NE 591: Advanced Reactor Materials

Fall 2021

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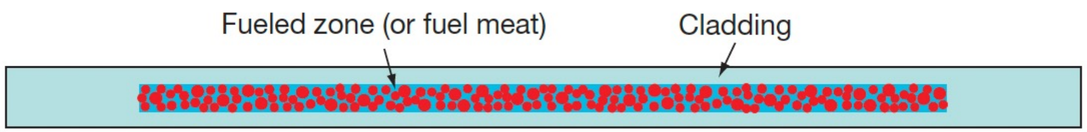
Last Time

- Wrapped up module 3 with nitride fuels
- Nitrides have a higher U density and higher thermal conductivity than oxides, with a higher melting point than metallic fuels
- Difficult fabrication, requiring atmospheric controls and enrichment of N, especially in thermal or transmutation applications
- Three stages in temperature, with gap closure leading to steady state behavior
- Nitride fuel undergoes restructuring, with central porous region, large grained region, and as-fabricated microstructure
- FCMI is a key life limiting phenomenon due to little creep in UN fuels

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



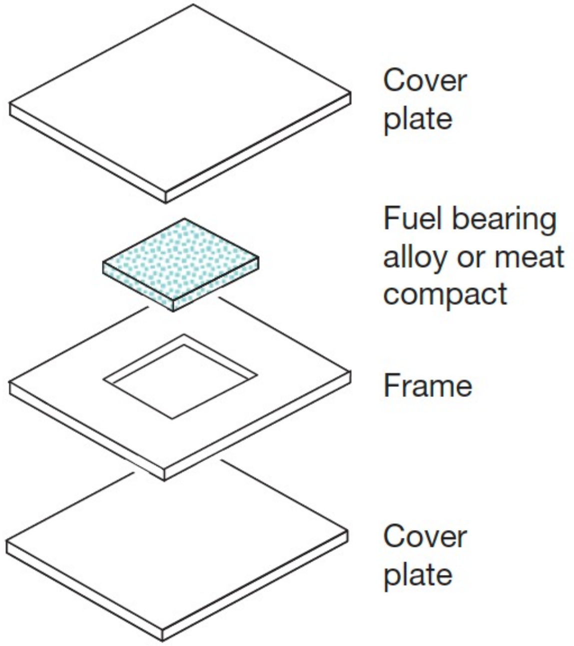
Intermetallic Fuels

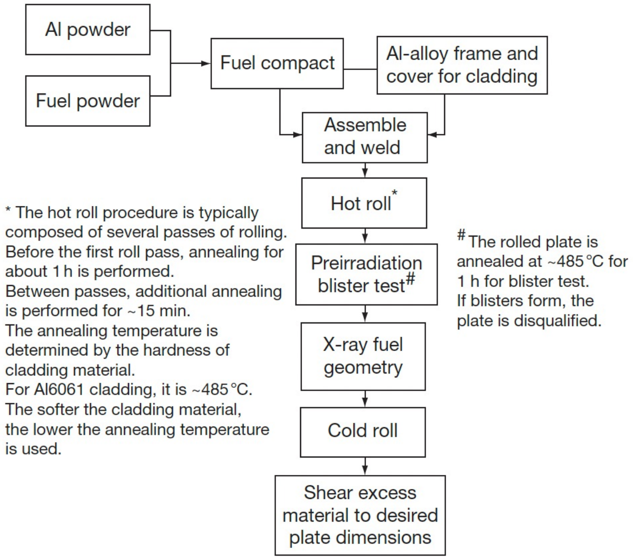
- U–Al, U–Si, and U–Mo fuels have been used in research reactors, with development from Al, to Si, to Mo driven by obtaining higher U densities
- Uranium metal in unsuitable, so intermetallics we developed to stabilize irradiation behavior
- The U-Al alloy was the first uranium intermetallic fuel chosen 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) and the Engineering Test Reactor (ETR)
- 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



