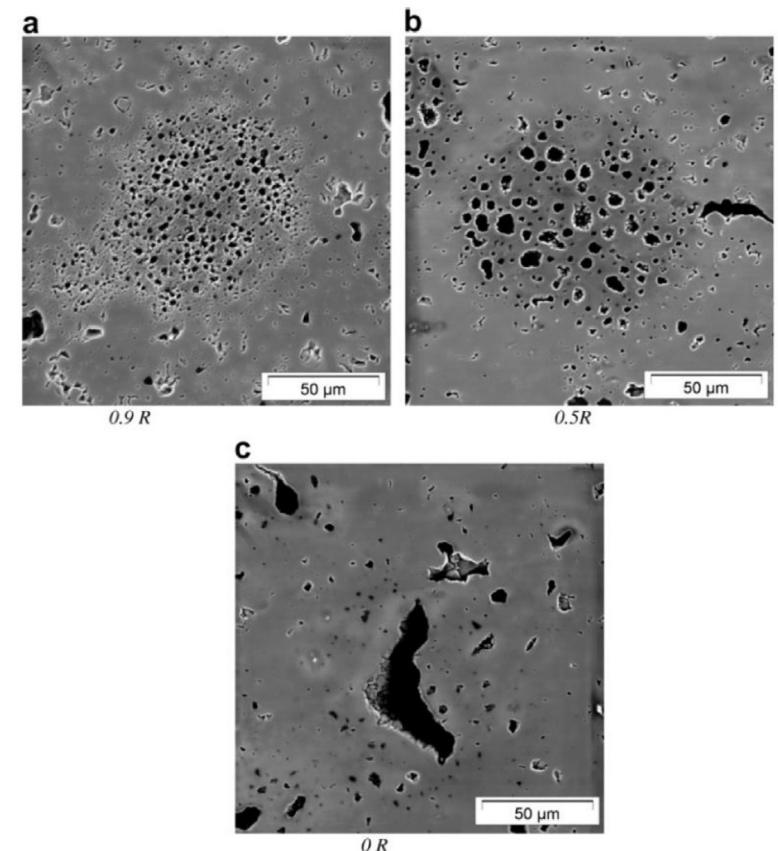


Redistribution of Pu

- This phenomenon is currently understood as an evaporation-condensation process
- The fuel at the edge of the pore closest to the centerline becomes gaseous inside the pore and deposits itself on the cooler region of the pore closest to the cladding
- UO₂ is the more volatile of the U/Pu heavy metal species present in the fuel matrix
- The high oxygen potential can lead to a high partial pressure of UO₃ within the self-contained pores
- Enriched regions of PuO₂ are left behind and deposited at the leading edge of the central void as the porosity agglomerates in the fuel center
- Some experiments on O/M ratio seems to point towards higher O potential leading to more redistribution
- While this is the working theory, it is not clear if this explanation can also account for the necessary pore velocities
- No experimentally proven substitution has been put forth as a replacement theory to the observed features

