NE 591: Advanced Reactor Materials

Fall 2021

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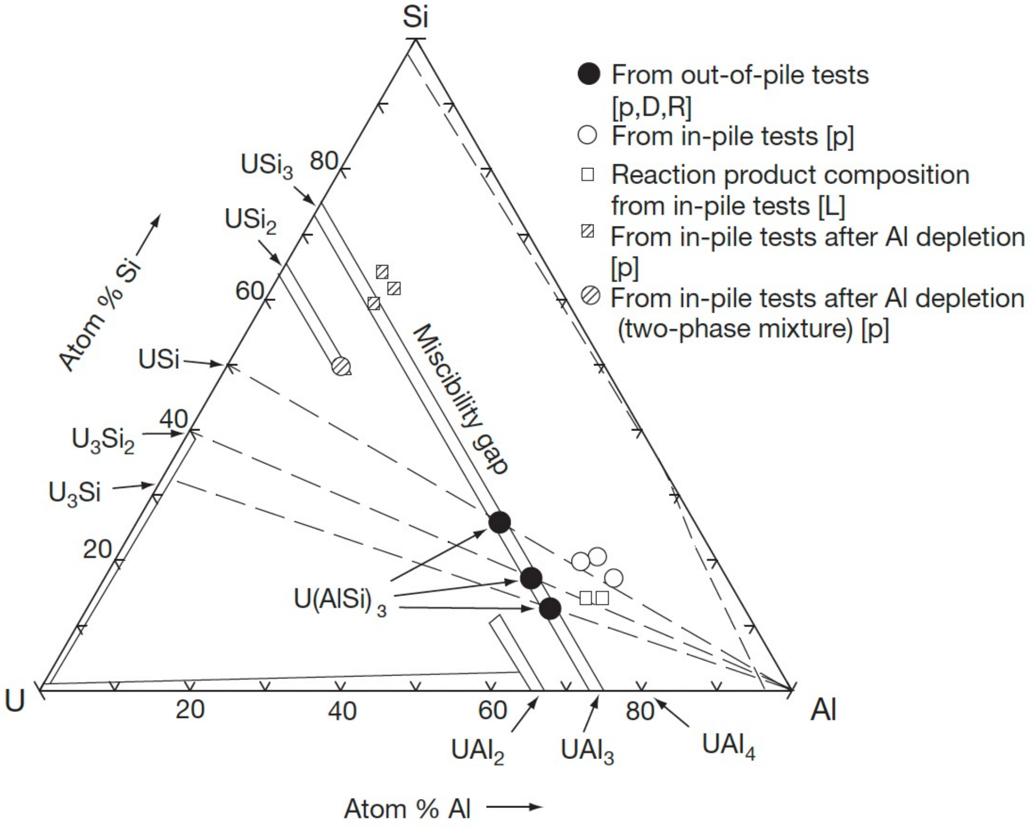
Last Time

- Introduction to research reactor fuel
- Key features:
  - low temperatures, no gap or plenum, high burnup
- Primary type is dispersed particles of metallic compound/alloy in a fuel block embedded in Al matrix
- Solid and gaseous swelling both affect intermetallic fuels
- Intermetallics can amorphize under irradiation, leading to increased swelling
- USi-type fuels have a higher density than UAlx, but swell significantly more
- U3Si2 has more stable bubble morphology than U3Si, due to their amorphous behavior

RESEARCH REACTORS

USi interaction with Al

- U3Si, U3Si2, and USi react with Al to form a single intermetallic compound, U(AlSi)3
- The solubility of Al in the USi phases is very low
- U(AlSi)3 has a composition intermediate between UAl3 and USi3, both of which are mutually soluble



USi interaction with Al

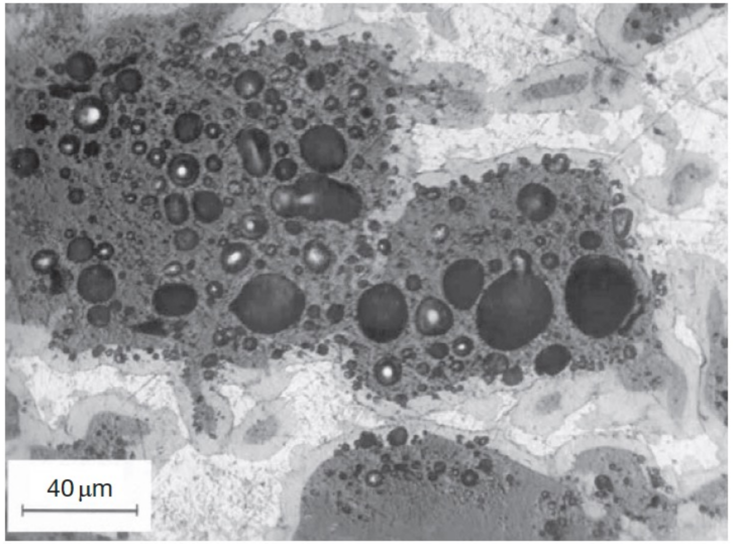
- Interaction layer growth is an interdiffusion controlled process, and can be investigated in out of pile experiments
- Out-of-pile tests are typically performed at high temperatures (600C) and have shown that interdiffusion is the rate-controlling process in IL growth of silicide–Al dispersion
- Fuel temperatures of typical in-pile tests are much lower (<200C) than the out-of-pile tests
- Simple extrapolations to the low temperature regime of the IL growth correlations for out-of-pile tests yield orders of magnitude smaller IL thickness values than observed
- This implies that thermally activated diffusion must be augmented by fission enhanced diffusion during irradiation

USi interaction with Al

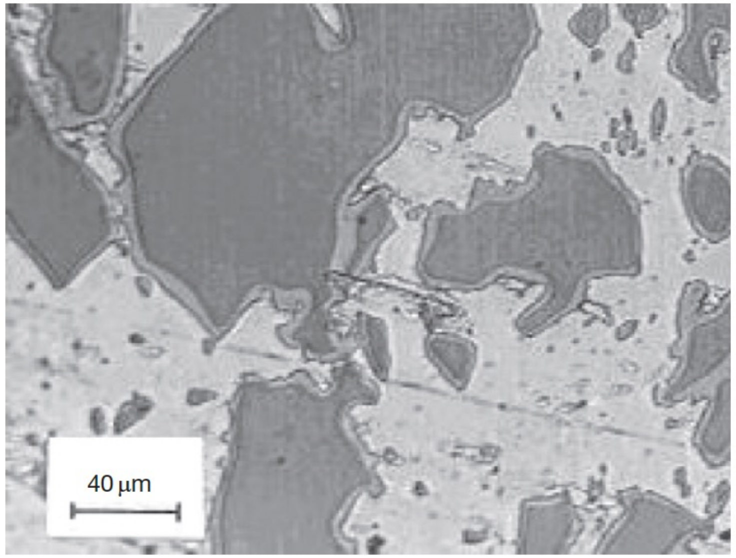
- The compositions in the interaction layer deviate from the exact stoichiometry of U(AlSi)3
- This indicates that the reaction products become amorphous during irradiation, which has been observed in in-pile tests
- Since the IL is amorphous, U, Al, and Si atoms exist in a mixture without crystalline restriction of stoichiometry
- The formation of gas bubbles in the ILs is important because of its potential effects on the IL growth rate
- The gas bubbles in the IL, on one hand, reduce the effective diffusion area and thereby reduce the IL growth rate
- On the other hand, they increase the IL volume itself, which results in a higher measured IL growth rate