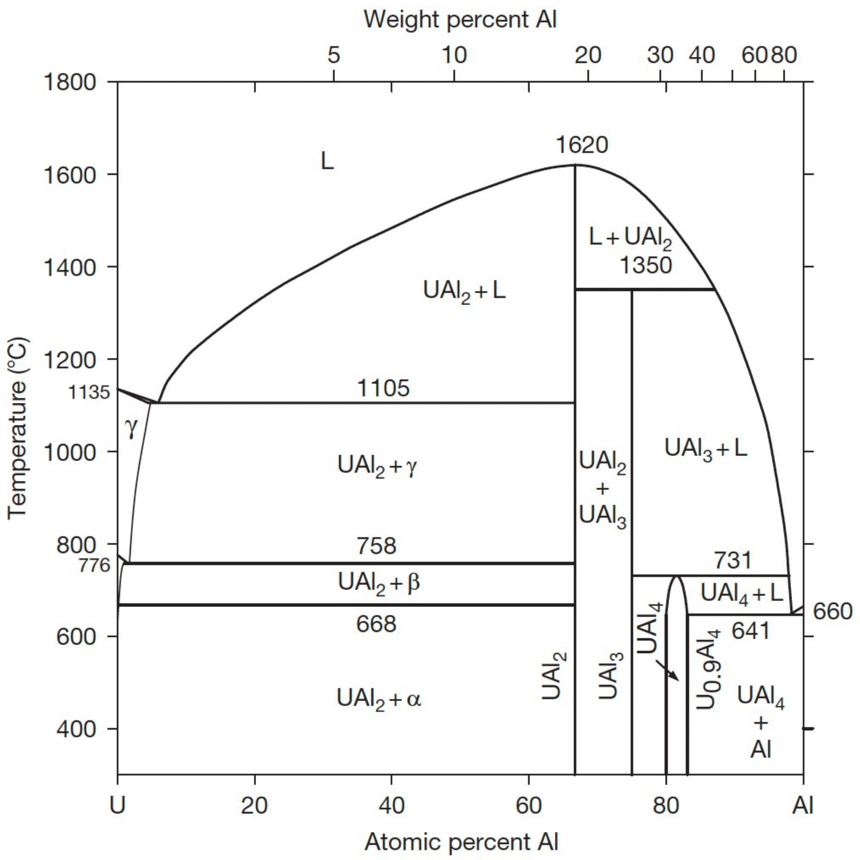


U-Al Alloys

- 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 UAlx
- UAlx 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
- UAlx 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

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 6.8 g/cc to 5.7 g/cc with decreasing U loading
- Thermal conductivity of dispersion fuels is largely governed by the matrix



Fuel Swelling

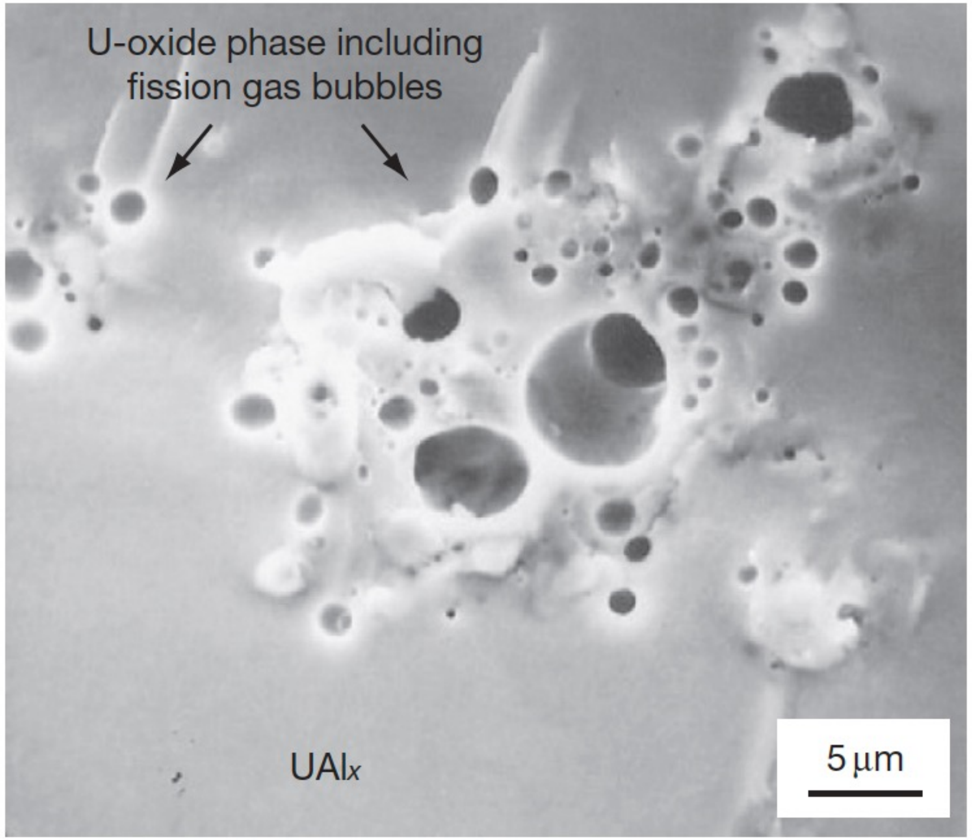
- Fuel swelling by fission products is conveniently divided into two distinct parts: solid and gaseous
- Solid FP swelling is due to the difference between the volume of a uranium atom and solid fission products
- Most fission gas atoms remain in the fuel, with solid FP swelling proportional only to 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

