BEHAVIOUR OF IRRADIATED URANIUM SILICIDE FUEL REVISITED

M. Ross Finlay*, Gerard L. Hofman, Jeffrey Rest, & James L. Snelgrove
Argonne National Laboratory
9700 South Cass Avenue
Argonne, IL 60439

*On assignment from the
Australian Nuclear Science and Technology Organisation (ANSTO)
PMB 1 Menai NSW 2234
Australia

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ABSTRACT

Irradiated U_3Si_2 dispersion fuels demonstrate very low levels of swelling, even at extremely high burn-up. This behaviour is attributed to the stability of fission gas bubbles that develop during irradiation. The bubbles remain uniformly distributed throughout the fuel and show no obvious signs of coalescence. Close examination of high burn-up samples during the U_3Si_2 qualification program revealed a bimodal distribution of fission gas bubbles. Those observations suggested that an underlying microstructure was responsible for the behaviour. An irradiation induced recrystallisation model was developed that relied on the presence of sufficient grain boundary surface to trap and pin fission gas bubbles and prevent coalescence.

However, more recent work has revealed that the U_3Si_2 becomes amorphous almost instantaneously upon irradiation. Consequently, the recrystallisation model does not adequately explain the nucleation and growth of fission gas bubbles in U_3Si_2. Whilst it appears to work well within the range of measured data, it cannot be relied on to extrapolate beyond that range since it is not mechanistically valid. A review of the mini-plates irradiated in the Oak Ridge Research Reactor from the U_3Si_2 qualification program has been performed. This has yielded a new understanding of U_3Si_2 behaviour under irradiation.

1. Introduction

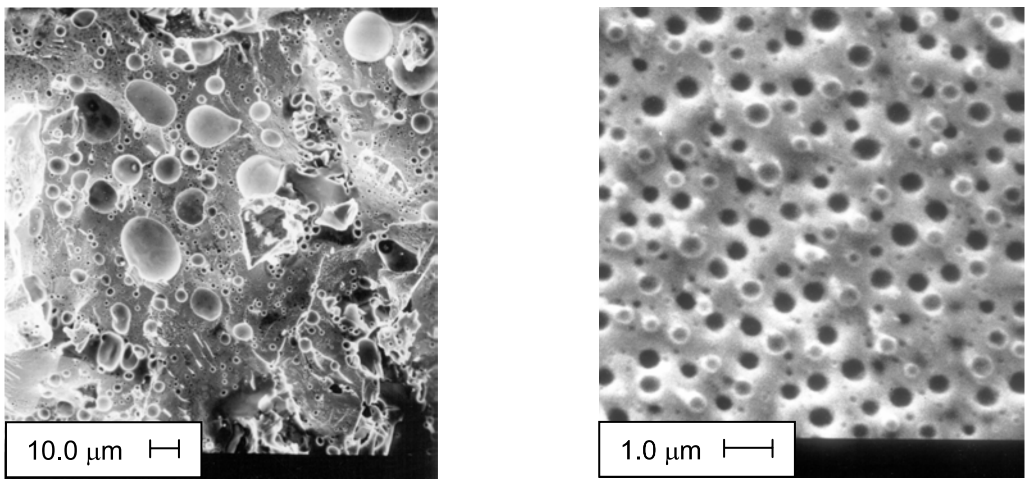
Previously, fission gas bubbles were considered to nucleate at approximately the time of grain recrystallisation and remain relatively constant in number throughout the irradiation. The larger bubbles were believed to be associated with grain boundaries and triple points and the smaller bubbles were located on grain boundary surfaces. The evidence that U_3Si_2 becomes amorphous when irradiated dictated that a new model be developed to explain fission gas behaviour. As a first pass, the data collected during the international qualification program for silicide fuels has been revisited.

Much of the detailed analytical work performed previously on U_3Si_2 fuel samples aimed to demonstrate the stability of the fuel at high burn-up. The lower burn-up samples were less extensively studied and therefore the quality and detail of the information available is limited. Whilst the trends observed are clear, some of the detail could be clarified with further study.

