NE 795: Advanced Reactor Materials

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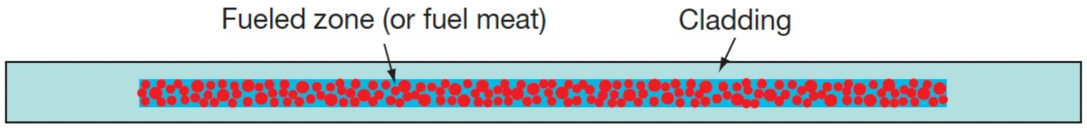
RESEARCH REACTORS

Intermetallic Fuels

- Uranium intermetallic fuels such as U–Al, U–Si, and U–Mo are chiefly meant for research and test reactors in which neutron production, instead of power generation, is the main purpose
- The operation temperatures of these fuels are lower than those UO2
- In general, the U intermetallic fuels can achieve much higher fission densities than oxide fuels
- Currently available research reactor fuels are predominantly in a dispersion form that is composed of fuel particles dispersed in an inert matrix (often Al)
- The fueled zone in a dispersion fuel plate, that is, the fuel particles–matrix mixture zone, is metallurgically bonded to the Al cladding



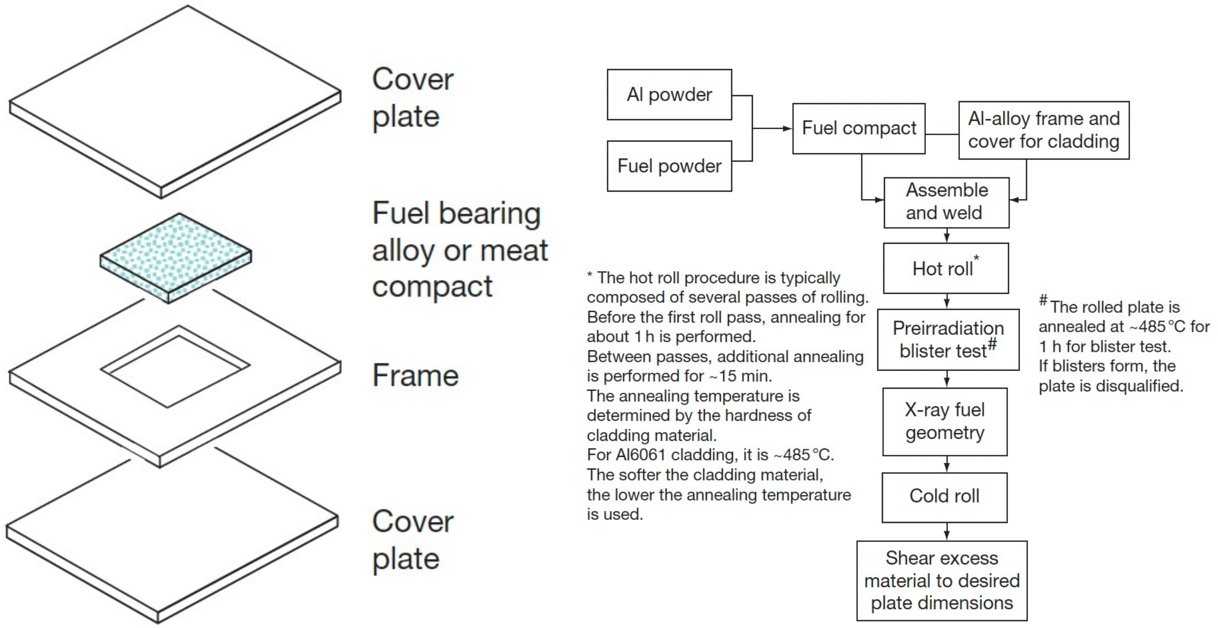
Intermetallic Fuels

- U–Al, U–Si, and U–Mo fuels have been used in research reactors, with development from Al, to Si, to Mo driven by obtaining higher U densities
- Uranium metal in unsuitable, so intermetallics we developed to stabilize irradiation behavior
- The U-Al alloy was the first uranium intermetallic fuel chosen for research and test reactor purposes, largely because of compatibility with Al cladding

Fuel	*Melting point (°C)*	*Physical density ($g\,cm^{-3}$)*	*Uranium loading ($g\,cm^{-3}$)*
U	1133	19.1	19.1
U–7Mo	1145	18.4	17.1
U–10Mo	1150	18.2	16.4
U_6Mn	726	17.8	17.1
U_6Fe	815	17.7	17.0
U_3Si[a]	930[b]	15.6	15.0
U_3Si_2[a]	1665	12.2	11.3
USi	1580	10.96	9.8
UAl_2[a]	1590	8.1	6.6
UAl_3[a]	1350[b]	6.8	5.0
UAl_4	731[b]	6.1	4.2
$U_{0.9}Al_4$[a]	641[b]	5.7	3.7
UAl_x[c]	NA	6.4	4.5
UC	2500	13.6	13.0
UN	2630	14.3	13.5
UO_2[a]	2875	10.96	9.7
U_3O_8[a]	[b]	8.4	7.1
Al[d]	660	2.7	0

U-Al Alloys

- U-Al was utilized as the fuel in the Materials Test Reactor (MTR; 1952-1970) and the Engineering Test Reactor (ETR: 1957-1981)
- Fabrication of U–Al alloys with high uranium contents poses difficulties during the rolling process, and uranium inhomogeneity increases proportionally with uranium content
- The application of monolithic U–Al alloy in higher power reactors was limited because of fabrication constraints and high fuel swelling



U-Al Phases

- There are three intermetallic compounds in the U–Al system: UAl2, UAl3, and UAl4
- UAl2 forms directly from the liquid, but UAl3 and UAl4 form by peritectoid reactions with aluminum
- UAl2 is fcc, UAl3 is $L1_2$ type, UAl4 is bco
- Densities range from 6.6 g/cc to 4.2 g/cc with decreasing U loading
- Thermal conductivity of dispersion fuels is largely governed by the matrix

