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TEM CHARACTERIZATION OF IRRADIATED U_3SI_2/AL DISPERSION FUEL

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ABSTRACT

The silicide dispersion fuel of U_3Si_2/Al has been recognized as a reasonably good performance fuel for nuclear research and test reactors except that it requires the use of high enrichment uranium. An irradiated U_3Si_2/Al dispersion fuel (~75% enrichment) from the high flux side of a RERTR-8 (U0R040) plate was characterized using transmission electron microscopy (TEM). The fuel plate was irradiated in the advanced test reactor (ATR) for 105 days. The average irradiation temperature and fission density of the fuel particles for the TEM sample are estimated to be approximately ~110°C and 5.4×10^{21} f/cm^3. The characterization was performed using a 200KV TEM with a LaB_6 filament. Detailed microstructural information along with composition analysis is obtained. The results and their implication on the performance of this silicide fuel are discussed.

1. INTRODUCTION

The silicide dispersion fuel of U_3Si_2/Al is currently recognized as the best fuel using high-enrichment uranium for research and test reactors. It has been tested using ion or neutron irradiation techniques and the material was shown to go amorphous at relatively low exposures [1,2]. The parameters that have been identified for influencing whether or not a phase will be amorphous are composition, fission density, fission rate, and temperature. The detailed microstructure characterization using TEM for U_3Si_2/Al was not performed in the past. Although U_3Si_2/Al silicide fuel has not been considered for RERTR low-enrichment fuel as a result of its unsatisfactory low fuel loading, a full detailed TEM characterization of the irradiated high-enrichment U_3Si_2/Al fuel will be very useful to understand the effects of different microstructure features on the fuel performance.

Due to the difficulty in fabricating spherical fuel particles of U_3Si_2 in the past, the irregular shape fuel flakes were typically used for the silicde dispersion fuel. This adds the complexity to characterization and modeling of the fuel meat as a function of irradiation. Kim et al reported the recent work using optical microscopy for the same silicide fuel plate (U0R040) on temperature and dose dependence of fission-gas-bubble swelling in U_3Si_2 [3]. The results showed a strong temperature effect on the fission gas morphology at high fission density. At low flux condition, the fission density, estimated temperature and bubble size are 3.2×10^{21} f/cm^3, 105 °C and 2 μm, respectively. The corresponding numbers at high flux condition are 6.1×10^{21} f/cm^3, 160 °C and 38 μm, respectively. The author estimated the fuel temperature from the interaction layer thickness based on a correlation for U_3Si_2/Al developed at Argonne National laboratory. Leenaers et al conducted comprehensive investigation on a U_3Si_2/Al dispersion fuel plate subjected to a cladding surface temperature of ~190 °C and fuel temperature of ~230 °C with a maximum fission density of ~1.3×10^{21} f/cm^3 [4]. They performed characterization using optical microscopy (OM), scanning electron microscopy (SEM) and electron-probe micro-analysis (EPMA). Their measurement suggests that the composition of the fuel-matrix-interaction (FMI) layer is close to $U_3Al_7Si_2$. The X-ray elementary map shows that fission product remains homogeneously distributed in the fuel grains except for Xe that starts to form sub-micron bubbles in the fuel grains. The fission products ejected out of the fuel particle is found to accumulate at the interface between FMI and Al matrix.

This work will report the microstructure characterization using TEM for U_3Si_2/Al fuel irradiated to high fission density. It enables the investigation of detailed microstructural features and composition down to nanometer resolution, therefore a complete set of microstructure information can be obtained for the irradiated U_3Si_2/Al fuel combining with the work described above.

2. EXPERIMENTS

The RERTR-8 dispersion fuel plate (U_3Si_2/Al, ~75% enrichment), labeled U0R040, was irradiated in the Advanced Test Reactor (ATR) at Idaho National Laboratory (INL). A small cylindrical punching of 1.0 mm diameter and roughly 1.4 mm in length was produced from the high flux side of the fuel plate at the Hot Fuel Examination Facility (HFEF) at INL. The estimated local fission density and irradiation time are 5.4×10^{27} f m^{-3} and 105 days, respectively. The fuel plate centerline temperature is calculated to be approximately 120 - 107°C using the PLATE fuel performance code [5]. The average fuel meat heat flux is ~294 W/cm^2 (beginning of life) and ~200 W/cm^2 (end of life). A standard TEM sample was prepared by mounting the fuel punching inside a 3.0 mm diameter molybdenum ring using epoxy in a glovebox at the Electron Microscopy Laboratory (EML), followed by mechanical wet-polishing down to ~100 μm, electrical jet-polishing for 40 seconds for each side, and precision ion polishing for several hours at low incident beam angles to perforation. Microstructural characterization was conducted using a 200 KV JEOL-2010 TEM with a LaB_6 filament.