The present study has focused on bubble nucleation and monitored changes in number, composition and size as a function of fission density. In the context of the following discussion, bubble nucleation refers to the point at which fission gas bubbles can be resolved in SEM micrographs. The distribution of bubble sizes was measured on a planar fracture surface of fuel particles and converted to a volumetric fraction using the Saltykov method [1].

2. Amorphisation

The behaviour of fission gas bubbles in U_3Si and U_3Si_2 has been demonstrated to be significantly different [2]. It was always recognised that U_3Si becomes amorphous when irradiated and exhibits breakaway swelling as a result (Figure 1,a)). The large free volume generated when U_3Si becomes amorphous permits rapid migration of fission gas atoms and fission gas bubbles. The bubbles coalesce in a dramatic manner and facilitate the gross swelling observed in U_3Si fuel plates.



a) b)

Figure 1. Fission gas morphology in a) U_3Si (73% burn-up, 4.3 x 10^{21} f/cm^3) and b) U_3Si_2 (96% burn-up, 5.2 x 10^{21} f/cm^3).

The uniform and stable distribution of fission gas bubbles in U_3Si_2 gave strong indications that they were associated with an underlying microstructural feature (Figure 1,b)). However, electron diffraction analysis of Kr ion irradiation tests on U_3Si_2 foils indicated that the material became amorphous [3]. There was some doubt over these results since it was not clear that the ion beam damage was representative of the complex irradiation damage caused by fission. More comprehensive neutron diffraction studies at the Intense Pulsed Neutron Source at Argonne National Laboratory [4] supported the conclusion above and revealed that U_3Si_2 contracted upon amorphisation. The reduced free volume of U_3Si_2 compared to U_3Si is believed to be the result of an increased number of silicon-silicon bonds. The smaller free volume is likely to reduce the mobility of fission gas atoms and fission gas bubbles as compared with U_3Si.

3. Bubble Study:

a) Bubble Number

The first major observation was the absence of the bimodal distribution of bubble sizes when the lower burn-up LEU samples were reviewed. The bimodal distribution was not observed until very high burn-up was achieved. At a fission density where bubbles were first observed, the distribution of bubble sizes was narrow and the number of bubbles, particularly at the peak size was high (Figure 2). On the swelling vs. fission density graph, this point is referred to as the 'knee'. At higher fission densities, the distribution was observed to broaden as the bubbles continued to grow by accumulating more gas. If the bubbles were growing at a constant rate then the distribution would have remained relatively uniform. However, the bubble distribution suggested that some bubbles grew at the expense of others. It is clear from Figure 2 that as the bubble diameter increased, the total number of bubbles decreased.

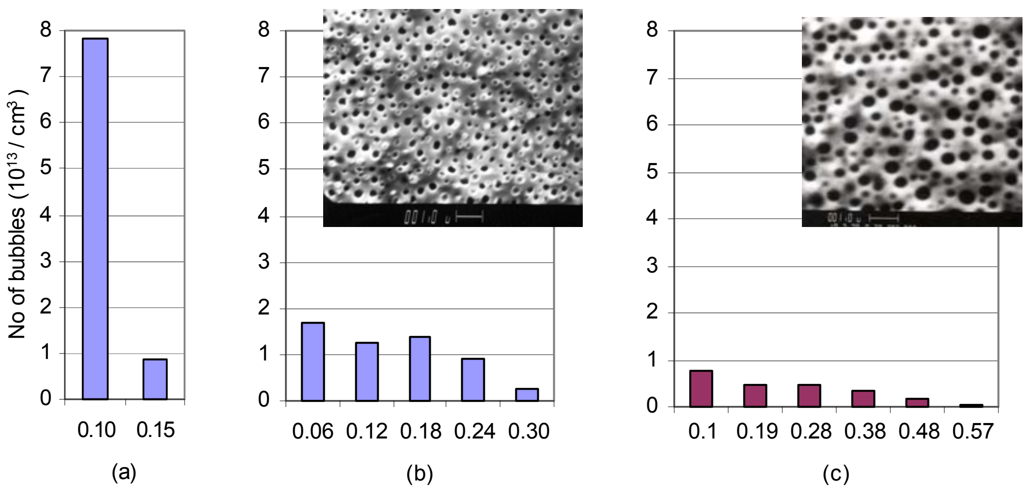


Figure 2. No of bubbles / cm^3 vs. bubble diameter (μm) in LEU fuel at fission densities of a) 2.8 x 10^{21}/cm^3, b) 4.2 x 10^{21}/cm^3, & c) 4.6 x 10^{21}/cm^3.