Micrographs of irradiated LEU U3Si–Al and U3Si2–Al

- The ILs of both fuels are generally uniform in thickness and free of visible fission gas bubbles
- The gas bubbles in the unreacted fuel serve as a boundary between the unreacted fuel and the ILs
- U3Si has dramatically higher swelling than U3Si2
- Both samples have similar burnup and temperature



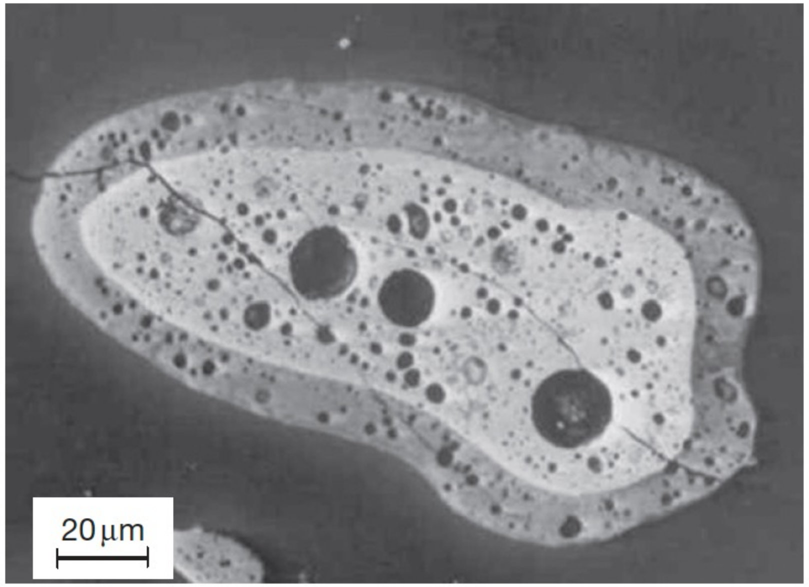
U3Si–Al



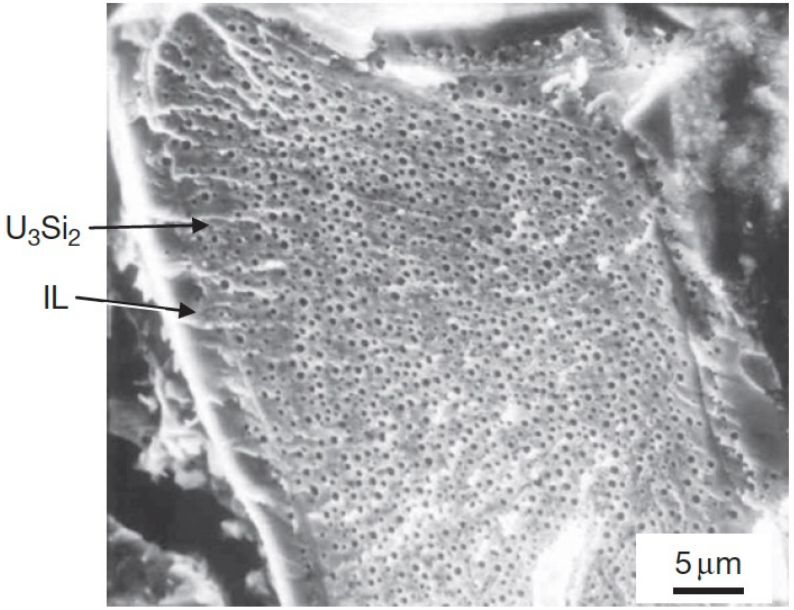
U3Si2–Al

Micrographs of irradiated HEU U3Si–Al and U3Si2–Al

- Gas bubbles are found in ILs of high-burnup HEU USi fuels
- These images are from ultra high burnup samples, ~4.5X the previous slide
- Thus, likely the formation of fission gas bubbles in the IL is dependent upon fission density
- Bubbles in the IL of U3Si2 appear later than in U3Si



U3Si–Al



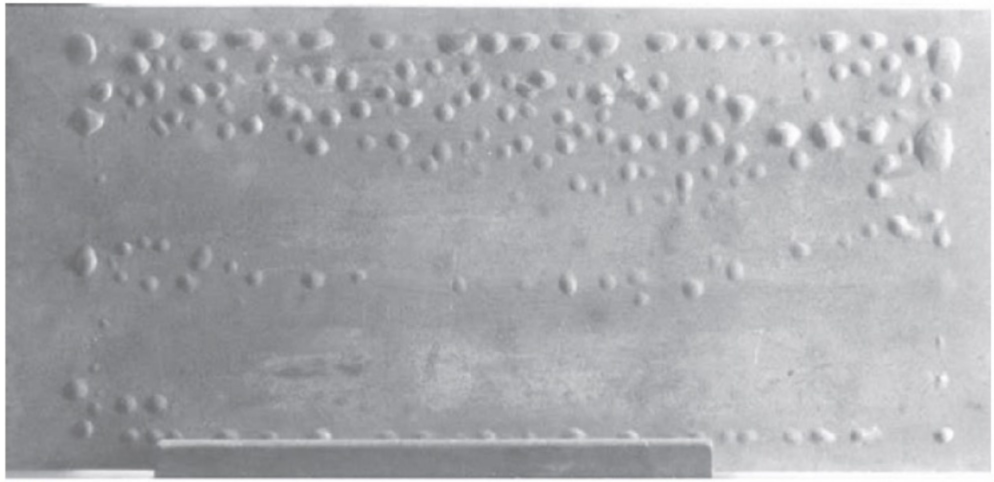
U3Si2–Al

Blister Testing

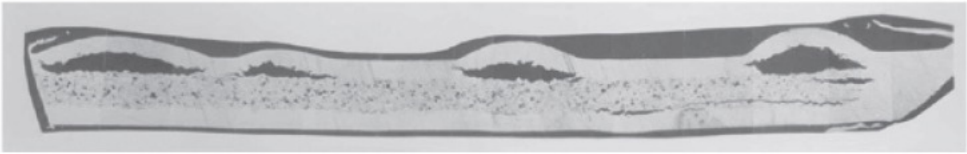
- A unique measure for sound fuel performance considered in research and test reactors is ‘blister threshold temperature’ testing with irradiated plates
- Because there is neither a gap nor a plenum, no fission gas release is possible outside of the fueled zone
- Fission gas and any gas included during fabrication remain in the fueled zone; in particular, fission gases are contained in pores or fission gas bubbles
- Gas pressure in large pores and fission gas bubbles, which may be insufficient to cause detrimental creep or yielding of fuel, could instead result in blistering of a fuel plate when the plate is heated to a certain temperature
- Two types of mechanisms can be considered for blistering: pore (or void) connection, and pressure rupture of fission gas bubbles