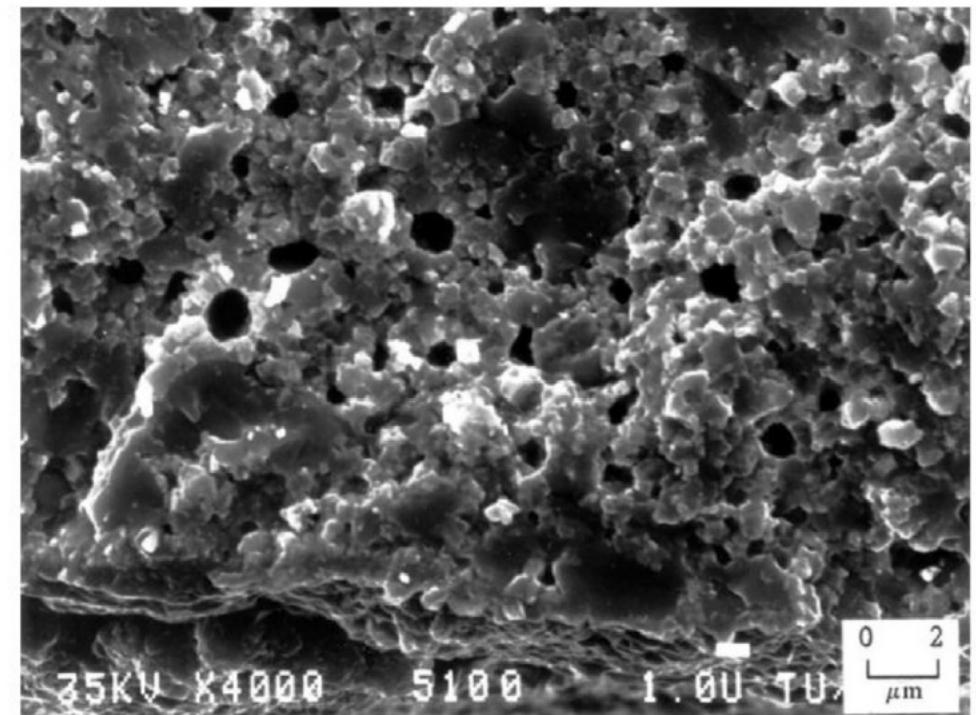
Pu-rich Agglomerates

- Regions of high Pu concentration form in the MOX fuel matrix due to incomplete mixing during fabrication
- Clusters of dispersed porosity form in high Pu concentration regions because of the high fission rate
- Thermal conductivity of the spots is also lower than the surrounding matrix, thus the PAs are both hotter and undergo a greater number of fission events in a very small region
- Burnup in these regions may be greater than 2-3 times that of the pellet as a whole
- The morphology of porosity in the agglomerates depends on the temperature, with smaller bubbles in cold regions and large bubbles in hot regions
- Porosity formed due to PAs are visually distinct from fission gas bubbles or pre-existing porosity



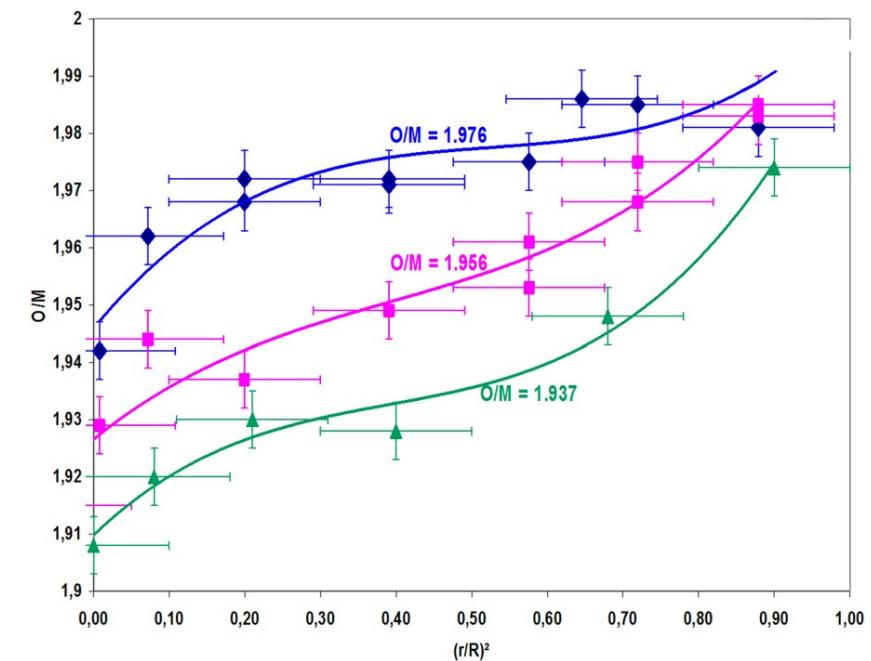
Pu-rich Agglomerates

- The presence of the high burnup structure (HBS) has been observed within the PA regions
- The HBS is basically a fine grained, cauliflower-like structure
- In MOX fuels, the HBS structure appears in fuels following burnups between 60 and 80 GWd/tM at temperatures below approximately 1100C
- PA's reach these local burnups at pellet burnups far below this threshold