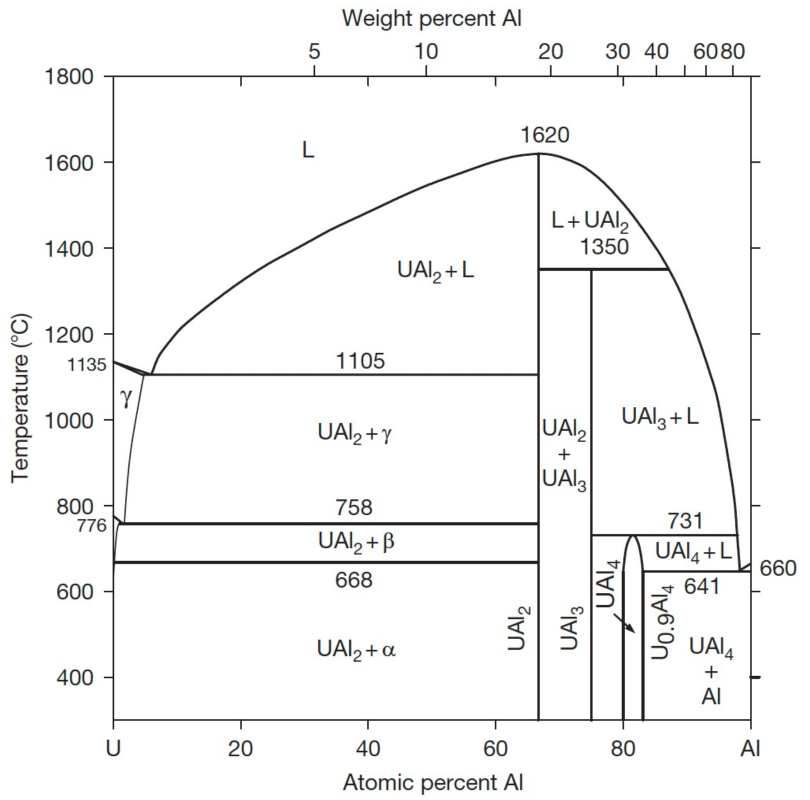


Table 1 The uranium weight percent, density and melting point of uranium aluminides

Compound	*Wt% U*	*Density (g/cm³)*	*Uranium density (g/cm³)*	*Melting point (K)*
UAl_2	81.52	8.14	6.64	1893
UAl_3	74.63	6.8	5.08	1623
UAl_4	68.8	6.06–6.10	4.16	1004
$U_{0.9}Al_4$	64.2–66.3	5.6–5.7	3.648	

U-Al Alloys

- The fuel form of U–Al alloy with a U density high enough to satisfy the need for high-power rectors is a mixture of UAl_2, UAl_3, and UAl_4, known as UAl_x
- UAl_x has positive features that enable its superior performance in high-power reactors
- Fuel swelling can be reduced by accommodating fission product swelling in the powder dispersions, which include pores left during fabrication
- UAl_x also has exceptional resistance to fission gas bubble formation
- In addition, fabrication with a uniform distribution of burnable absorbers is possible
- Typical powder lots used in the ATR contained phase fractions of 7.6 wt% UAl_2, 78.6 wt% UAl_3, and 13.8wt% UAl_4
- These phase fractions can be modified based upon the fabrication process

Fuel Swelling

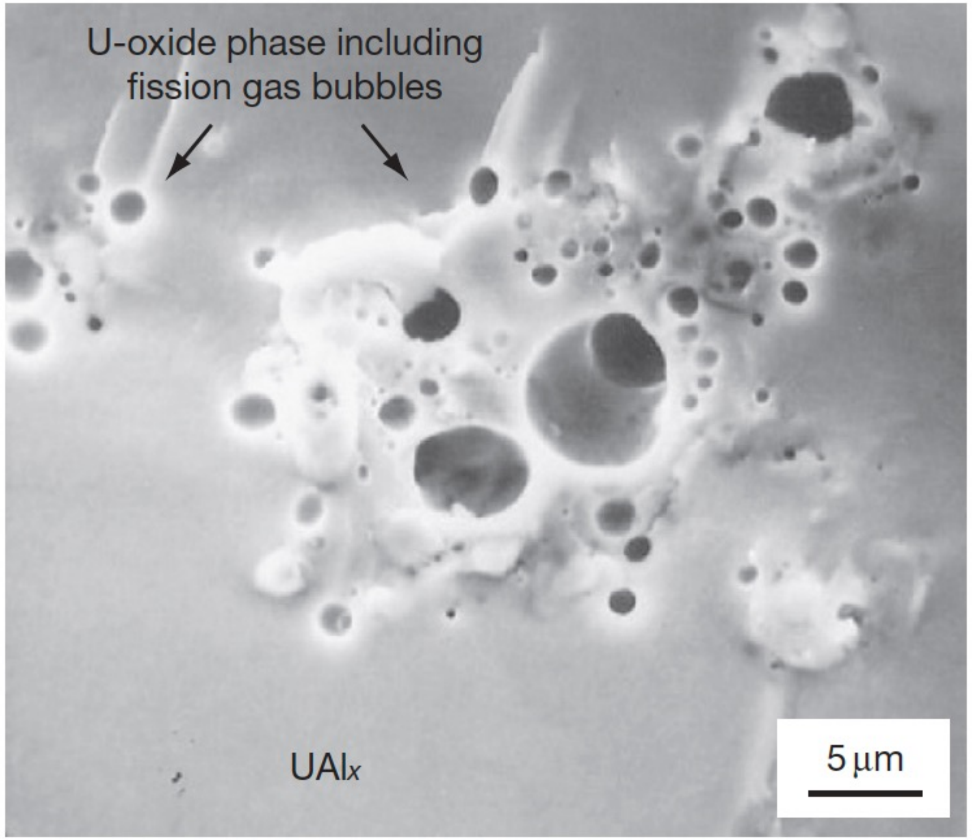
- Fuel swelling by fission products is divided into two distinct parts: solid and gaseous
- Solid FP swelling is due to the difference between the volume of a uranium atom and solid fission products
- Most fission gas atoms remain in the fuel, with solid FP swelling proportional only to burnup; independent of fabrication method, fuel type, temperature, etc.
- Thus, solid swelling is applicable across other intermetallic fuels, with derivations from U-Zr being modified for UAl, USi, and UMo fuels

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

- The solid FP swelling for UMo is given by the above equation, where fd is fission density in 10^{27} fissions/m^3
- 50% burnup is approximately 4×10^{27} f/m^3