The trend continued beyond the point at which a secondary nucleation of bubbles occurred. At that point (Figure 3), the bubble density increased due to the secondary nucleation. However, if the new peak was subtracted from the total number of bubbles, the number of bubbles from the primary nucleation continued to decrease.

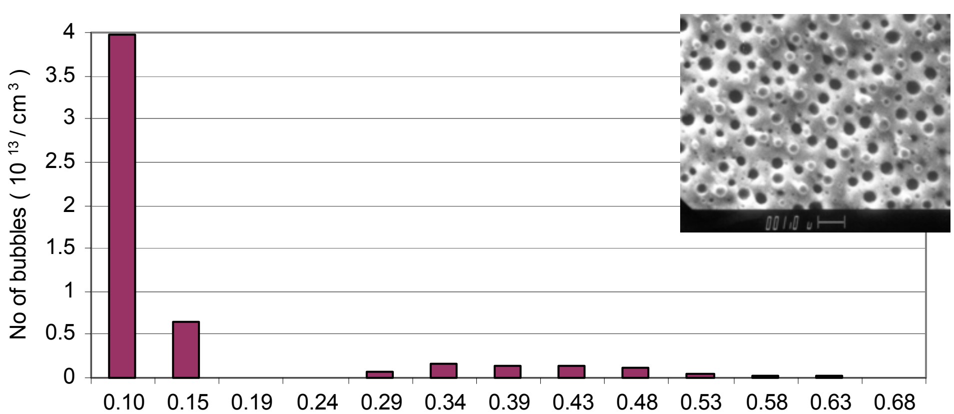


Figure 3. No of bubbles / cm^3 vs. bubble diameter (μm) in LEU fuel at a fission density of 5.2 x 10^{21}/cm^3.

Figure 4 shows clearly that the total bubble population decreased dramatically with a small increase in fission density. Despite the absence of any clear proof in the SEM micrographs, it is reasonable to assume that coalescence had occurred. Although this contradicted the previously considered numerical stability of the fission gas bubbles, it was clear that the number of fission gas bubbles decreased. For LEU fuel, the number of bubbles decreased by approximately a factor of 4 before a second population of smaller bubbles appeared. Beyond this point, the number of larger bubbles continued to decrease, although the rate was not as rapid. This observation was difficult to reconcile with the bubble morphology. Generally, the bubbles were uniformly dispersed throughout the fuel particles with little evidence of coalescence or bubbles situated adjacent to one another. However, calculations indicate that the bubbles disappeared at a rate of ~ 1 bubble every 2-3 minutes, per 1000 μm^3. Given that each of the SEM micrographs examined represented a cross section through such a volume it was not so surprising that little evidence for coalescence was found.