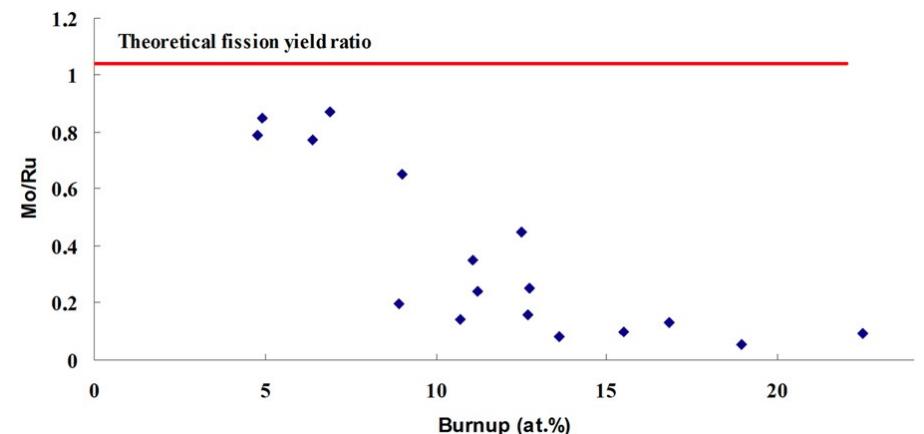
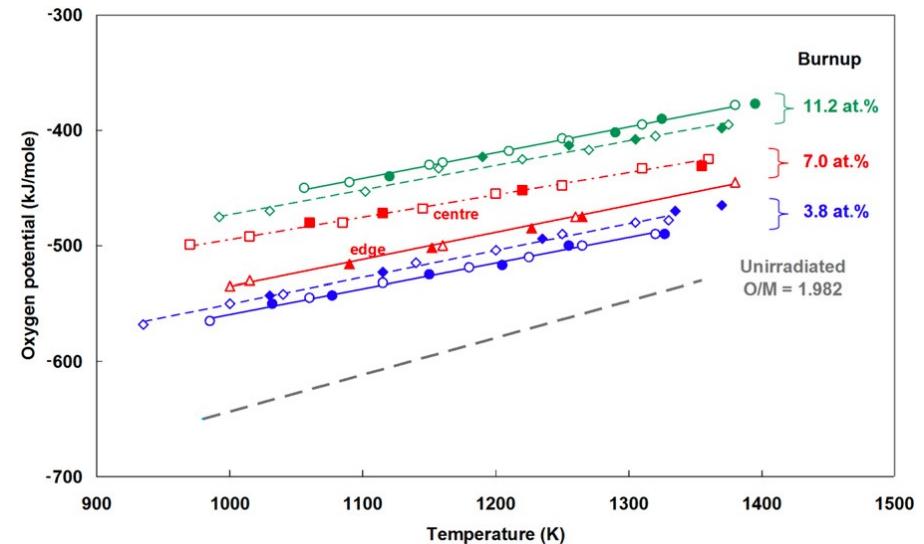
Oxygen Redistribution

- The as-fabricated oxide pellets used as fuel in fast reactors are always hypostoichiometric with an initial O/M typically in the range 1.93–2.00
- Oxygen is redistributed radially, migrating down the thermal gradient, thus bringing the composition close to stoichiometry near the periphery, whereas the O/M ratio becomes very low in the hottest area
- Oxygen transport is likely a combination of vapor and solid diffusion



O/M Ratio

- Fission releases two oxygen atoms, which cannot be fully bound by the fission products, this increases the O potential in the fuel as dissolved O
- The O potential increases until the point where Mo starts to oxidize, leaving the metallic inclusions
- The O/M ratio increases until Mo starts to oxidize, then maintains at approximately 2.0 or thereabouts