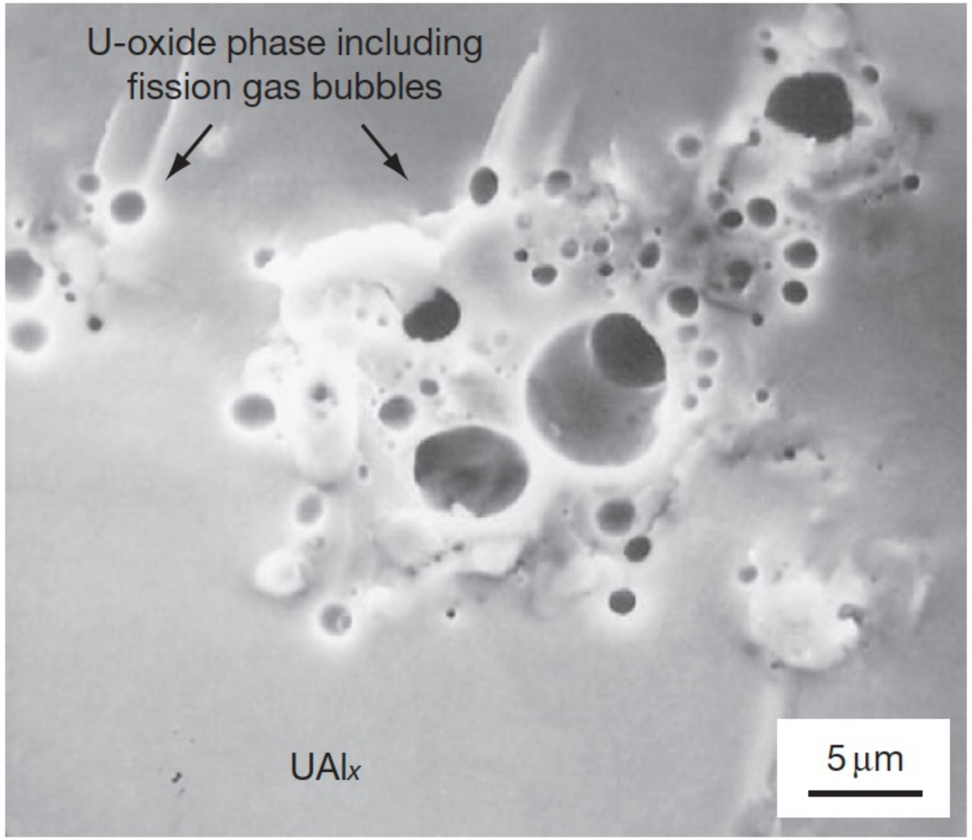
Fuel Swelling

- Gaseous FP swelling is due to the formation of fission gas bubbles and is more difficult to quantify
- Historical examinations on UAlx fuels showed no large fission gas bubbles in the fuel
- Thus, fission gas bubbles were sufficiently small to be beyond the scope of 1980s era SEM
- However, oxide inclusions showed large fission gas bubbles
- Oxides are present due to fabrication



Fuel Swelling

- It is unclear whether the oxide clusters acted as reservoirs absorbing fission gas, or whether UAlx helps retard bubble formation
- It is possible that nanoscale bubbles are forming, but are undetectable via SEM (I would argue this is necessary)
- The gas bubble swelling rate is estimated by subtraction of solid fission product swelling from the total swelling of the plate

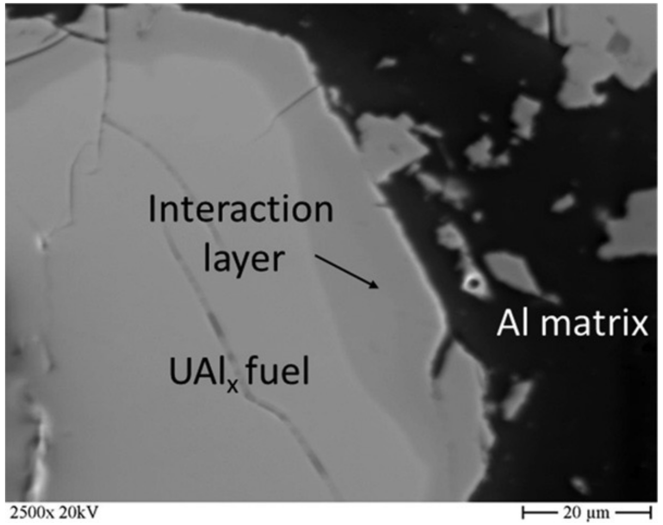


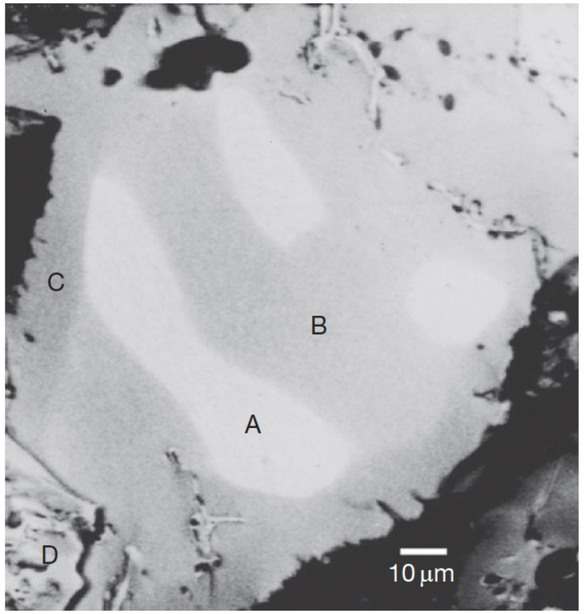
Amorphization

- The performance of all U intermetallic fuels is closely related to whether they are crystalline or amorphous during irradiation
- The U intermetallic fuels tend to be amorphized by damage in the crystal structure caused by highly energetic fission fragments and low temperatures inhibiting recombination
- Amorphization of a crystalline material is accompanied by an increase in volume, which facilitates atomic mobility, enhancing diffusion
- Fission gas mobility is also high in amorphous materials and the fuel material is more readily deformed by the growing gas bubbles
- Thus, fission gas bubble growth in an amorphous material is faster
- The three U–Al intermetallics undergo amorphization depending on the fission rate and temperature
- The lower the irradiation temperature and the higher the fission rate, the more readily the fuel becomes amorphous