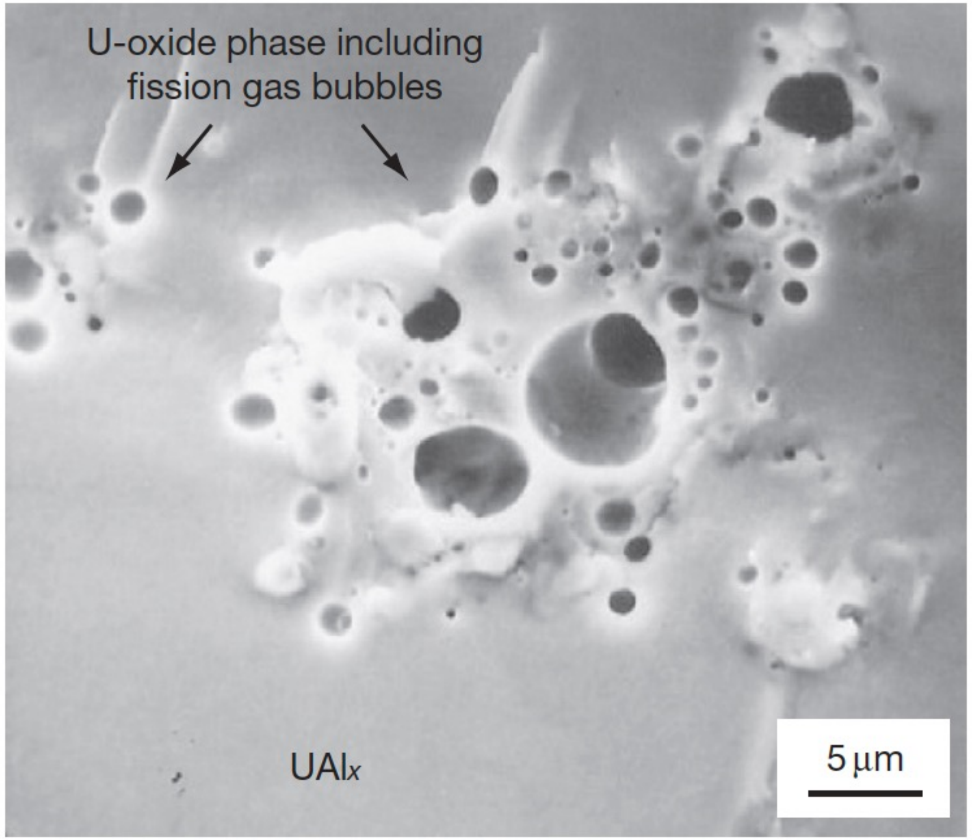
Fuel Swelling

- 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)
- A direct quantification of the gas bubble swelling rate is currently impossible
- Instead, the gas bubble swelling rate is estimated by subtraction of solid fission product swelling from the total swelling