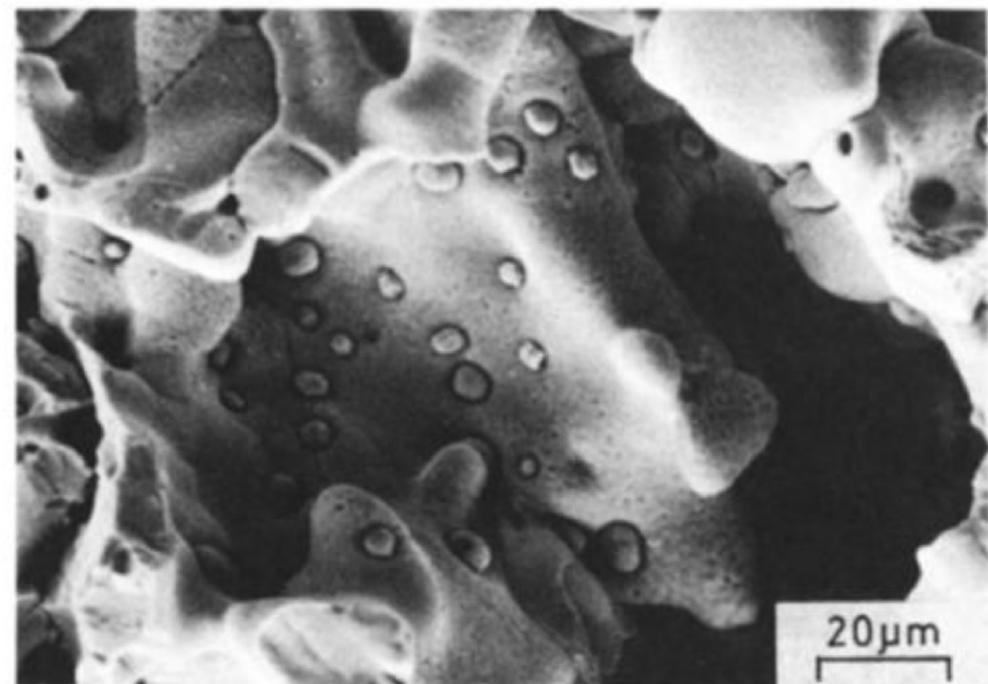
Solid Fission Products

- Fission products in oxide fuels can be grouped into 4/5 categories
- Fission gases and volatile species
- Metallic precipitates
- Oxide precipitates
- Soluble oxides
- LWR fuel vs Pu-containing MOX fuel, we see a higher concentration Ru, Rh, Pd, and a lower concentration of Zr and Mo
- Target higher burnups, so we have a very high inventory of fission products

Fission Product	Concentration (ppm)		Fission Product	Concentration (ppm)	
	U-235	Pu-239		U-235	Pu-239
Kr	120	60	Sn	32	35
Rb	130	60	Sb	14	14
Sr	260	100	Te	140	170
Y	180	60	In	80	100
Zr	1000	650	Xe	1050	1150
Nb	7	7	Cs	960	950
Mo	890	790	Ba	390	310
Tc	220	210	La	290	260
Ru	480	800	Ce	690	630
Rh	130	230	Pr	340	260
Pd	110	580	Nd	980	870
Ag	8	80	Pm	90	110
Cd	8	35	Sm	140	220
In	1	4	Eu	20	40

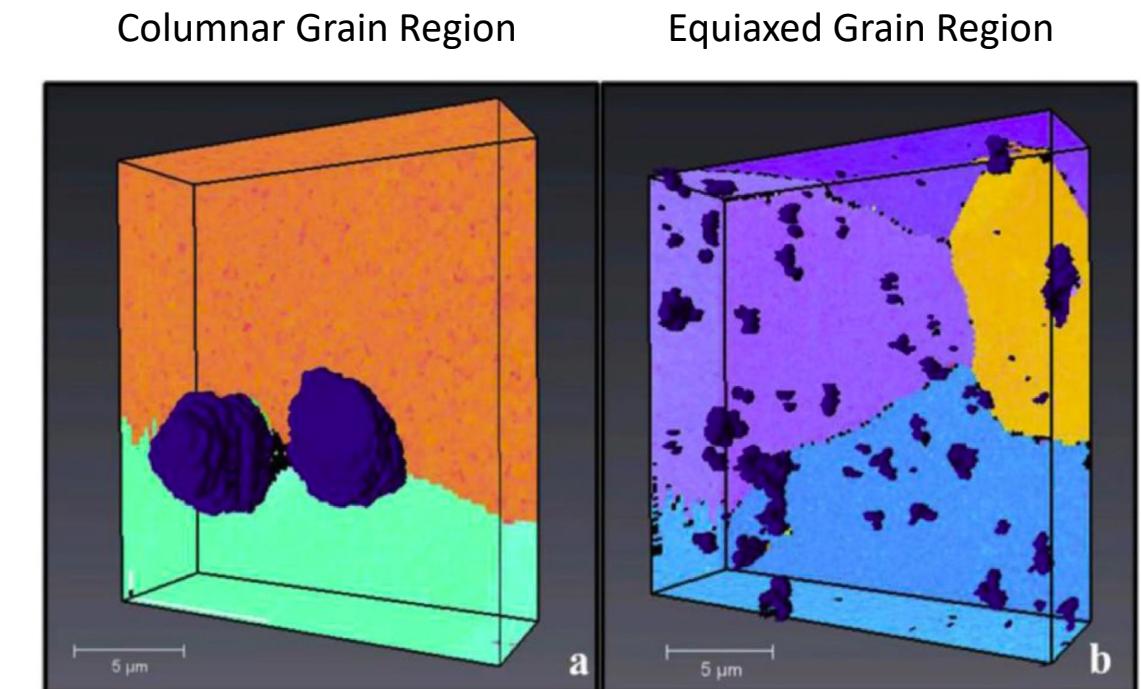
Metallic Inclusions

- Mo, Tc, Ru, Rh, and Pd form prominent phases in irradiated nuclear fuels commonly referred to as “white inclusions,” “noble metal,” or “five-metal” precipitates
- The particles exist as a solid solution taking on the hexagonal close packed (hcp) structure
- The particle size, frequency, and composition exist over a wide range, depending on the burnup and position found within the pellet