UAl-Al Interaction

- UAlx and Al react during irradiation even at low temperatures due to irradiation-enhanced interdiffusion
- UAl2 and UAl3 react with matrix Al to generate UAl4, and since there are no higher content compounds, UAl4 stays stable with Al
- In the image, A is UAl2, B is UAl3, C is UAl4, and D is U oxide
- Measured reaction data of UAlx–Al from in-pile tests are scarce



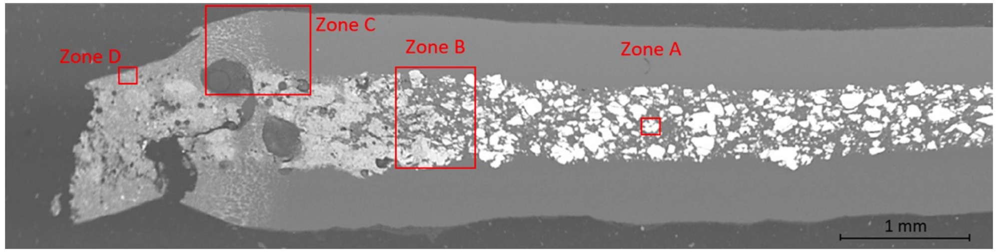


Fission Gas Bubbles

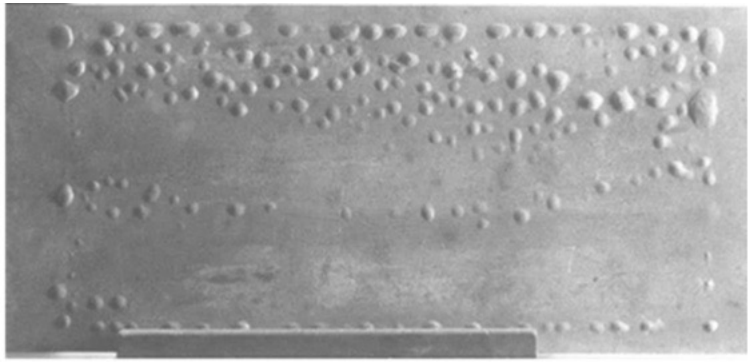
- The fuel kernel and the interaction layers can both become amorphous
- Even in the amorphous phases, no large fission gas bubbles have been observed
- Relatively recent TEM work has showed that at 20% burnup, Xe is still in solid solution in the amorphized phases
- Conversion of UAl2 to UAl3 and UAl4 results in a volume reduction of the fuel, which generates extra space for fission products to reside, increasing the effective solubility
- The high resistance of UAlx to large fission gas bubble formation and a higher as-fabricated porosity lead to a lower overall plate thickness increase in UAlx/Al compared to other fuel dispersion systems

Off-normal behavior

- Most common accident scenario is a channel blockage, resulting in loss of coolant flow
- In the extreme, this can lead to fuel melting
- Higher temperatures at a minimum will lead to bubble formation, coalescence, and swelling
- Temperature increases can result in the blistering of the plates, a delamination of the cladding from the fuel, and potential burst of cladding and release of fission products



(a)



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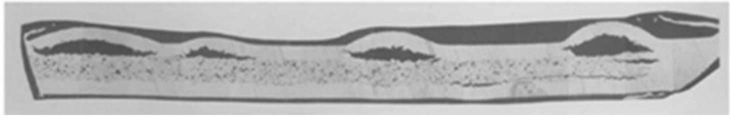


U-Al Summary

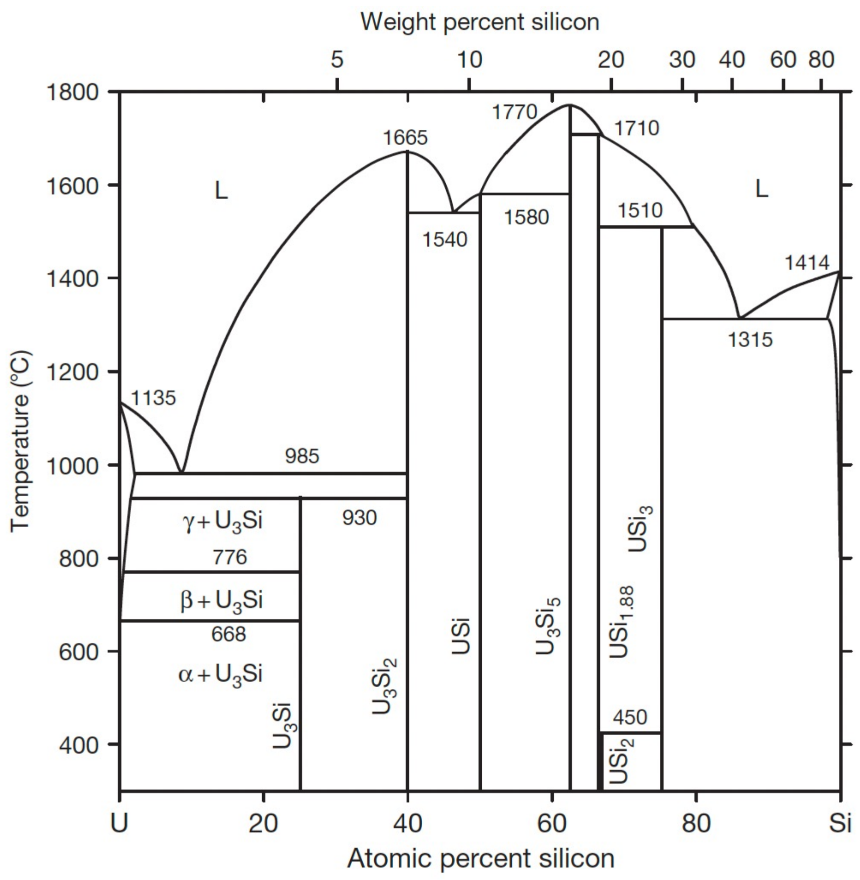
- UAlx fuels are in dispersion form in an aluminum matrix
- The three uranium aluminides undergo amorphization depending on the fission rate and temperature
- UAl_4 amorphizes most readily and UAl_2 least readily
- UAlx–Al dispersions have lower fueled zone swelling than any other type fuel dispersions due to low fission gas bubble swelling
- UAlx fuels had limited utilization due to the requirement of very high U enrichment in relatively low U density alloys
- Additionally, UAl_2 is highly pyrophoric, leading to difficulties in fabrication, significantly increasing costs