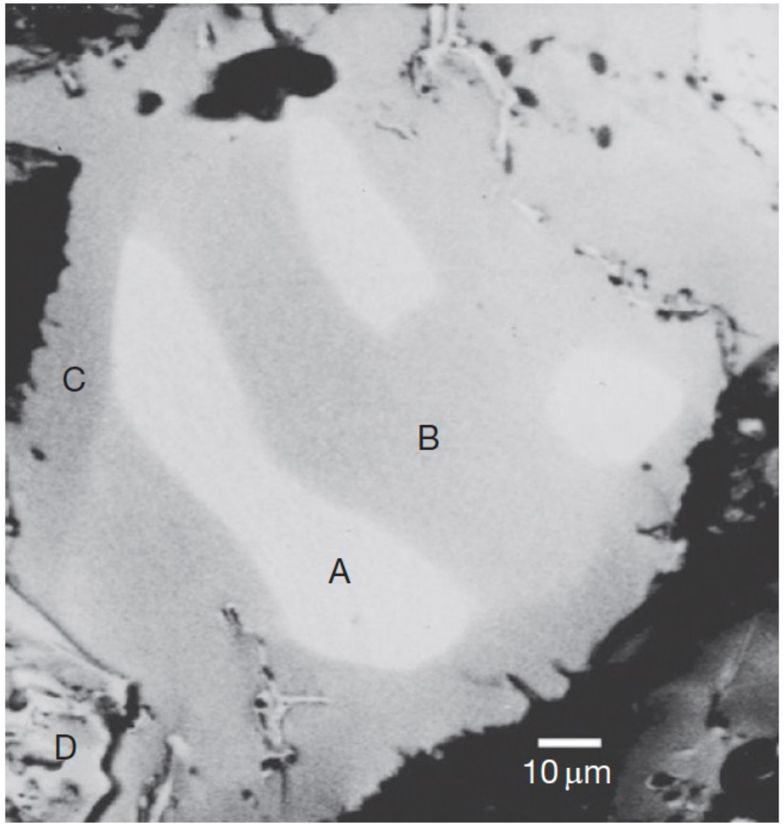


Amorphization

- 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



U-Al Summary

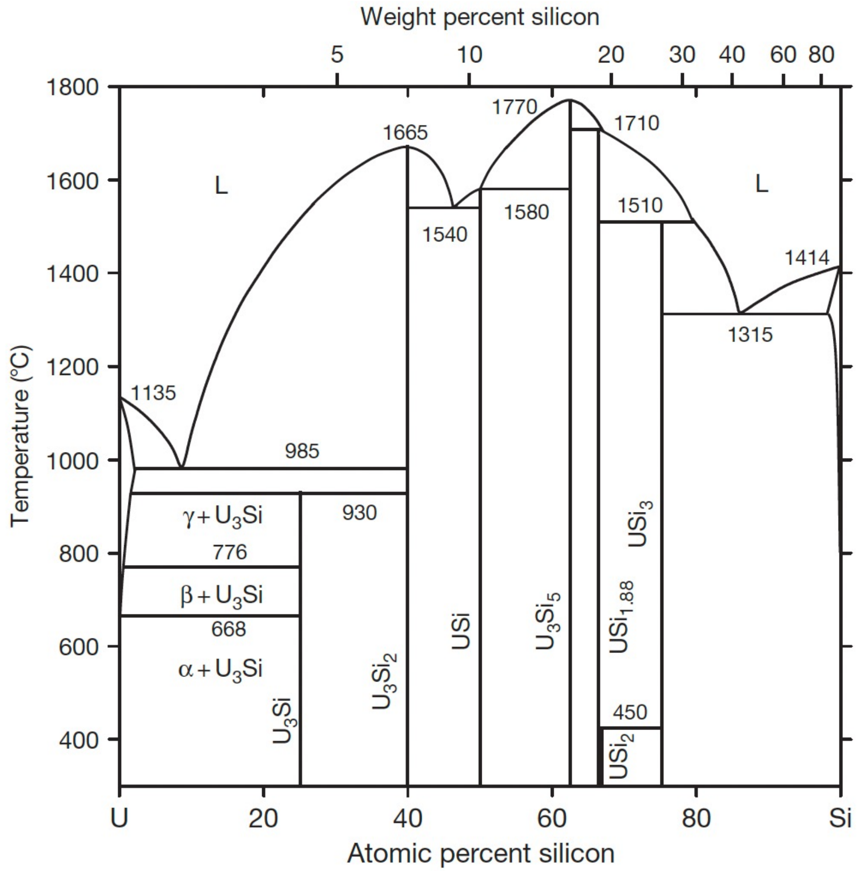
- UAlx fuels are in dispersion form in an aluminum matrix
- The three uranium aluminides undergo amorphization depending on the fission rate and temperature
- UAl_4 amorphizes most readily and UAl_2 least readily
- UAlx–Al dispersions have lower fueled zone swelling than any other type fuel dispersions 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
- To use a fuel with reduced enrichment, keeping the fuel phase volume the same in the fueled zone, requires using a fuel having 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 interest in commercial LWR application