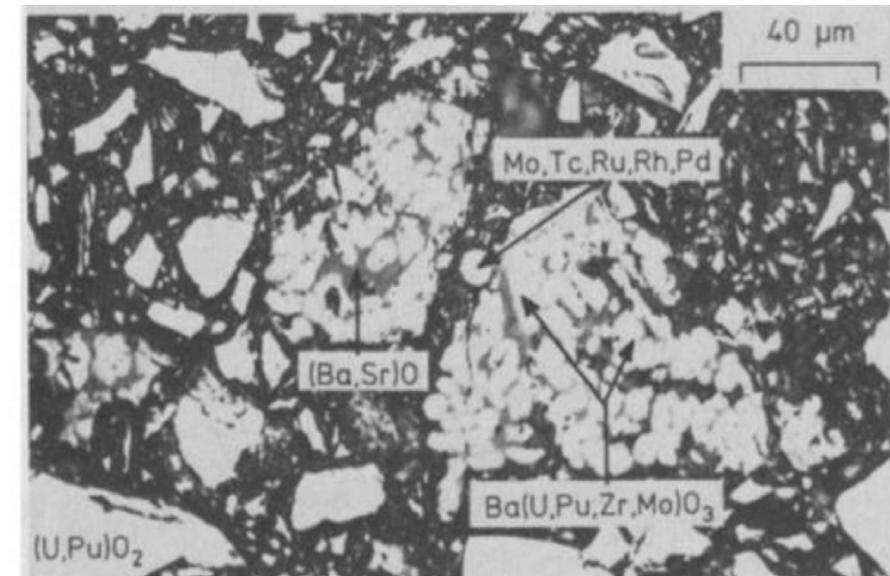
Metallic Inclusions

- In the columnar grain region of the fuel, the particles are commonly $5\text{-}10 \mu\text{m}$ in diameter , collecting primarily on the grain boundaries
- Particles tend to be much smaller ($2 \mu\text{m}$ and below) in the equiaxed and as-sintered regions, but occur more frequently intragranularly
- The particles form as a result of fission product phase agglomeration, as opposed to nucleation and growth process



Oxide Phases

- Oxides containing Sr, Zr, or the rare earth (RE) elements form solid solutions with either UO₂, PuO₂, or both at low concentrations
- Barium is only soluble to 1.6 at% in MOX fuels and thus precipitates a separate oxide phase at higher concentrations
- These oxides, commonly referred to as the “grey phase,” form ABO₃ perovskite structures, in which A=(Ba_{1-x-y}, Sr_x, Cs_y, x,y <<1) and B=(U, Pu, Zr, Mo, RE)
- The particles are primarily Ba rich, followed by Zr, U, Pu, Mo, Sr, and trace amounts of the remaining products
- Due to the sheer number of constituents, the structures are largely unknown
- Grey phase is typically found in the equiaxed or outermost regions of the columnar grains commonly intermixed with other constituent oxides