RERTR

- The US DOE initiated the RERTR (Reduced Enrichment for Research and Test Reactor) program in 1978 to convert the world's research and test reactors using high-enrichment uranium (HEU) to those using low-enrichment uranium (LEU)
- An enrichment in 235U of 20 at.% is the threshold between HEU and LEU
- Reactors were/are using mainly UAlx and U3O8 dispersion fuels
- To use a fuel with reduced enrichment while keeping the fuel phase volume the same in the fueled zone requires using a fuel with a higher uranium density to compensate for the reduced fissile fraction in LEU
- The fuel form developed to accomplish this is U3Si2, which allows the highest possible uranium loading among the qualified fuel types

U-Si

- In the U–Si system, U3Si, U3Si2, and USi are the compounds of interest for candidate fuels chiefly because of their high uranium density: 15.3, 12.2, and 10.96 g/cc, respectively
- U3Si2 and USi form directly from liquid, but U3Si forms only by a peritectoid reaction at 925C
- U3Si and U3Si2 are of key interest, due to their higher U density
- U3Si2 is also of some interest in commercial LWR application

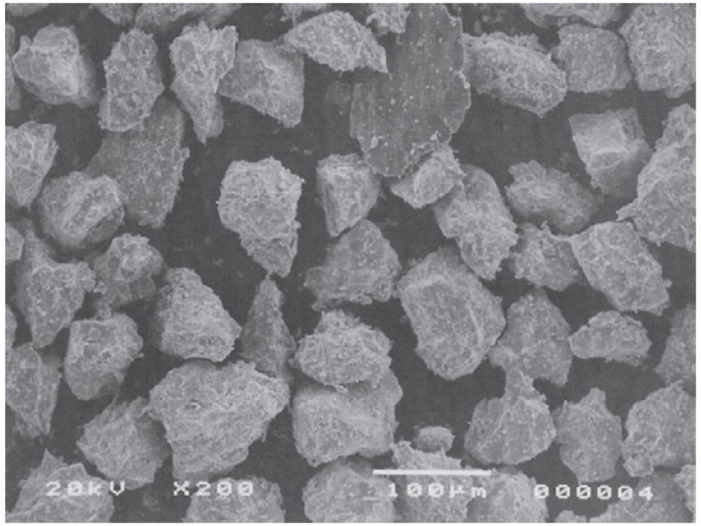


USi Fabrication

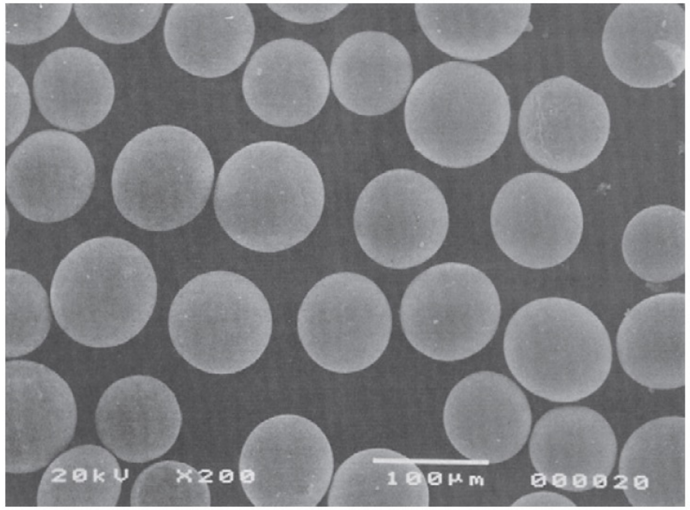
- In practice, it is almost impossible to fabricate the exact stoichiometric form of one of these U-Si compounds
- Typically, a higher content of Si is required to suppress the formation of solid solution U, or Si-lean U-Si compounds
- The secondary phases typically reside inhomogeneously in a fuel particle, which causes inhomogeneous size distributions of fission gas bubbles inside the fuel particles
- Alloy ingots of U–Si are made by mixing and melting of uranium and silicon with a desired Si/U ratio
- The ingots are sometimes annealed in an inert atmosphere to complete compound formation
- These ingots are then broken into smaller particles by a powder fabrication process
- U3Si is more ductile than U3Si2, and requires significantly more work to break into small particles

USi Fabrication

- The fragmentation/comminution process results in jagged and irregular powders
- An atomization technology widely used in powder metallurgy is applied to fabricate spherical powders of U3Si2 and U3Si, involving liquid fuel droplets and centrifugal force
- Atomized powder has several advantages over comminuted powder: 1) surface-to-volume ratio is smaller, so reaction with matrix is less; 2) high homogeneity and fewer impurities; 3) lower residual stresses and defects