Blister Testing

- In the typical blister test, the sample plate is held at a specified temperature for 30–60 min during each annealing step
- The temperature at which blisters form is termed the ‘blister temperature’
- Images of a U3Si2–Al dispersion fuel plate after a postirradiation blister test at 450C



(a)



(b)

USi Blistering

- For typical fuel particle loadings, miniature scale plates of U_3Si_2 and U_3Si were blistered in the range of 515–530C
- An increase in fuel loading dropped the blister temperature by about 75C
- When boron is added, the blister threshold temperature decreases by about 100C, similar to that observed in UAl_x fuels
- Boron is added as a burnable absorber in certain research reactor fuel designs as a means of flux/temperature balancing to avoid hot spots
- The blister threshold temperature for U–Si intermetallic dispersion fuels is less sensitive both to burnup and to fuel volume loading than UAl_x–Al dispersion fuels

USi Summary

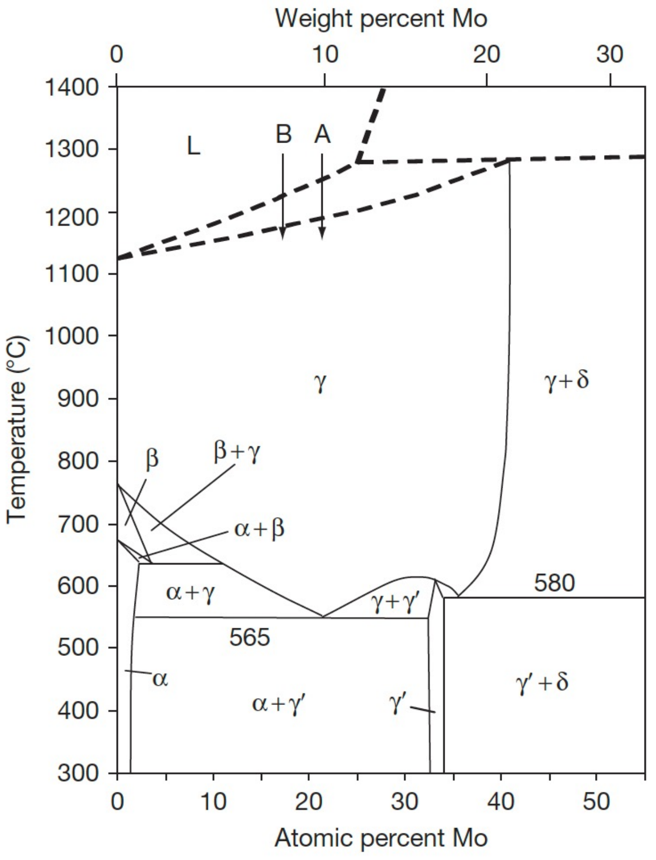
- U3Si2 is presently considered the best qualified fuel in terms of uranium loading and performance for research and test reactors
- U3Si is unsuitable for a plate-type geometry because of unstable swelling, it is still applicable for fuel rods
- The ILs in U3Si2/Al are free of porosity formation at reasonable burnups and the IL growth is considered reasonably slow
- Both U3Si and U3Si2 are amorphized under irradiation, but have inherent differences in fission gas bubble growth
- U3Si has excessive breakaway swelling, whereas U3Si2 has stable, albeit still large, swelling

RERTR to UMo

- Failure to convert high-power research reactors using HEU to LEU U3Si2 resulted from the need for fuels of even higher uranium density
- The fuel development effort has shifted to uranium–molybdenum alloys with Mo content ranging 6–10wt%, in both monolithic and dispersion fuel forms
- Since 1997, the U–Mo alloys have been irradiation-tested, driven by US leadership
- This program is now called the United States High Performance Research Reactor (USHPRR) Program
- Similar programs work in conjunction with the USHPRR in Argentina, Canada, France, South Korea, and Russia

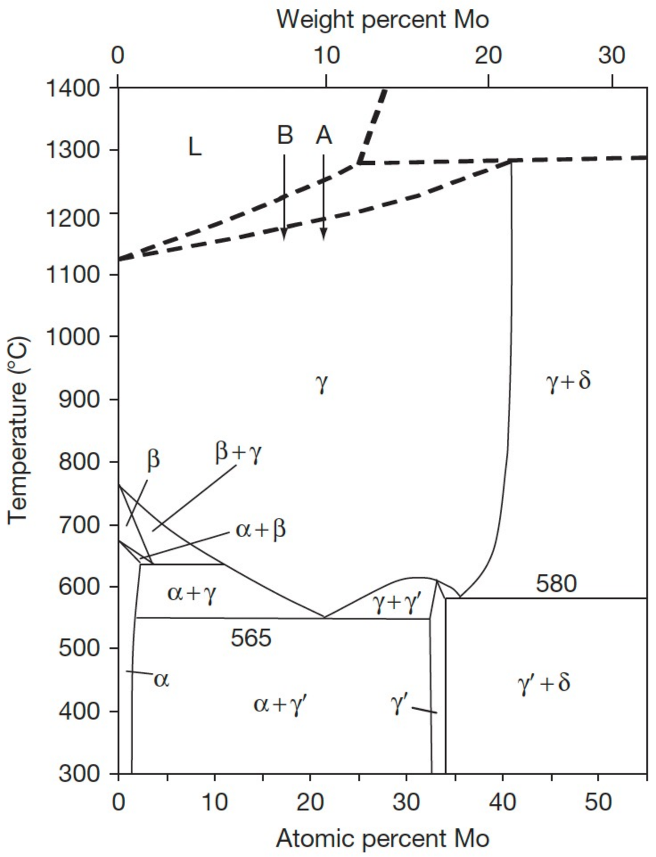
UMo

- It was recognized early on in the development of fast reactor fuels that molybdenum is one of the strongest gamma-stabilizers of the transition-metal elements, even stronger than Zr, and that it enables alloys with U to have relatively high U density
- A disadvantage of Mo as an alloying element is that it has higher neutron absorption cross sections than Si and Al, but not sufficiently significant to be problematic
- The solubility of Mo extends to 22 wt% (or 41 at.%) in the gamma-phase, but it is limited to a few percent in the alpha and beta-phases.