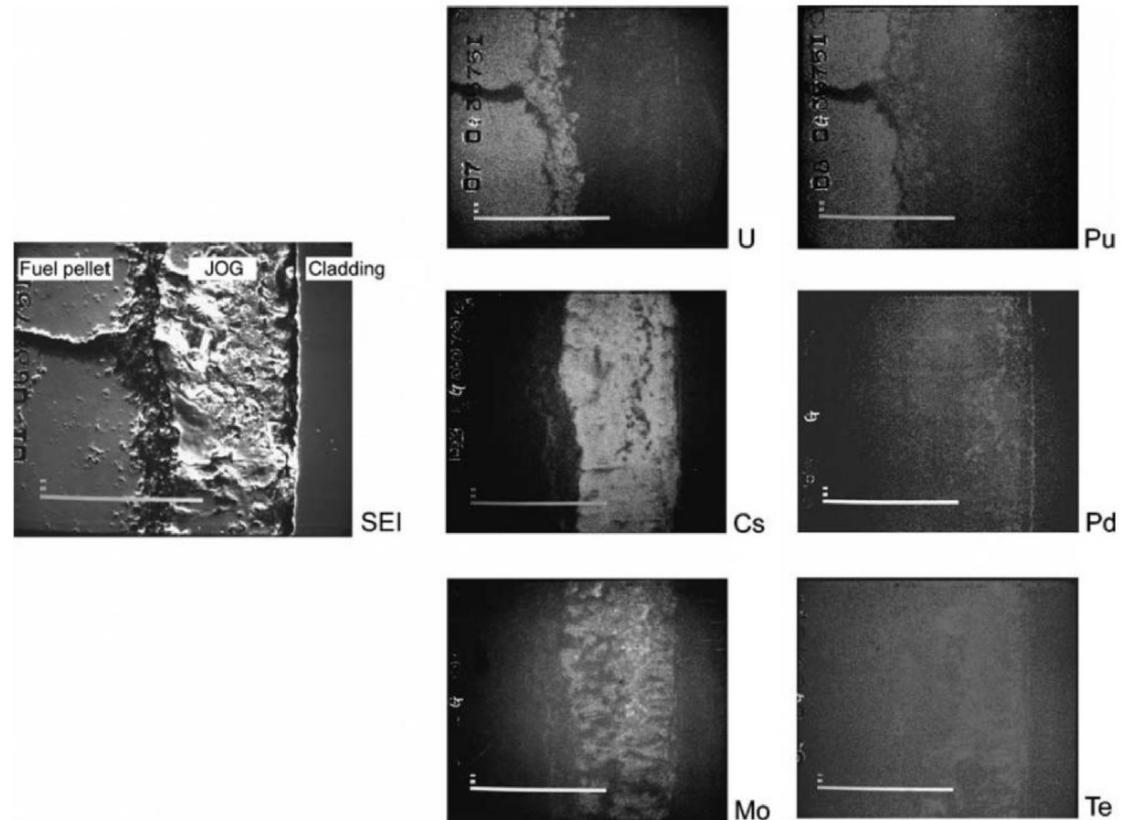


Joint Oxide Gain

- The volatiles class of fission products produced during reactor operation are of particular interest to fuel-cladding interactions
- Cs, Te, and I all evaporate at low operating temperatures and migrate to the coolest part of the fuel assembly where they react with fuel or cladding constituents
- Mo has a tendency to combine with Cs and O to become volatile and migrate toward cooler fuel regions
- This has been termed Joint Oxide Gain (JOG)
- JOG is an oxide buildup formed on the fuel surface between the pellet and cladding
- After gap closure, there remains a minimal residual gap
- Primarily Cs_2MoO_4 or $\text{Cs}_2(\text{U}, \text{Pu})\text{O}_4$, the JOG structure is irregular and dense, found in regions where the peak fuel temperature is lowest