3. RESULTS

An overview of low magnification bright field TEM image of irradiated U_3Si_2 fuel particle is shown in Figure 1. Unlike the irregular shape bubbles for the U-7Mo fuel particles, bubbles in silicide fuel particle are circular. The size of these bubbles is approximately in the range of 10 – 1000 nm. Note that, in contrast to optical microscopy, bubbles greater than 1 μm are difficult to be captured in a TEM image. The size distribution of bubbles shown in the figure is based on 325 bubble counts. The average size and volume of these bubbles are estimated to be ~94 nm and 1.1×10^6 nm^3, respectively, with a bubble number density approximately ~1.05×10^{20} m^{-3}. The corresponding bubble volume fraction in the fuel particle is estimated to be approximately ~11%.

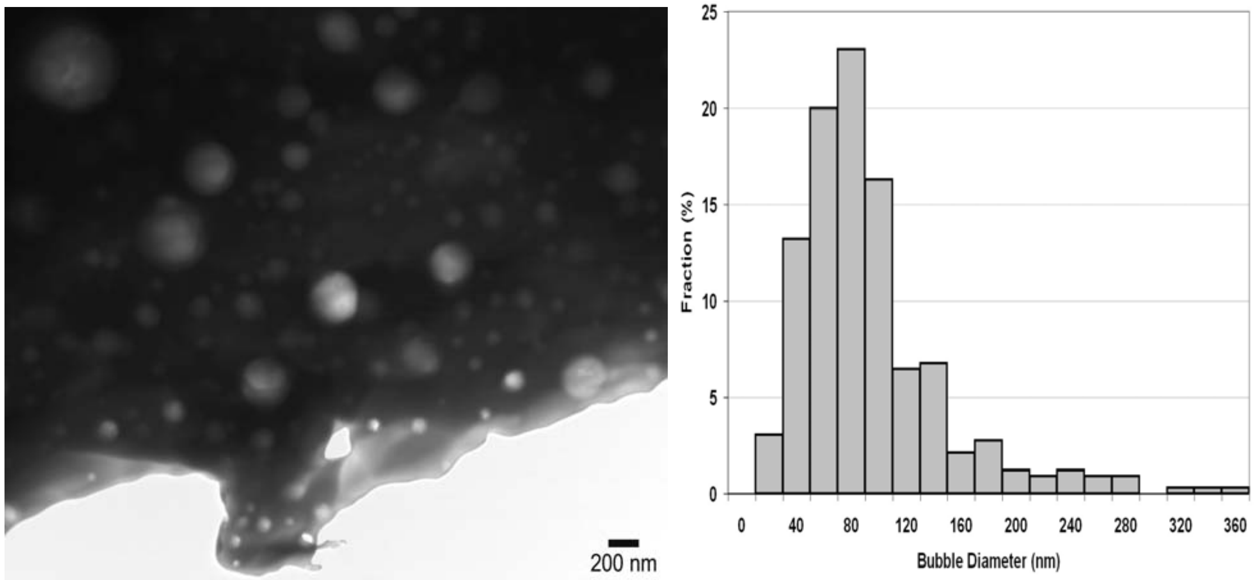


Fig 1. Bubbles and their size distribution in the irradiated U_3Si_2 fuel particle.

Figure 2 shows the fuel matrix interaction (FMI) layer on the left and the aluminum matrix on the right. The composition data of energy dispersive spectroscopy (EDS) measurements for the marked spots are listed in Table 1. At this relatively low magnification, The FMI area on the left of the image (spot A-D) appears clean. High concentration bubbles are observed in a narrow region (typically < 1 μm) of FMI next to the interface of FMI and Al matrix. It was noticed that this narrow region of FMI has a lower U (< 5%) and Si (< 9%) content comparing to a typical composition (U > 10% and Si > 10 %) for FMI layer. The Si content measured in the Al matrix (spot I–K) is likely the result of transmutation of Al into Si by $^{27}Al(n,\gamma)^{28}Al \rightarrow {}^{28}Si + \beta$ reaction. Fission product of Zr, Nd, Y and Ba are detected in the low U and Si zone of FMI layer. A typical value of 2-3 at% Xe is often detected in these bubble areas