UMo Phases

- The gamma-phase undergoes a eutectoidal decomposition at 565C, transforming to the dual-phase mixture of the orthorhombic alpha-phase and the ordered tetragonal gamma'-phase which has the nominal stoichiometry of U2Mo
- This transformation is slow when the molybdenum content is more than about 6 wt%, so a gamma-phase metastable U–Mo alloy with 6–12 wt% Mo can be obtained by quenching the alloy melt into the gamma-phase



Gamma Stability

- The radiation stability of UMo depends on its ability to retain the gamma phase
- At research reactor temperatures, the gamma phase wants to transform into the alpha/gamma’ two phase system
- Radiation counteracts the driving thermodynamics by disordering the gamma’ phase, retaining the gamma phase

- The critical fission rate is the rate at which the minimum number of displacements that maintain the gamma-phase are in balance with the thermodynamic tendency to transform to the alpha/gamma’-phases

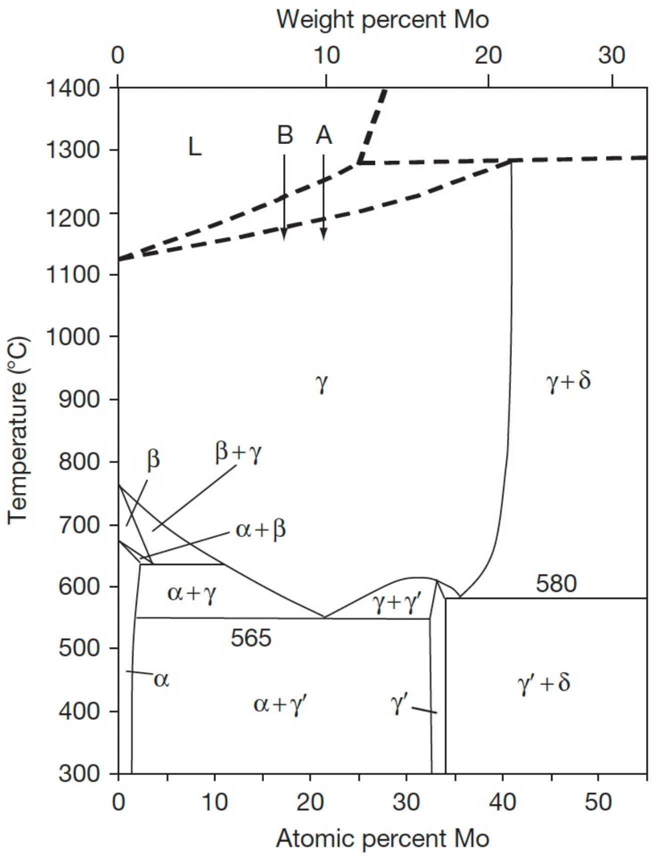
Temperature (K)	*Critical fission rate ($m^{-3}s^{-1}$)*
644	8.8×10^{17}
658	2.2×10^{18}
672	4.8×10^{18}
686	9.2×10^{18}

UMo Fabrication

- Dispersion fabrication is unique from monolithic fabrication
- UMo dispersion fuels are fabricated in a similar manner to USi dispersion fuels
- Both comminution and atomization processes can be applied
- The UMo alloy is quite ductile, which poses problems for the comminution process
- Alloys can be lightly oxidized to assist in comminution
- The comminuted powders have more equiaxially shaped grains and a more homogeneous distribution of grains than the atomized powder fuel because there is no thermal process involved during fabrication
- However, they are heavily cold-worked and contain a high concentration of dislocations which can polygonize and serve as nucleation sites for gas bubbles

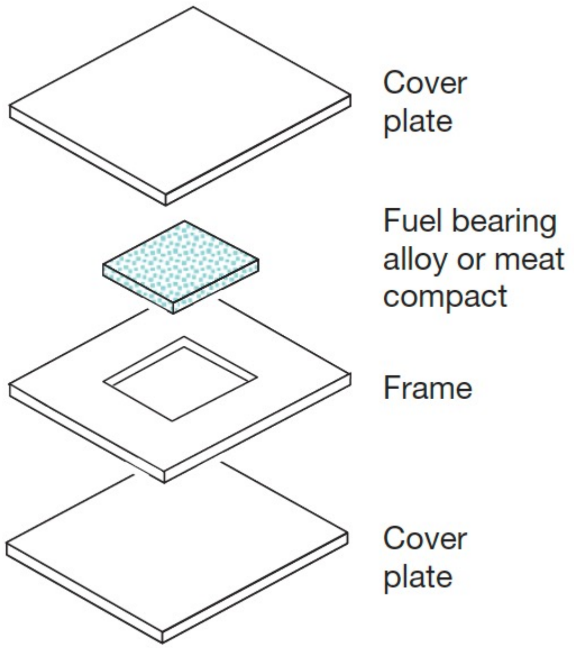
UMo Fabrication

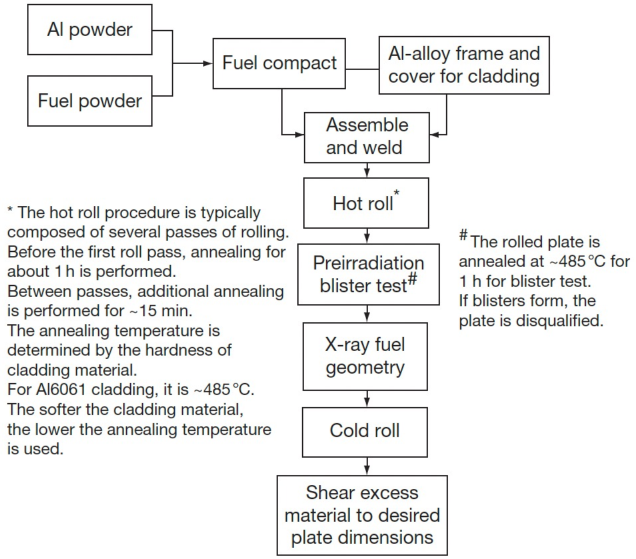
- The microstructure of the atomized powder consists of a ‘cellular’ solidification structure which is commonly found in rapidly cooled alloys that have a pronounced solidus–liquidus gap
- Mo-rich phases solidify first upon cooling
- As the cooling progresses, the solid phase volume increases, while, simultaneously, the Mo content in the solid phase decreases
- If cooling is too rapid, Mo rich islands will form inside a network of a Mo lean matrix