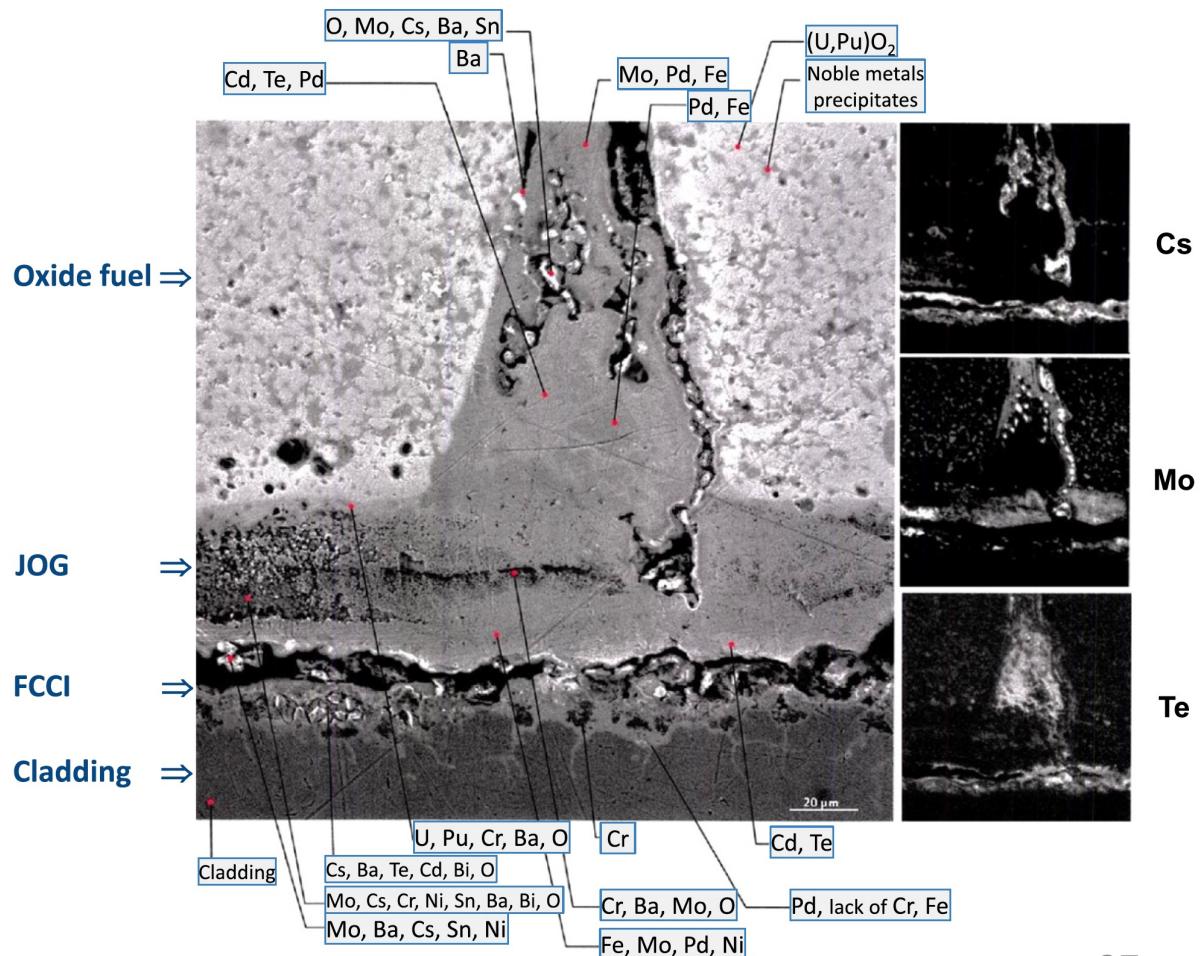
Joint Oxide Gain

- The volatile constituents of the JOG structure evaporate from the fuel pellet at high temperatures and condense to become solid at the cooler top or bottom of the fuel assemblies
- It is believed that the existence of JOG aids in thermal transport of the fuel, as the oxide structures have higher thermal conductivity than a fuel-cladding gap filled with fission gases



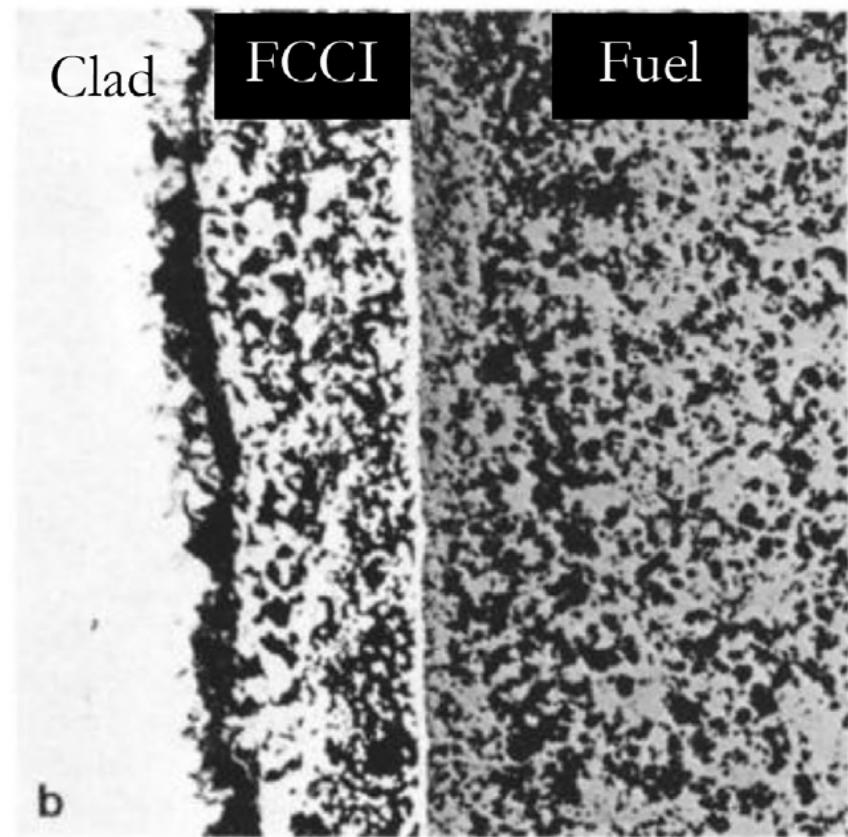
Joint Oxide Gain

- JOG acts as a mechanical buffer, limiting the amount of PCMI, or stresses in the cladding
- JOG reduces fuel swelling, by allowing fission products to leave the fuel into a preferable chemical state
- Fission products in the JOG play a predominant role on FCCI and on the resulting strong corrosion