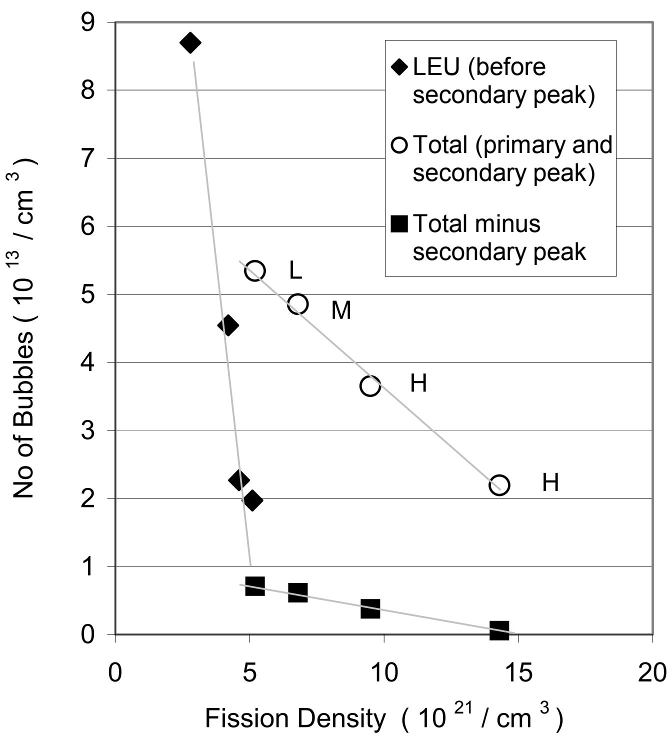


Figure 4. No of bubbles per cm^3 in irradiated U_3Si_2 fuel particles. L = LEU, M=MEU, H=HEU

b) Fission Gas Atoms in Bubbles

The number of fission gas atoms stored in bubbles was calculated and compared against the total number of atoms generated. Two very interesting observations were made. Firstly, the percentage of gas atoms stored in bubbles was very small (Figure 5). Secondly, the higher enrichment fuels, that is, MEU and HEU, that generate a larger number of fission gas atoms, store a smaller fraction of the gas generated in those bubbles. It was surprising to discover that an HEU fuel that had a bubble volume fraction of 68% only contained between 5 & 20% of the total gas atoms generated. The surface energies of bubbles generated in common nuclear fuels such as UO_2 are not well known and therefore are even less understood in amorphous alloy fuels. Hence, an upper and lower bound value was used.

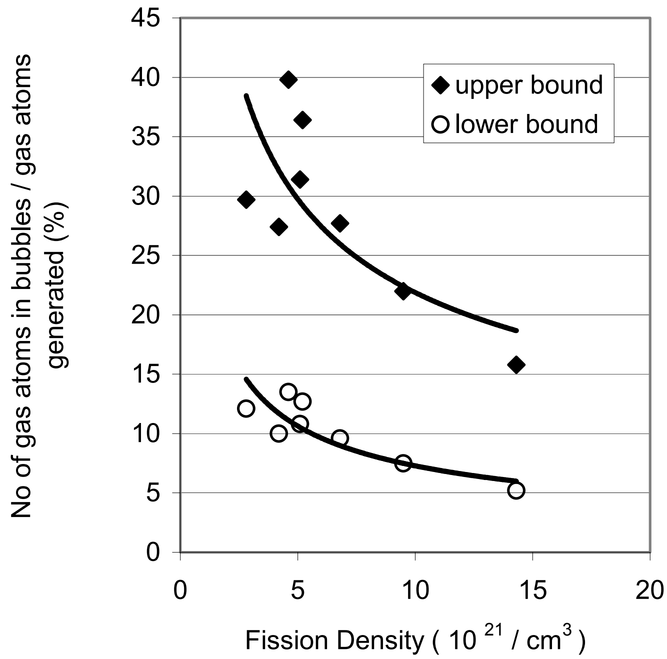


Figure 5. Number of fission gas atoms in bubbles as a percentage of the total fission gas atoms generated.

4. Swelling Behaviour

a) Influence of fission rate on fission gas solubility

The knee is defined as the point at which fission gas bubbles are first observed. At that point, the swelling rate of the fuel particle accelerates compared to the swelling rate when fission gas atoms are retained in solution. Rest and Hofman [5] demonstrated that the higher fission rate of HEU fuels shifted the knee to a higher fission density compared to the lower fission rate of the LEU fuels. At a higher fission rate, more fission fragment-gas atom collisions occur that provide the energy to retain the fission gas atoms in solution. Although the fission rate dependence of the knee position was recognised, individual fission-rate histories of the various mini-plates were not considered. The swelling curves beyond the knee were determined as linear fits of the data for the three general levels of fission rate experienced in the LEU, MEU and HEU plates, as illustrated in Figure 6. In hindsight, it is clear that this interpretation of the data was simplistic.