UMo Fabrication

- The U–Mo fuel uses the same plate fabrication method as other U intermetallic fuels
- However, the hot rolling procedure can have significant effects on the performance of the fuel
- The thermal process changes particle characteristics and can enhance the interaction between the particles and the matrix





Fuel Swelling

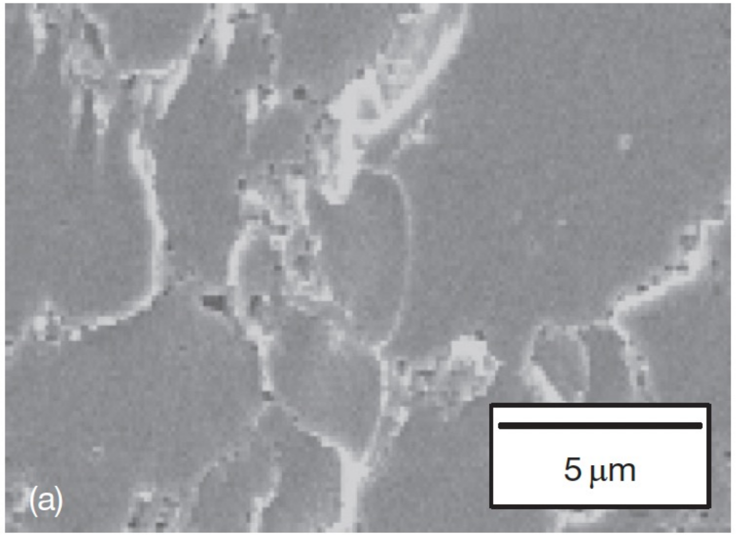
- Fuel swelling by solid fission products is also applicable for U-Mo fuels

$$\left(\frac{\Delta V}{V_0}\right)_s = 4.0 f_d$$

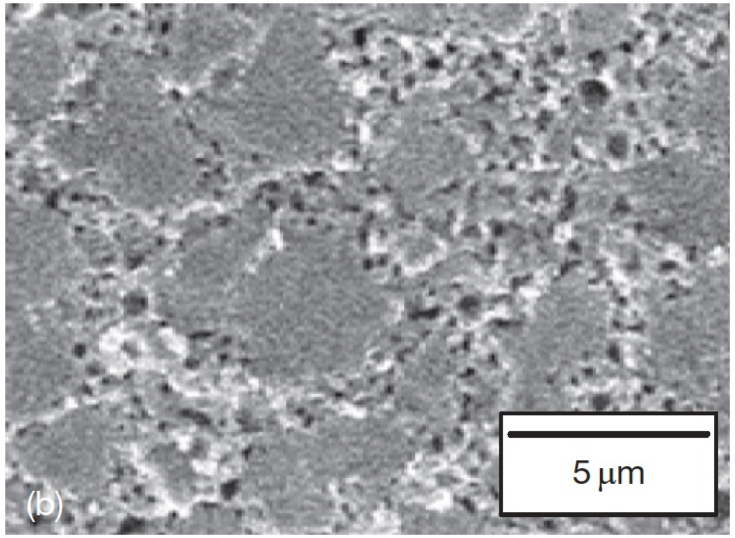
- The fuel swelling due to fission gases is unique in the UMo system
- U–Mo swelling, specifically, swelling by gas bubble growth, is known to have two distinct rates: slow at low burnup and much faster at high burnup
- The phenomenon underlying the transition is grain refinement or ‘recrystallization’ of the gamma-phase U–Mo
- After this transition, gas bubble agglomeration accelerates, resulting in faster swelling

Recrystallization + Swelling

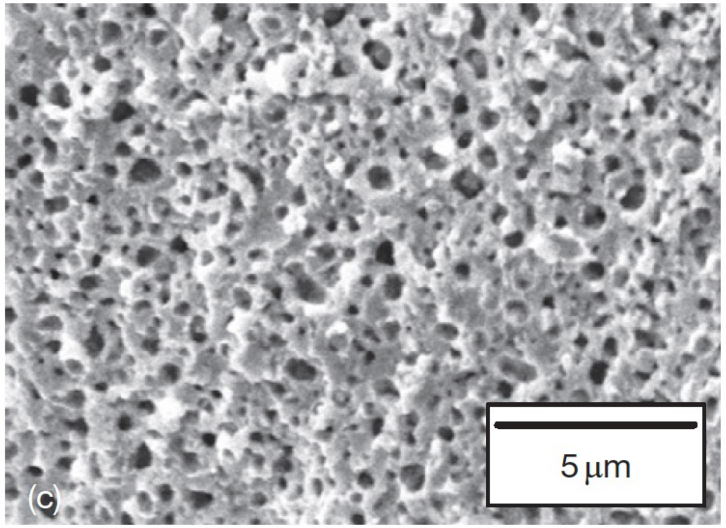
- The evolution of fuel microstructure by fission gas bubble formation and growth is shown with three different burnups
- In an SEM, fission gas bubbles first appear along grain boundaries, with no large bubbles in the fuel