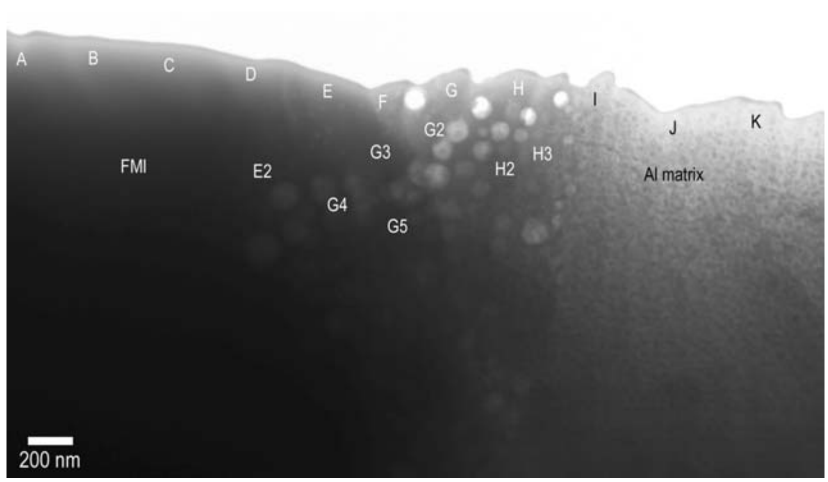


Fig 2. Microstructure of FMI (left) and Al matrix (right). EDS data of the marked spots are shown in Table 1

Table 1. EDS measurement (at.%) at spots marked in Figure 2.

Spot	U	Si	Al	Mo	Note
A	12.7	12.9	74.1	0.3	FMI, lack of bubbles
B	13.1	11.7	73.8	1.3	FMI,
C	12.8	11.7	75.1	0.5	FMI,
D	12.4	11.4	75.7	0.6	FMI,
E	9.6	10.4	79.2	0.8	FMI,
E2	11.1	10.1	78.5	0.4	FMI,
F	10.8	11.4	77.6	0.2	FMI,
G	2.0	7.5	88.1	2.4	Low U & Si FMI, high concentration bubbles,
G2	2.2	8.4	81.4	2.3	Low U & Si FMI, Zr-2.4, Nd-1.8, Y-1.6, Ba-0.7
G3	4.1	8.6	81.1	1.4	Low U & Si FMI, Zr-2.1, Nd-1.4, Y-0.9
G4	4.6	8.6	79.7	1.7	Low U & Si FMI, Zr-2.1, Nd-1.9, Y-1.1, Ba-0.7
G5	2.4	6.9	84.6	1.5	Low U & Si FMI, Zr-2.0, Nd-2.0, Y-0.8
H	1.2	8.4	80.5	2.8	Low U & Si FMI, Zr-3.6, Nd-2.1, Y-1.4
H2	1.0	6.9	82.2	2.7	Low U & Si FMI, Zr-3.0, Nd-2.1, Y-1.6, Ba-0.7
H3	0.4	5.3	88.2	1.8	Low U & Si FMI, Zr-1.8, Nd-1.1, Y-1.2
I	0.5	2.8	96.1	0.7	Al matrix
J	0.4	3.3	95.7	0.5	Al matrix
K	1.1	4.3	94.7	0	Al matrix

A more complete interface microstructure of Al matrix, FMI and fuel particle is shown in Figure 3. The thickness of FMI layer in this case is approximately ~5 μm. This time a narrow region of FMI with high concentration bubbles is located next to the interface of FMI and fuel instead of the interface of FMI and Al matrix. Unlike the narrow bubble zone in Figure 2, the EDS measurement listed in Table 2 indicates no noticeable difference in composition between this narrow region and the rest of the FMI. Again, large part of FMI appear clean with no bubbles at this magnification. Note that the EDS measurements of FMI listed in both Table 1 and Table 2 do not match the compositions for $U(Si, Al)_3$ type phase.