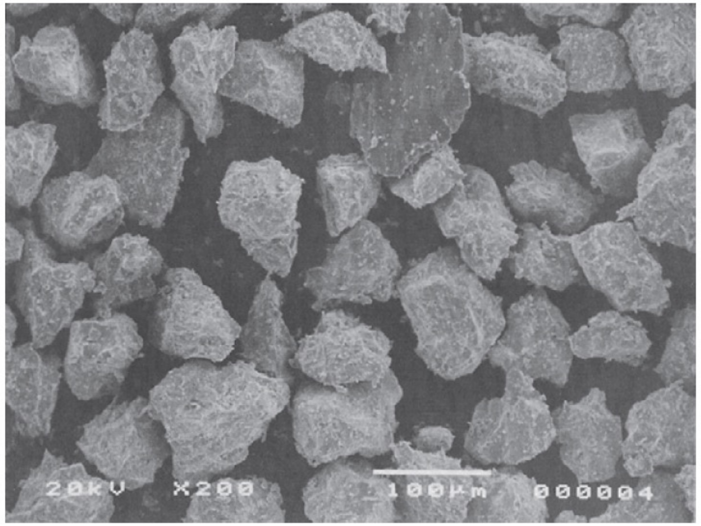


USi Fabrication

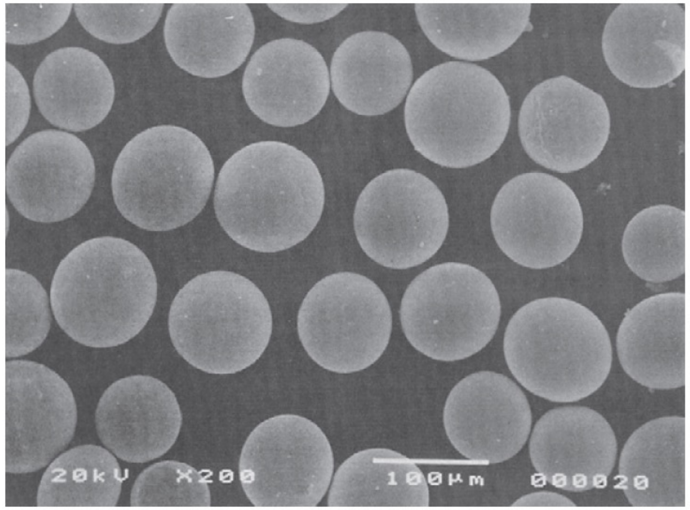
- In practice, it is almost impossible to fabricate the exact stoichiometric form of one of these U-Si compounds
- Typically, a higher content of Si is required to suppress the formation of solid solution U, or Si-lean U-Si compounds
- The secondary phases typically reside inhomogeneously in a fuel particle, 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, are 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