From a review of the individual fission rate histories, it has been possible to identify a knee point for each mini-plate. The position of the knee is based on a correlation between the fission density at the knee and the instantaneous fission rate at the knee. The correlation, shown in Figure 7, indicates that a higher instantaneous fission rate shifts the knee to a higher fission density. It is important to use the instantaneous fission rate, because the behaviour of the fission gas will be determined by the fission-rate at that time, and not by an average fission rate. Therefore, the fission gas solubility is not fixed but is fission rate dependent. If the instantaneous fission rate is above the threshold value, then the fission gas will be retained in solution and no bubbles will appear. If the instantaneous fission rate is at or below the threshold then bubbles will appear.

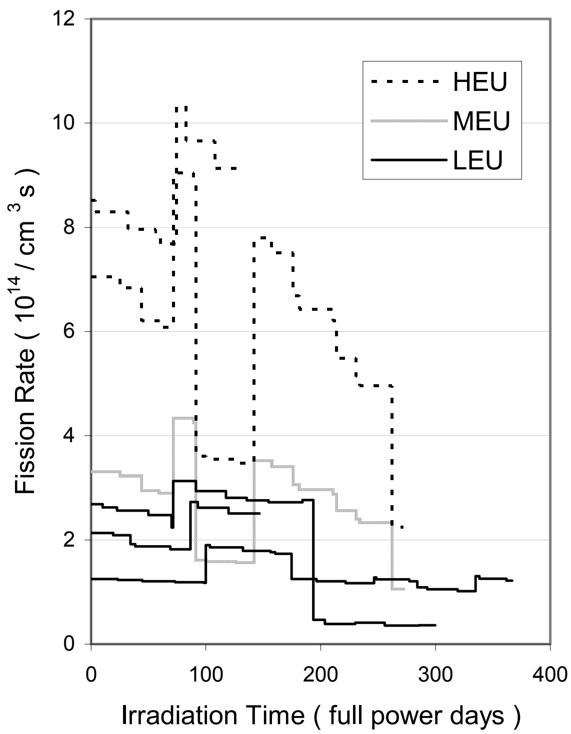


Figure 6. Fuel particle fission rate history of U_3Si_2 mini-plates irradiated in the Oak Ridge Research Reactor.

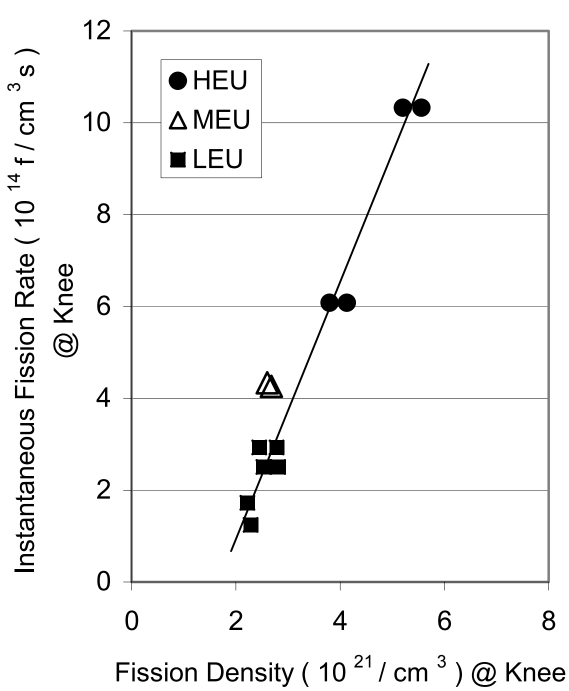


Figure 7. Illustration of the fission rate dependence of the knee point. The data points shown represent the two best estimates of the position of the knee point for a selected number of mini-plates.

b) Influence of Uranium/Silicon Ratio on Fission Gas Diffusivity

Although the fission rate effect can explain the appearance of the knee, it is doubtful, that it can explain the increase of fission gas solubility beyond the knee, or the secondary nucleation of fission gas bubbles. Despite the step changes in fission rate, illustrated in Figure 6, the general trend is for the fission rate of each mini-plate to decrease as a function of fission density. Based on the argument presented in Section 4a), the solubility would be expected to decrease as a function of fission density. However, a comparison of the mini-plate at the knee point compared with the mini-plate at the point of secondary nucleation (Figure 8) shows that the amount of fission gas in stored in solution has increased. This observation is not consistent with the fission rate effect detailed in Section 4a), and indicated that another factor was influencing the behaviour of fission gas in solution.