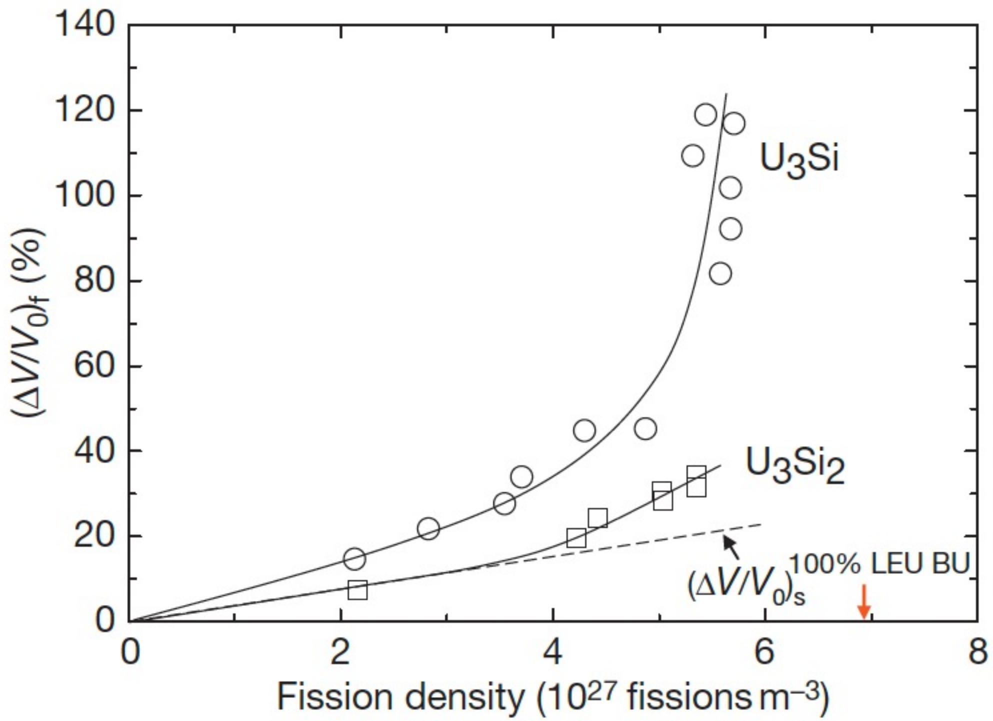
Comminution



Atomization

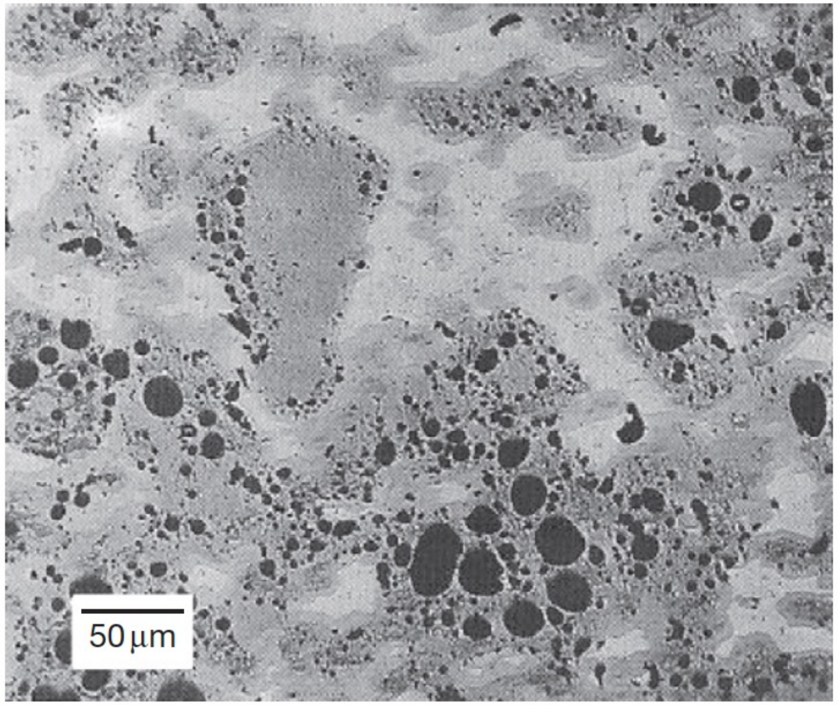
USi Fuel Swelling

- Solid fission product swelling is treated as identical to that in UAlx fuels, but fission gas swelling is markedly different
- Large swelling for U-Si phases, more so for U3Si
- Fuel swelling kinetics of U–Si fuel particles is well documented in the literature
- Again, gaseous swelling is estimated by subtracting solid FP swelling from the total swelling



Amorphous Swelling

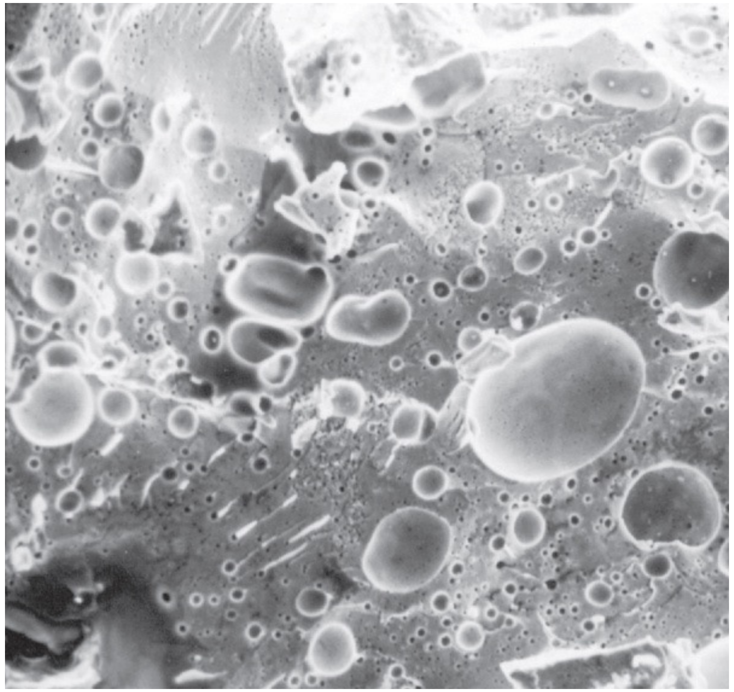
- U3Si and U3Si2 are known to become amorphous under irradiation at sufficiently low temperatures
- The primary damage in the crystal is due to highly energetic fission fragments
- In the amorphous fuel, fuel swelling depends on the viscosity of fuel
- Fission gas mobility is also high in amorphous material and the fuel material is more readily deformed by the growing gas bubbles



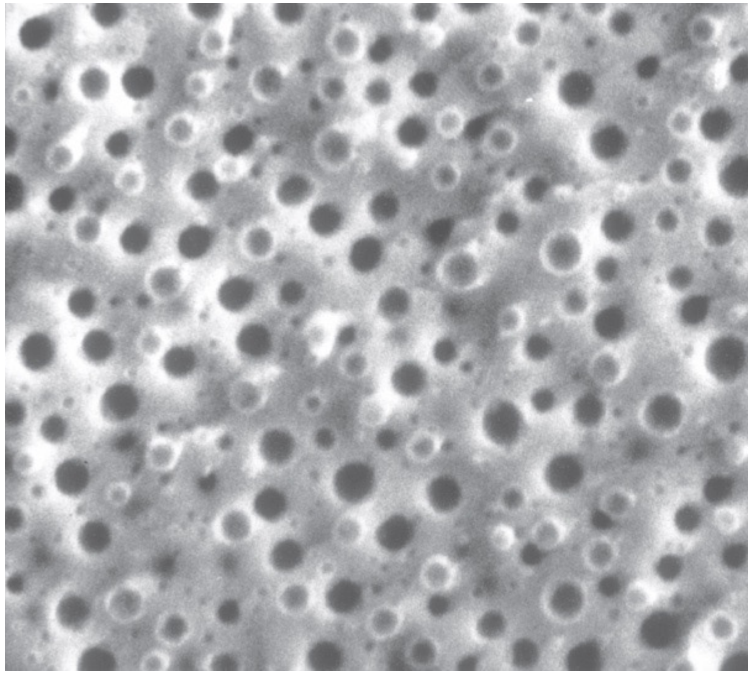
U3Si fission gas bubbles at 4.5E27 f/m3

USi Swelling

- Figures shows fuel microstructures and the fission gas bubble morphology of irradiated U3Si and U3Si2 at 100C to 15% and 19% burnup