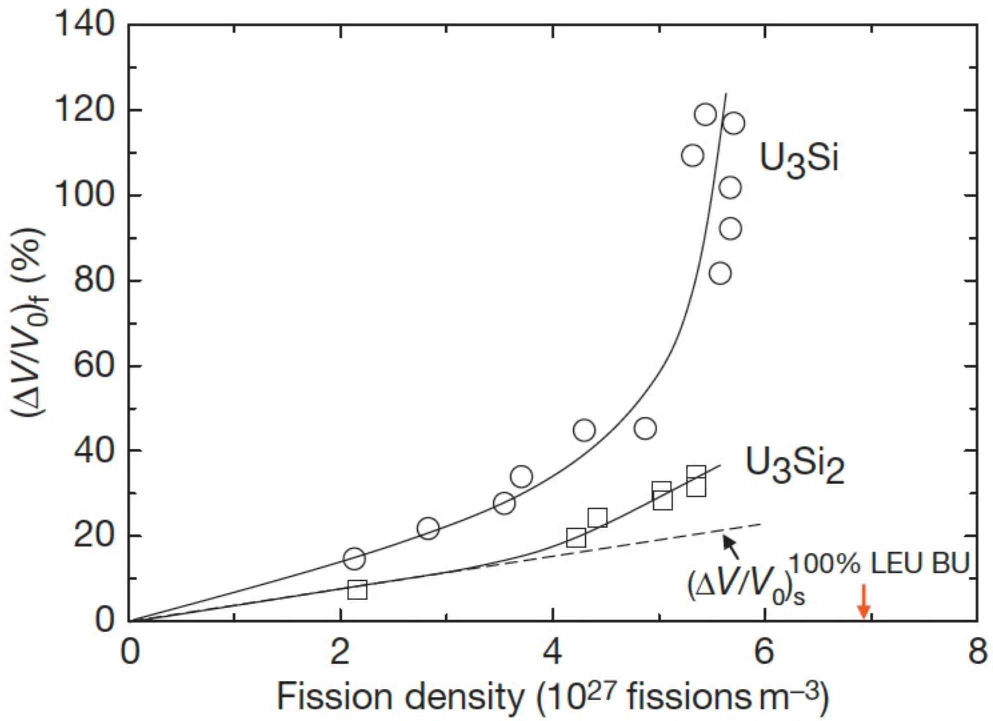
Comminution



Atomization

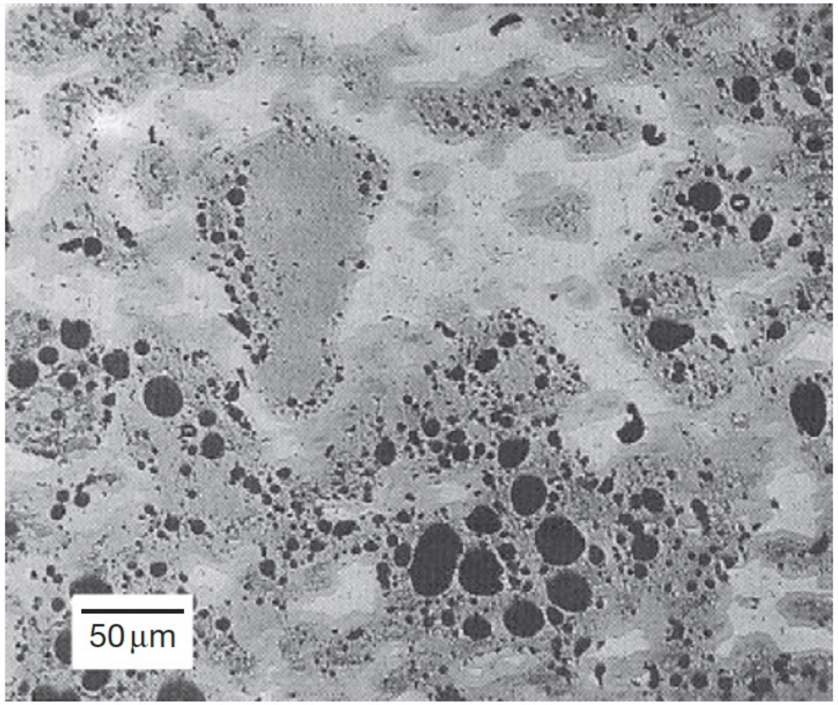
USi Fuel Swelling

- Solid fission product swelling is treated as identical to that in UAlx fuels, but fission gas swelling is markedly different
- 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

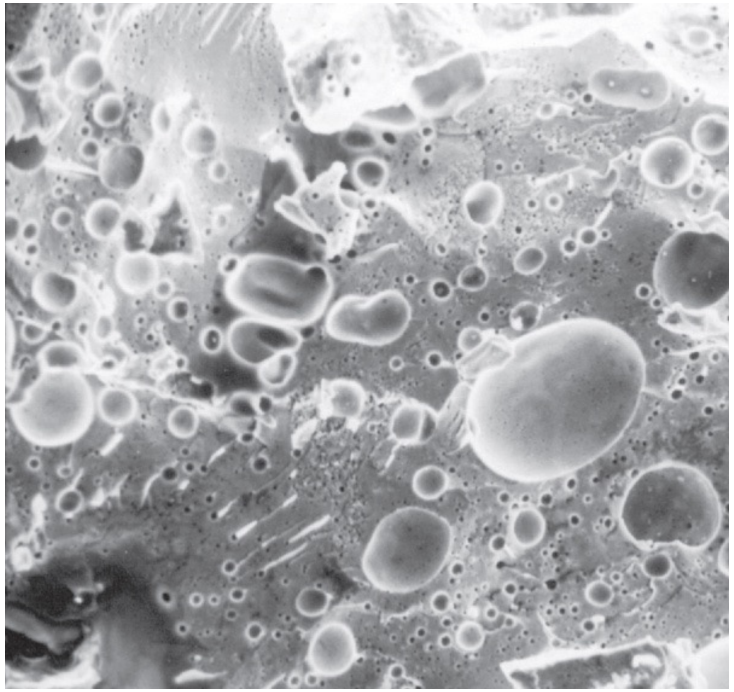
- U3Si and U3Si2 are known to become amorphous under irradiation at sufficiently low temperatures
- The primary damage in the crystal is due to highly energetic fission fragments
- In the amorphous fuel, fuel swelling depends on the viscosity of fuel
- Fission gas mobility is also high in amorphous material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