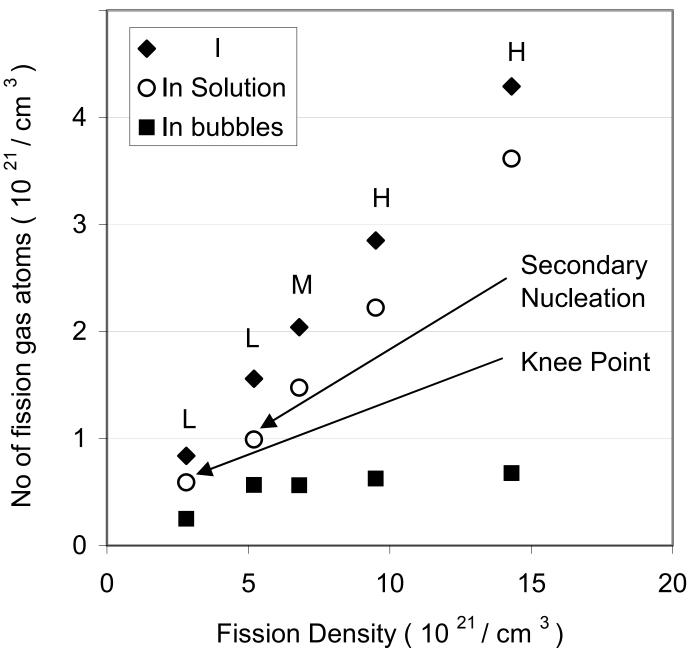


Figure 8. Fission gas atom behaviour as the fission density increases.

As the uranium burns, the uranium content decreases, relative to the amount of silicon present. Figure 9 illustrates how the uranium-to-silicon ratio changes as a function of fission density. The silicon-to-silicon bonds, which are much stronger than the uranium-silicon bonds probably reduce the diffusivity of fission gas atoms in solution. Therefore, migration of fission gas atoms to fission gas bubbles becomes more difficult and as a result, more fission gas is stored in solution. This effectively increases the solubility limit, which continually changes, and is influenced by the uranium-to-silicon ratio and the fission rate. Fission gas is produced, however, at a faster rate than the increasing solubility limit can accommodate, and at some point fission gas bubbles nucleate again.

There are parallels between the changes in fission gas solubility and the growth of the interaction layer between the fuel particle surface and the aluminium matrix. Hofman et al. [6] were able to derive a correlation for the growth of the interaction layer for LEU fuels but were unable to apply it to the MEU and HEU U_3Si_2 fuels or to USi fuels. The rate of growth of the interaction layer in those fuels was too low to fit the correlation. It is now considered that the change in silicon-to-uranium ratio reduced the diffusivity of aluminium in much the same way that it is believed to affect the diffusivity of fission gas atoms in solution.