35% BU



65% BU

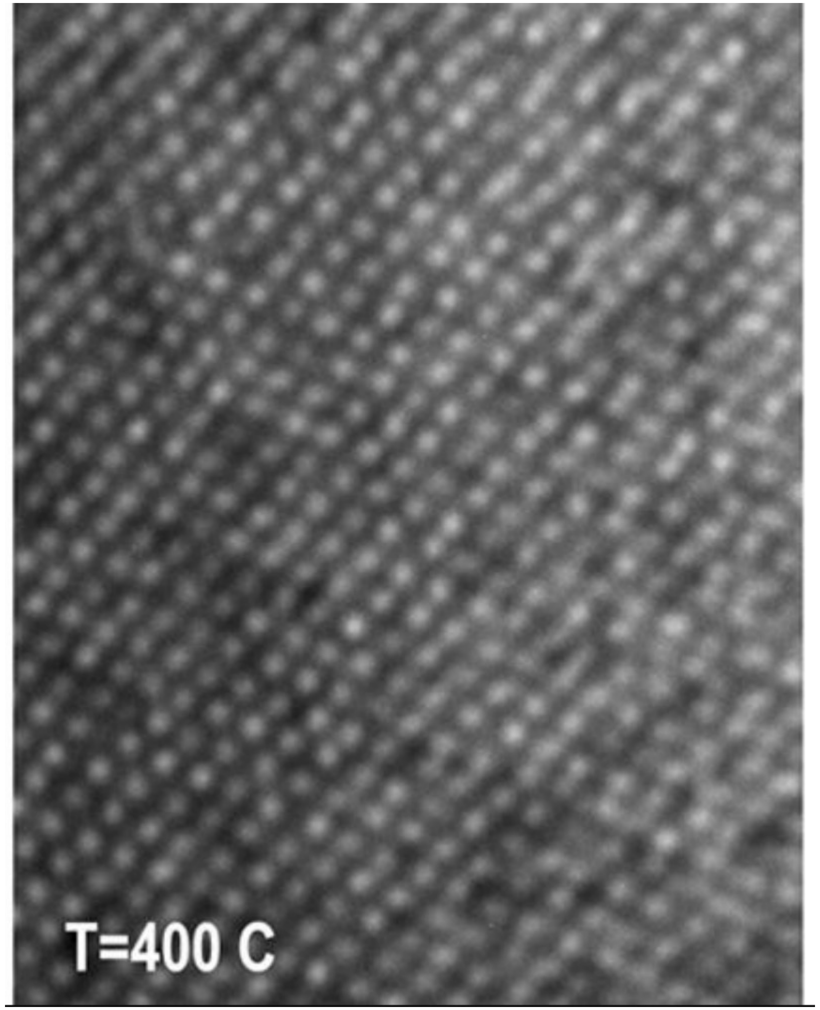


80% BU

Fission Gas Superlattice

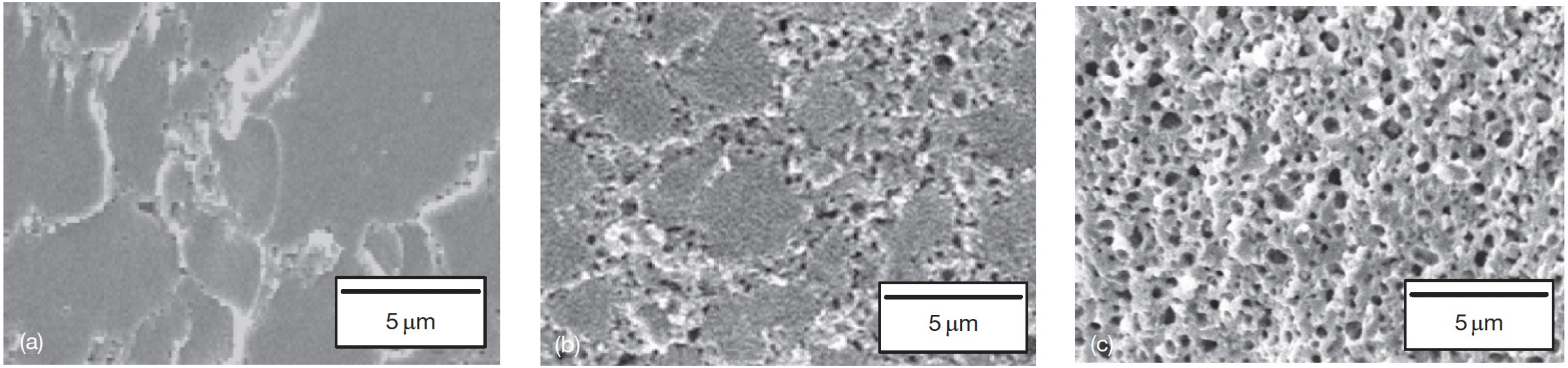
- TEM analysis has identified in the low BU regime a fission gas superlattice of 2nm sizes bubbles
- As the bubbles are small, even though their number density is large, these bubbles are too small to produce much fuel volume increase
- The Young-Laplace equation denotes a force balance, and the ideal gas law gives an approximation of the pressure
- Thus, these small bubbles are highly pressurized and contain large amounts of gas

$$\Delta p = \frac{2\gamma}{R} \qquad PV = nRT$$



Recrystallization + Swelling

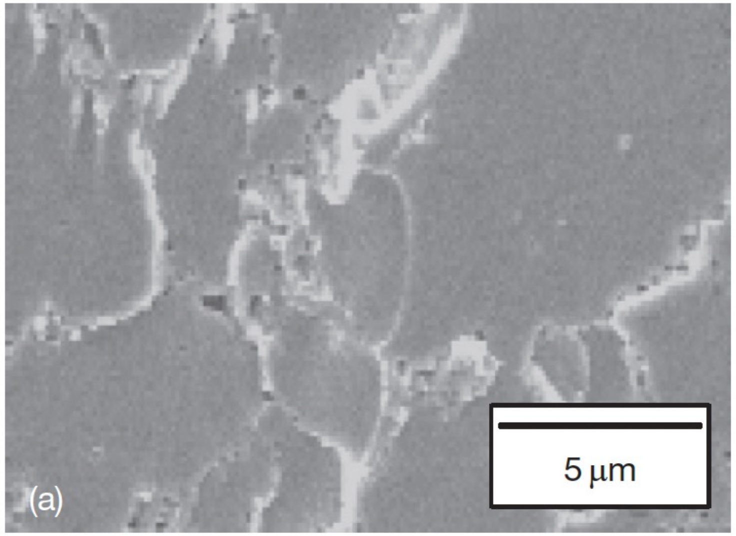
- As burnup increases (2.5–3.5E27 fissions/m3), the bubble population increases in the grain boundaries and additional bubbles progressively appear at newly formed grain boundaries as grain refinement continues
- At this stage, the average bubble size also increases with fission density as the number density increases, both of which increase the fuel swelling rate