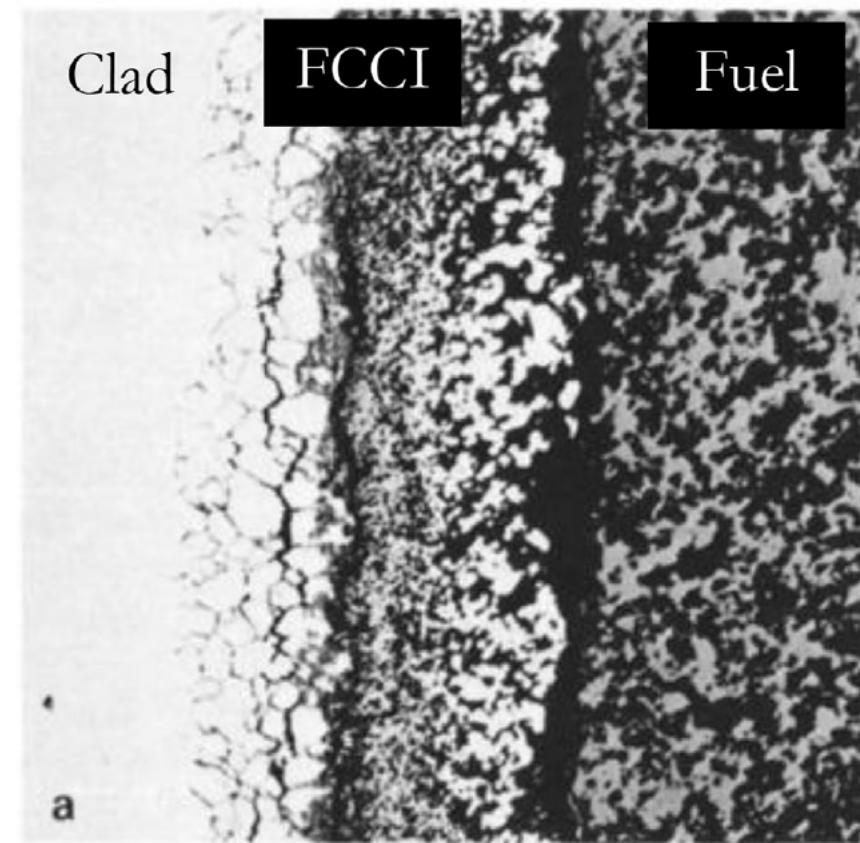
MOX FCCI

- The cladding inner surface temperature of LWR MOX fuels do not reach sufficiently high temperatures under normal operating conditions to initiate detrimental oxidation and chemical attack
- FCCI manifests itself in three primary modes: matrix attack, intergranular attack, or combined, which demonstrates the properties of both matrix and intergranular attack
- Matrix FCCI attack corresponds to the localized oxidation of the cladding material, with primarily oxidation of the Cr in the stainless steel



MOX FCCI

- Intergranular attack modes occur due to the depletion of Cr in grain boundaries due to the formation of Cr₂₃C₆ carbides allowing penetration of corrosive species
- Oxygen and volatile fission products (Cs, Te, I, etc.) are the primary culprits of FCCI initiation in oxide fuel systems
- In MOX fuels, the oxygen potential of the system is the greatest difference from LWR UO₂
- The preferential formation of noble metals rather than oxide formers leads to an excess of available oxygen in the system



MOX FCCI

- Under normal operation, stainless steel cladding forms a chrome oxide (Cr_2O_3) layer that acts to protect the cladding from corrosion
- Cs is generally unreactive with stainless steel claddings, but reacts with the protective oxide layer to create Cs-chromates (Cs_2CrO_4 or $\text{Cs}_2\text{Cr}_2\text{O}_7$) when excess oxygen is present
- The decay of the protective oxide layer causes deeper penetration of the FCCI into the cladding
- Iodine is primarily bound to Cs in the form of CsI , and can lead to an enhancement in oxidation in hyperstoichiometric fuels
- Tellurium is highly active when combined with Cs to create Cs_2Te , which can dissolve cladding constituents in the presence of high oxygen potential
- The O/M ratio of the fuel before and during irradiation are significant factors, and FCCI can potentially be limited by operating with a hypostoichiometric initial fuel composition

MOX Summary

- Phenomena of interest: Restructuring, O and Pu redistribution, Pu agglomerates, fission product chemistries, JOG formation, and FCCI
- O/M ratio is one of the most significant factors in determining the nature of actinide redistribution, fission product precipitate chemistries, and FCCI formation
- The effects of fission product precipitates and Pu agglomerates on fuel thermal behavior is highly localized with little discernible influence on the overall fuel burnup behavior

QUESTIONS?