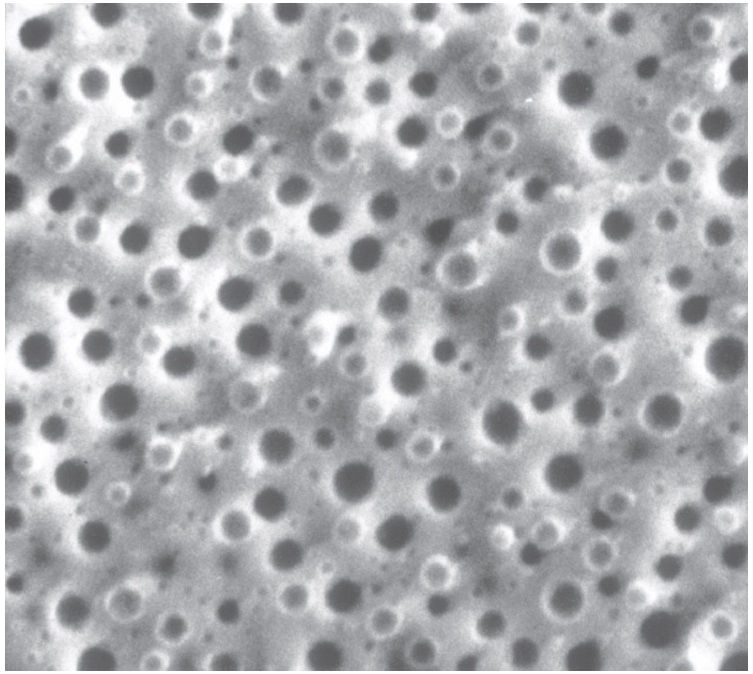
U3Si fission gas bubbles at 4.5E27 f/m3

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

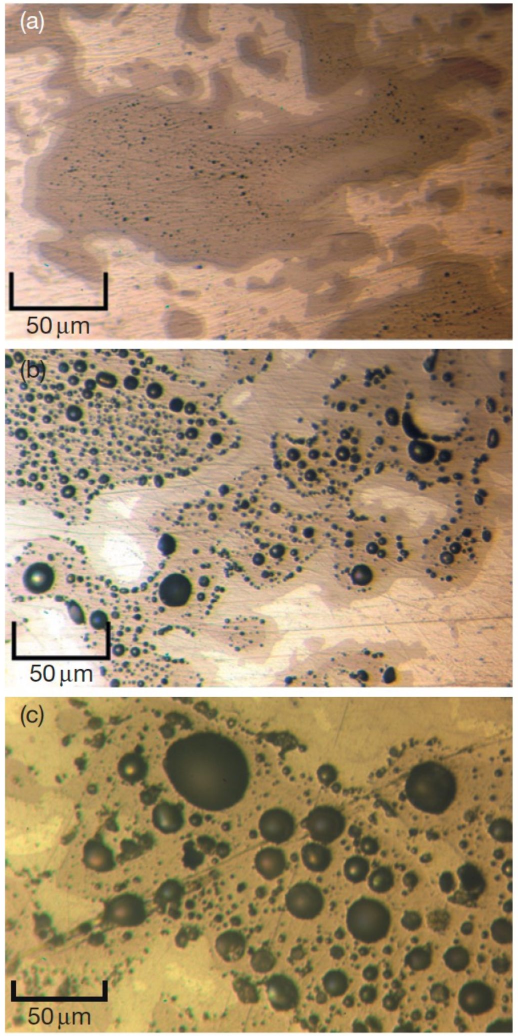
- Both U3Si and U3Si2 are amorphous during research reactor irradiation
- Fission gas bubble growth in U3Si is high and unstable, while that of U3Si2 is generally lower and stable
- An explanation is the correlation between free volume and viscosity
- In that U3Si has larger free volume than U3Si2

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

- 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

USi Swelling

- 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