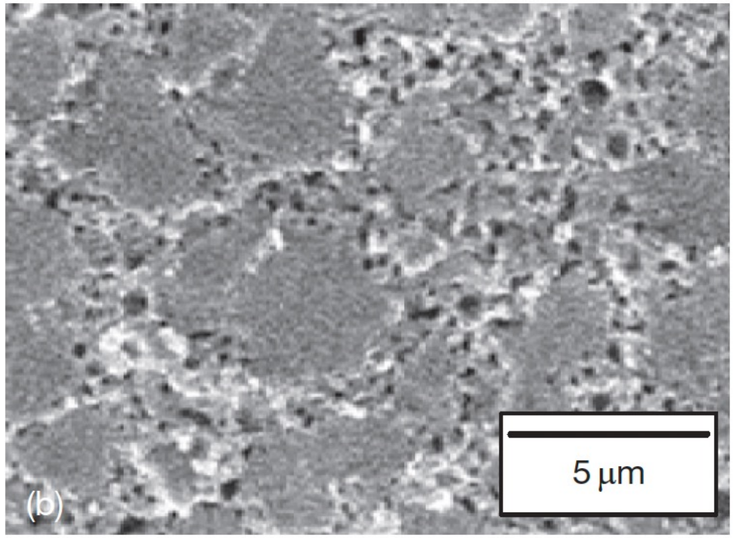
35% BU | 65% BU | 80% BU

Recrystallization + Swelling

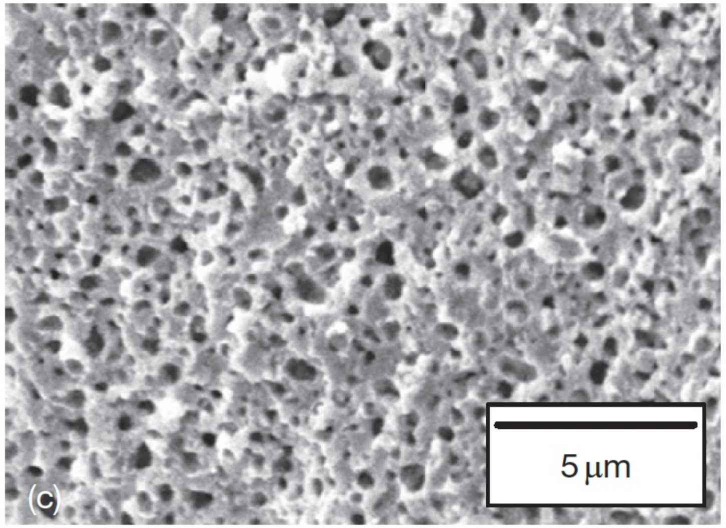
- At higher burnup, large bubbles uniformly span the entire fuel cross section as the grain refinement is nearing completion



35% BU



65% BU



80% BU

UMo Gaseous Swelling

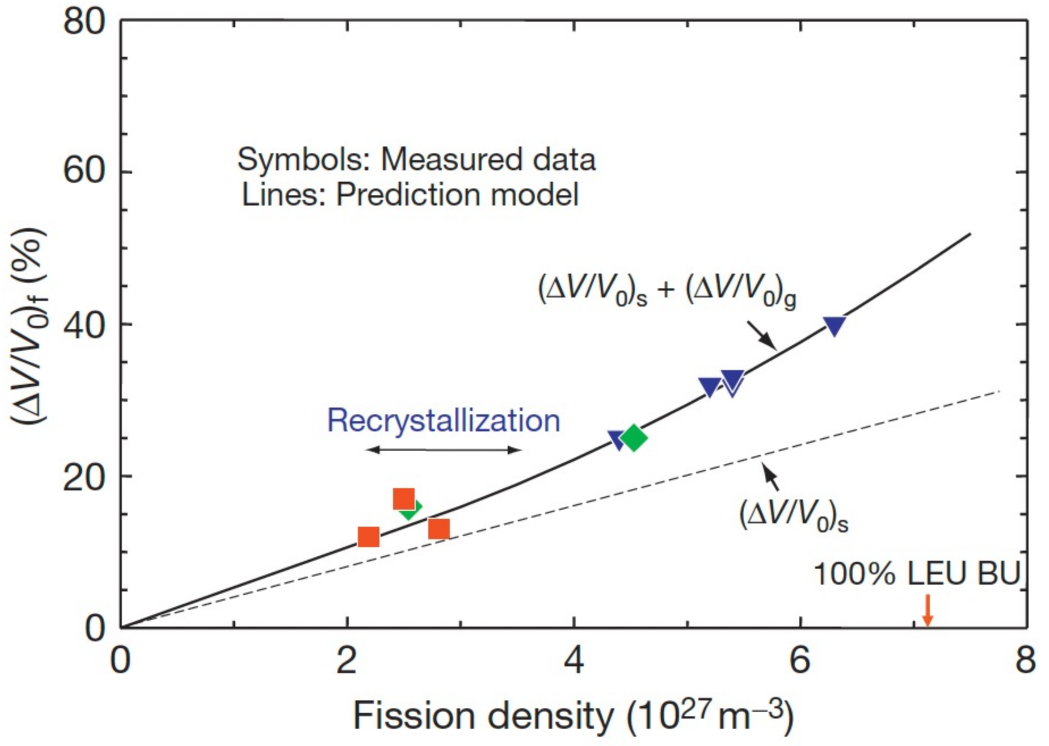
- Total swelling of U–Mo fuel is obtained from plate thickness changes before and after irradiation
- The gas bubble swelling is obtained by subtracting the solid fission product swelling
- The data can be fit to a linear function at low fission density, and a quadratic function at higher fission density

For $f_d \leq 3 \times 10^{27}$ fissions m^{-3},

$$\left(\frac{\Delta V}{V_0}\right)_g (\%) = 1.0 f_d$$

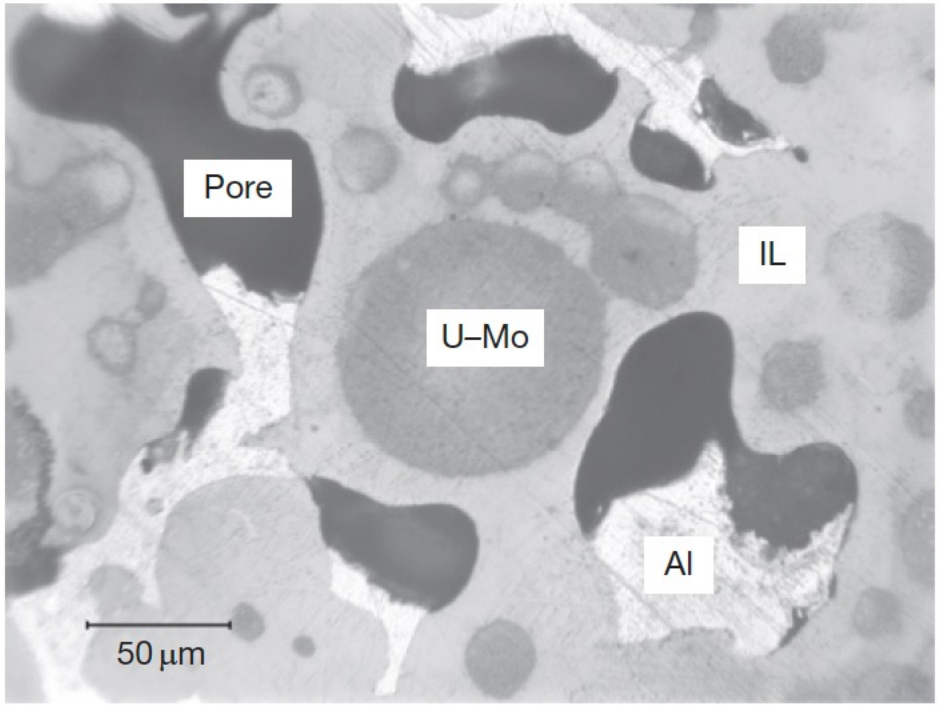
For $f_d > 3 \times 10^{27}$ fissions m^{-3},

$$\left(\frac{\Delta V}{V_0}\right)_g (\%) = 3.0 + 2.3(f_d - 3) + 0.33(f_d - 3)^2$$