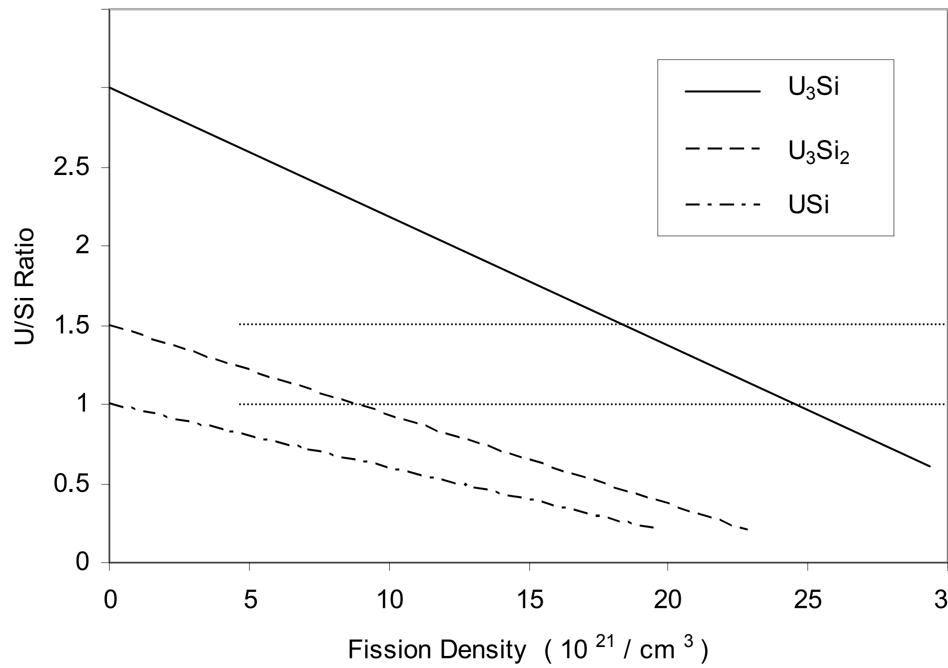


Figure 9. Change in the uranium-to-silicon ratio vs. fission density as 93% enriched U_3Si, U_3Si_2 and USi are burned.

c) Fuel Particle Swelling

Based on the information provided in Section 4a) and b) above, a new fuel particle-swelling graph has been produced (Figure 10). The position of each knee is based on the correlation shown in Figure 7. The swelling curve of each fuel has been illustrated as non-linear. This is particularly evident for the high burn-up HEU mini-plate. As the uranium-to-silicon ratio decreases and the proportion of gas in the fission gas bubbles continues to decrease, the swelling rate is also expected to decrease. In the absence of data points at intermediate fission densities, the shape of the curves are a best estimate, based on the arguments presented in Section 4a) and b). A comparison of the swelling data plotted in Figure 10 with the original data, as reported by Hofman et al. [2] will reveal some differences. The current analysis of swelling has included an assessment of the effect of the growth of the interaction layer.

The fission rate effect and the changing uranium-to-silicon ratio both influence bubble behaviour and ultimately fuel particle swelling. It is difficult to separate the two effects and identify their individual influence. The fission rate effect is likely to dominate at the lower fission densities when the change in the uranium-to-silicon ratio is small. However at the higher fission densities, that is, in MEU and HEU fuels, the change in the uranium-to-silicon ratio is significant and expected to exert a strong influence. This is reflected in the decrease in the rate of swelling shown for the HEU fuel mini-plates.