U3Si



U3Si2

USi Swelling

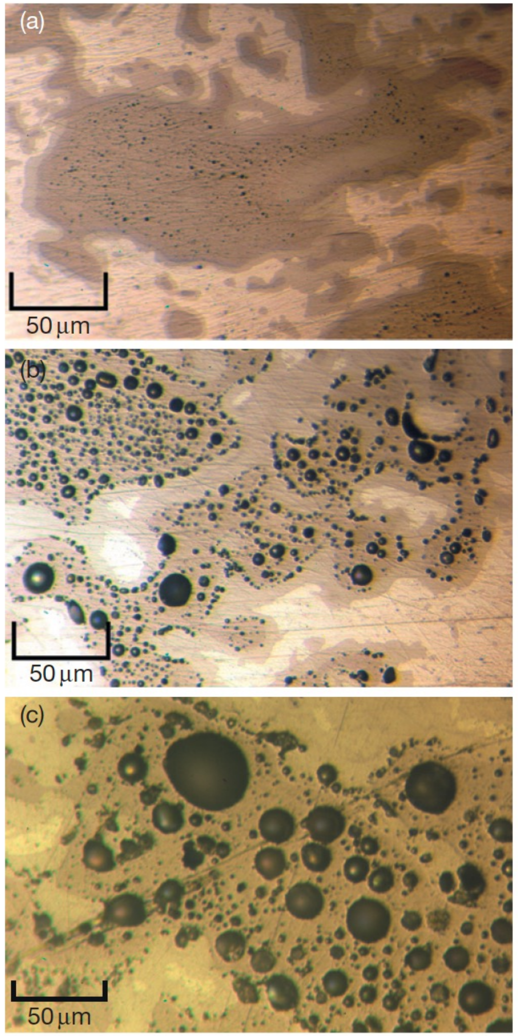
- Both U3Si and U3Si2 are amorphous during research reactor irradiation
- Fission gas bubble growth in U3Si is high and unstable, while that of U3Si2 is generally lower and stable
- An explanation is the correlation between free volume and viscosity, in that U3Si has larger free volume than U3Si2
- Thus U3Si viscosity is relatively lower

$$\eta = \eta_0 \exp\left(\frac{C}{\Delta V_R}\right)$$

- The additional Si bonds in U3Si2 have a large effect on the amount of free volume in the glassy state, and therefore also on the fluidity of the fuel, and thus the swelling behavior
- Amorphization is a prerequisite for this low-temperature high-swelling behavior

U3Si2 Swelling w/ temperature

- The bubble morphology from higher temperature tests is available
- Bubble growth in U3Si2 can be enhanced to the level of U3Si if the temperature is increased by about 60C (albeit at higher burnups)
- It appears that the low bubble growth advantage of U3Si2 provided by the high Si/U ratio is negated if the temperature is increased