UMo-Al Interaction

- The interaction layer (IL) formation between U–Mo fuel particles and matrix Al poses potential fuel failure risks
- Pores tend to form in thick ILs
- Variable composition of the IL is possible because of its amorphous nature during irradiation
- Amorphization is usually accompanied by an increase in volume that facilitates atomic mobility, enhancing diffusion



UMo-Al Interaction

- The IL growth correlation follows a parabolic law, dependent upon the fission rate, temperature, and time

$$Y^2 = Af_r^{0.5} t \exp\left(-\frac{q}{T}\right)$$

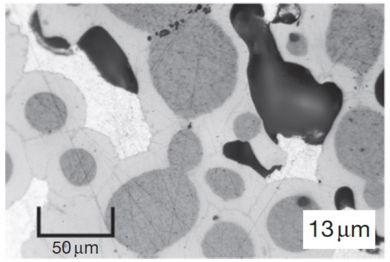
- The Al/(U+Mo) ratio of the interaction product in the (U–Mo)–Al dispersion from out-of-pile tests is in the range 3.5–7.6
- Based upon our knowledge of the U-Al system, the Al/U ratio is 2, 3 or 4
- Thus, Mo is facilitating the formation of higher Al content compounds
- As the Mo content increase, , the formation of (U,Mo)Al3, is suppressed, and the Al content in the IL increases
- The formation of high-Al content IL is unfavorable because: 1) its lower density, leading to more swelling; and 2) high Al content linked to IL pore development

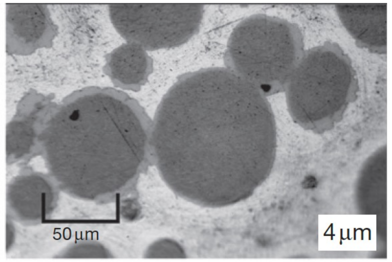
Alloying Additions

- A method to suppress the formation of UAl_4 in the U–Al system depends on finding an element to suppress the peritectoid reaction UAl_3 + Al ->UAl_4
- There are a number of additives which have been identified to inhibit this reaction, most notably Ge, Si, Sn, and Zr
- In the US, Si was primarily investigated in UMo dispersion fuels to inhibit Al_4 formation and suppress IL growth
- Si dramatically reduces the IL thickness
- The ILs of Si-added plates are commonly uneven, with different thicknesses on different particles
- This is due to the non-uniform concentration of Si
- At higher burnups, the IL continues to grow and the effect of Si is weakened

Addition of Si

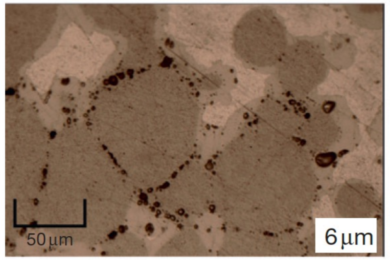
U–7Mo/Al–0.2Si
R5R020 (C5)
BU = 60%
Time = 135 EFPD
RERTR–6

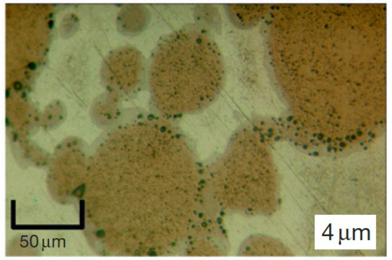




U–7Mo/Al–2Si
R2R010 (C3)
BU=57%
Time=135 EFPD
RERTR-6

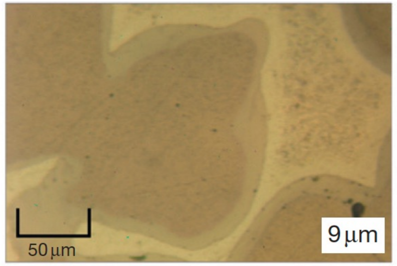
U–7Mo/Al–2Si
R2R078 (C3)
BU = 78%
Time = 98 EFPD
RERTR–9A

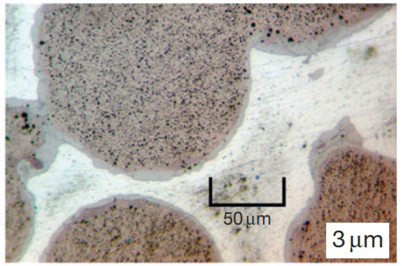




U–7Mo/Al–4.8Si
R3R108 (C2)
BU = 78%
Time = 98 EFPD
RERTR-9A

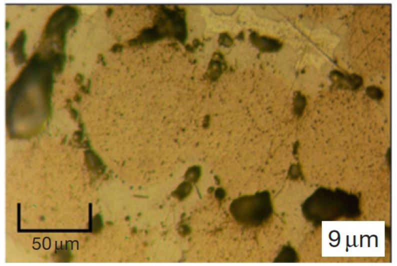
U–7Mo/Al–0.1Si
R0R010 (B3)
BU = 86%
Time = 90 EFPD
RERTR–7

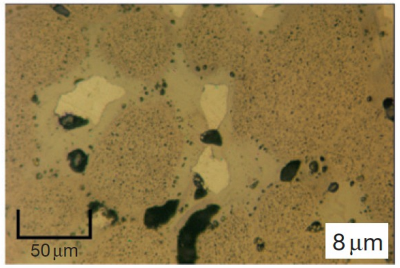




U–7Mo/Al–2Si
R2R040 (B2)
BU = 86%
Time = 90 EFPD
RERTR-7

U–7Mo/Al–2Si
R2R088 (B6)
BU = 119%
Time = 115 EFPD
RERTR–9B





U–7Mo/Al–3.5Si
R6R018 (B7)
BU = 119%
Time = 115 EFPD
RERTR-9B

Summary

- USi interaction with Al leads to $U(Al,Si)_3$ phases which can amorphize
- Fission gas bubbles largely are retained in the fuel, with bubbles appearing in the interaction layer at very high burnups
- Blister testing is used as a safety test to determine temperature limits of safe fuel operation, with typical BTEs around 450-550C
- UMo dispersion fuels allow for greater U density
- Mo stabilizes the gamma phase, and the gamma is additionally stabilized under irradiation
- Fuel swelling is critical in UMo fuels, with the unique feature of a fission gas superlattice
- Subsequent recrystallization leads to breakaway swelling
- Addition of Si can suppress the interaction layer formation in UMo particles