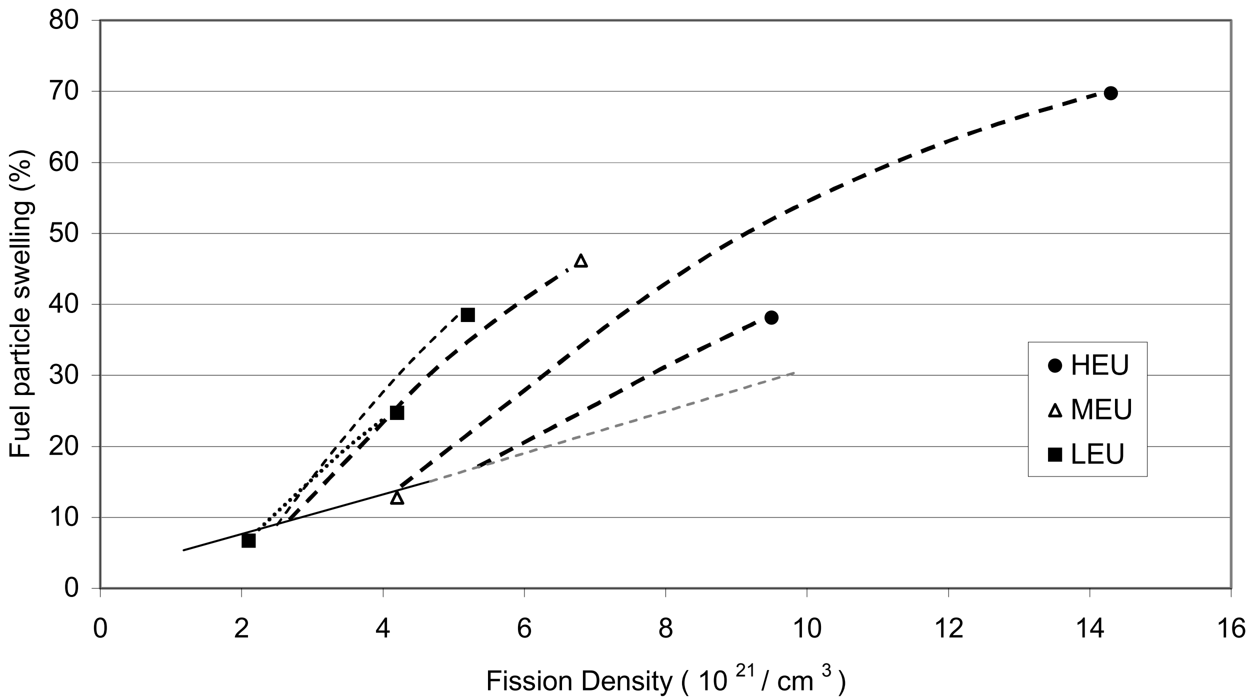


Figure 10. Swelling behaviour of U_3Si_2 fuel particles.

5. Conclusions

A review of data from the U_3Si_2 qualification program has been completed and has provided a new understanding of the swelling behaviour of amorphous U_3Si_2 fuel particles. The following conclusions have been drawn.

- U_3Si_2 becomes amorphous under irradiation; however, the fission gas and swelling behaviour remains stable and benign.
- The bi-modal distribution of bubbles is not generated at the knee, it emerges at very high fission density.
- Coalescence of fission gas bubbles occurs at a very slow rate, and is not evident from bubble morphology.
- Most of the fission gas generated is retained in solution, with less than 30% of the fission gas atoms generated present in visible bubbles.
- The position of the knee is determined by the individual fission rate history of each fuel plate.
- The decrease in the uranium-to-silicon ratio with burn-up results in a larger fraction of silicon-to-silicon bonds and facilitates the increased solubility of fission gas.
- The influence of the fission rate and the U/Si ratio is likely to promote a non-linear swelling rate.

6. References

1. DeHoff, R., & Rhines, F., *Quantitative Microscopy,* McGraw Hill, 1968, pg 167.
2. Hofman, G.L., Rest, J., Birtcher, R.C., & Snelgrove, J.L., *Correlation of Irradiation Induced Microstructural Changes and Fission Gas Swelling in Uranium Compounds*, Proceedings of the International Meeting on Reduced Enrichment for Research and Test Reactors, Newport, Rhode Island, September 23-27, 1990.
3. Birtcher, R.C., Wang, L.M., Allen, C.W., & Ewing, R.C., *Disordering and Amorphization of* U_3Si *and* U_3Si_2, Proceedings of XIIth International Congress Electron Microscopy, 1990, pg 534.
4. Birtcher, R.C., Richardson, J. W., & Mueller, M. H., *Amorphization of* U_3Si_2 *by Ion or Neutron Irradiation*, Journal of Nuclear Materials, 244, 1997, pg 251-257.
5. Rest, J., & Hofman, G.L., *Dynamics of irradiation-induced grain subdivision and swelling in* U_3Si_2 *and* UO_2 *fuels*, Journal of Nuclear Materials, 210, 1994, pg 187-202.
6. Hofman, G.L., Rest, J., Snelgrove, J.L., Wiencek, T. & Koster van Groos, S., *Aluminum-*U_3Si_2 *Interdiffusion and its Implications for the Performance of Highly Loaded Fuel Operating at Higher Temperatures and Fission Rates*, Proceedings of the International Meeting on Reduced Enrichment for Research and Test Reactors, Seoul, Korea, October 7-10, 1996.