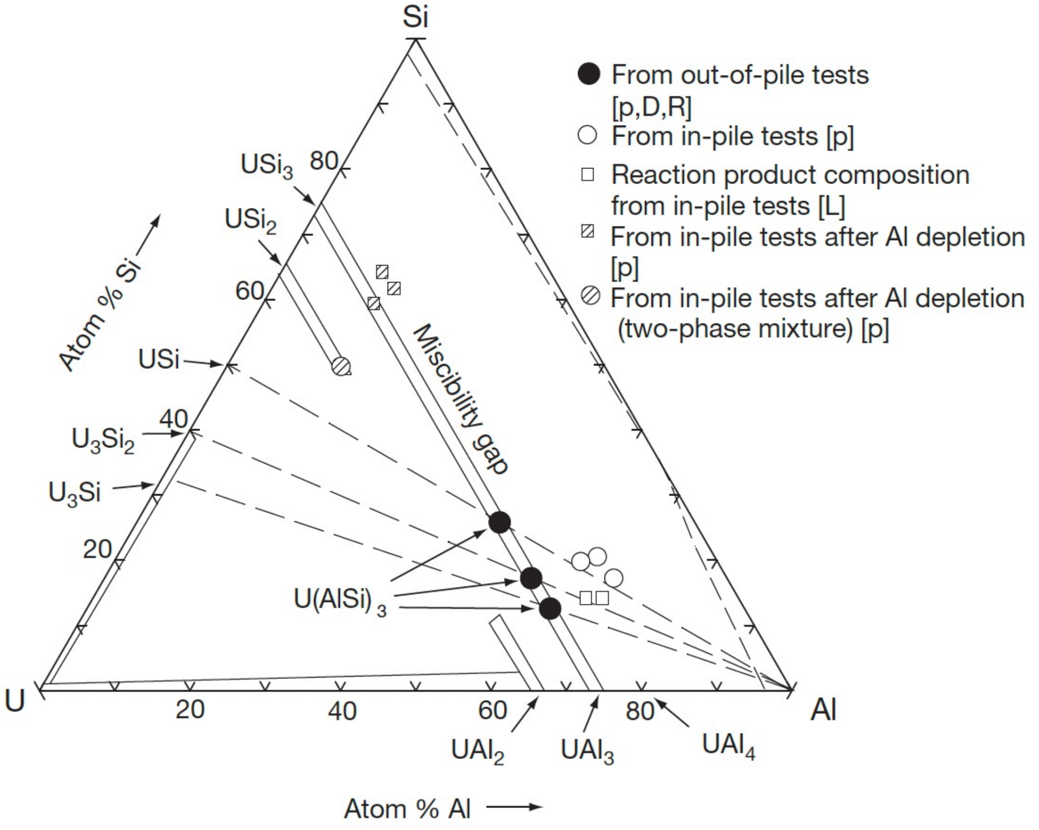
T=105 C and FD=3.2E27 f/m3

T=136 C and FD=5.4E27 f/m3

T=160 C and FD=6.1E27 f/m3

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

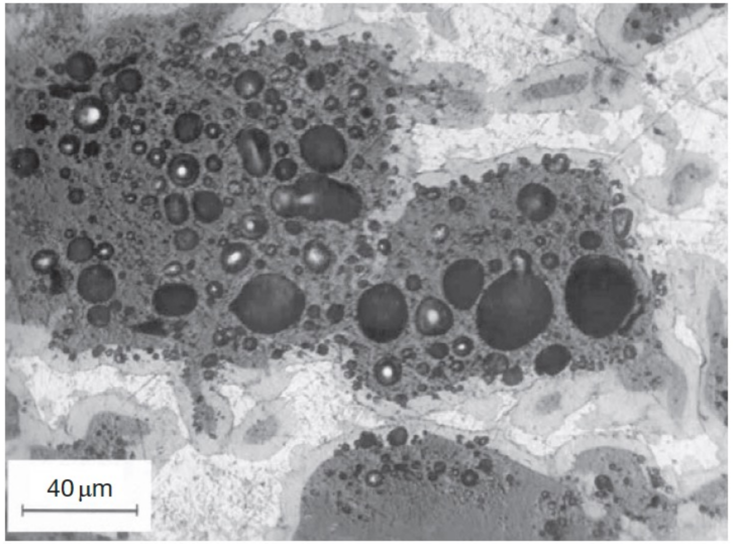
USi interaction with Al

- 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

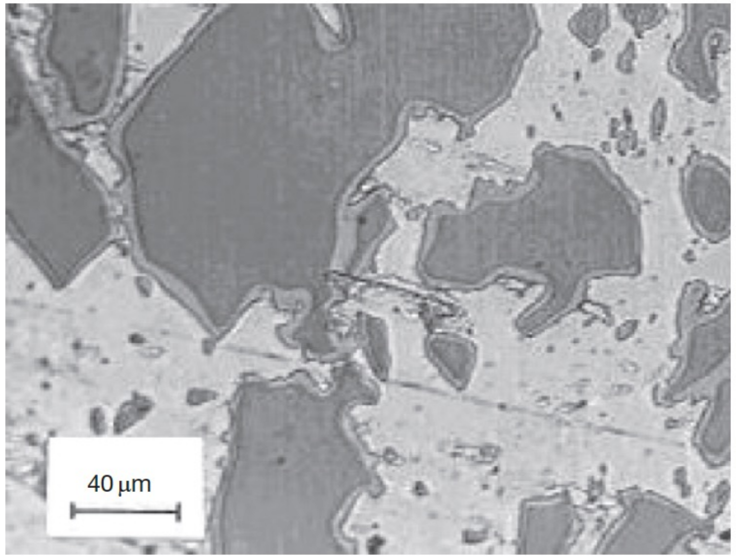
- The formation of gas bubbles in the ILs is important because of its potential effects on the IL growth rate
- The gas bubbles in the IL reduce the effective diffusion area and thereby reduce the IL growth rate, limiting breakaway IL formation

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



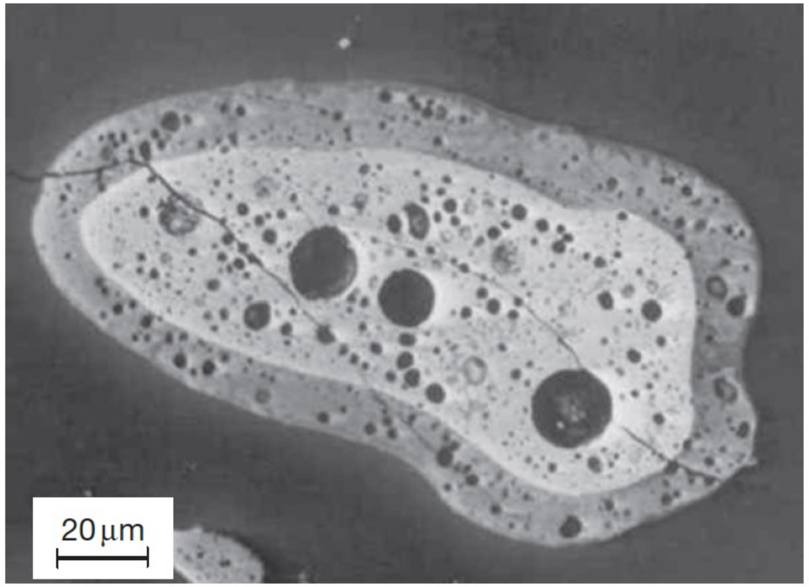
U3Si–Al



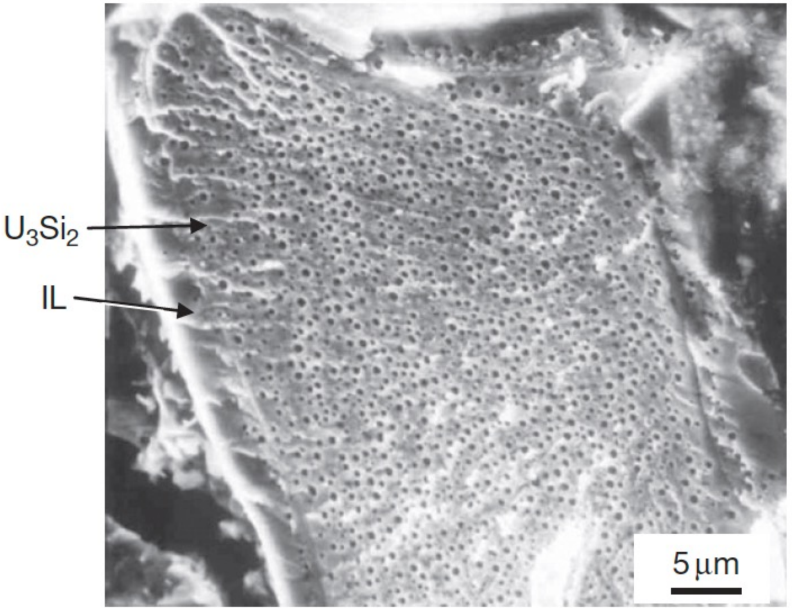
U3Si2–Al

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