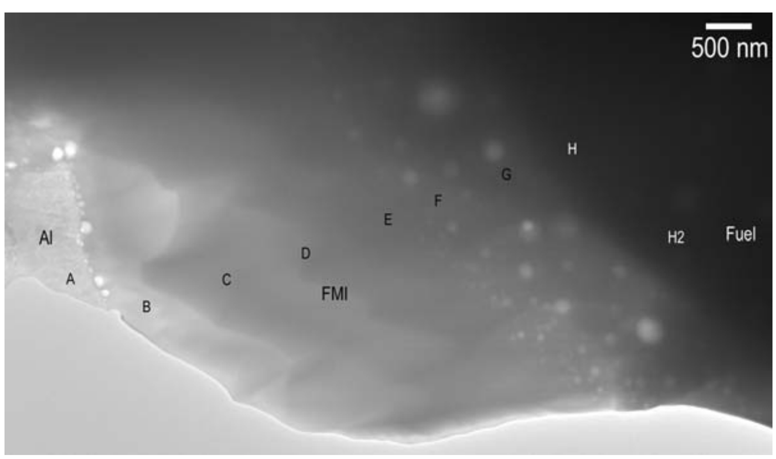


Fig 3. Microstructure of Al matrix (left), FMI (middle) and Fuel particle (right) in irradiated U_3Si_2/Al Fuel. Composition measurements of the marked spot are listed in Table 2.

Table 2. EDS measurement (at.%) of areas marked in Figure 3

Spot	U	Si	Al	Mo	(Si+Al)/U	Note
A	0	0.9	98.3	0.9	n/a	Al matrix
B	9.1	10.8	77.5	2.5	9.7	FMI, lack of bubbles
C	14.0	14.0	71.0	0.9	6.1	FMI, lack of bubbles
D	15.6	14.5	69.5	0.5	5.4	FMI, lack of bubbles
E	16.6	14.7	68.2	0.6	5.0	FMI, lack of bubbles
F	17.4	14.5	67.3	0.8	4.7	FMI, high concentration bubbles
G	20.0	16.5	62.7	0.7	4.0	FMI, high concentration bubbles
H	48.5	34.4	17.4	0	n/a	Fuel
H2	61.1	31.4	4.6	2.9	n/a	Fuel

The selected area diffraction (SAD) patterns for fuel particles indicate that most part of the fuel is amorphous with some scattered nano-crystalline grains, as shown in the Figure 4 (left). The inset shows the overlap of a single diffused ring from amorphous phase with discrete rings from nano-crystalline grains. These nano-grains, shown as white features in the weak beam dark field image using the ring, have a size up to ~10 nm. In most areas of a fuel particle, the single diffused ring always present while the discrete rings are often weak and even become invisible. The pictures on the right of Figure 4 show the high resolution view of a FMI area imaged using over-focus (middle) and under-focus (right) condition. The small white spots such as those highlighted in the boxes are believed to be the small gas bubbles at sizes below ~2 nm. The inset shows a single diffused ring for the amorphous FMI layer. Fission product of 3.7 at% Zr is detected in this FMI area. There are uniformly distributed white features shown in FMI with weak contrast at size around 5-10 nm. The nature of these features is not identified.

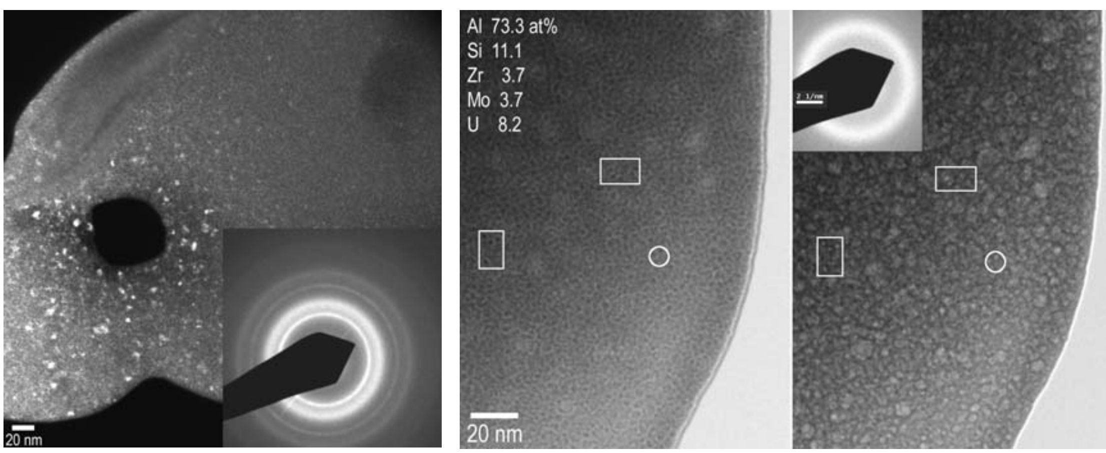
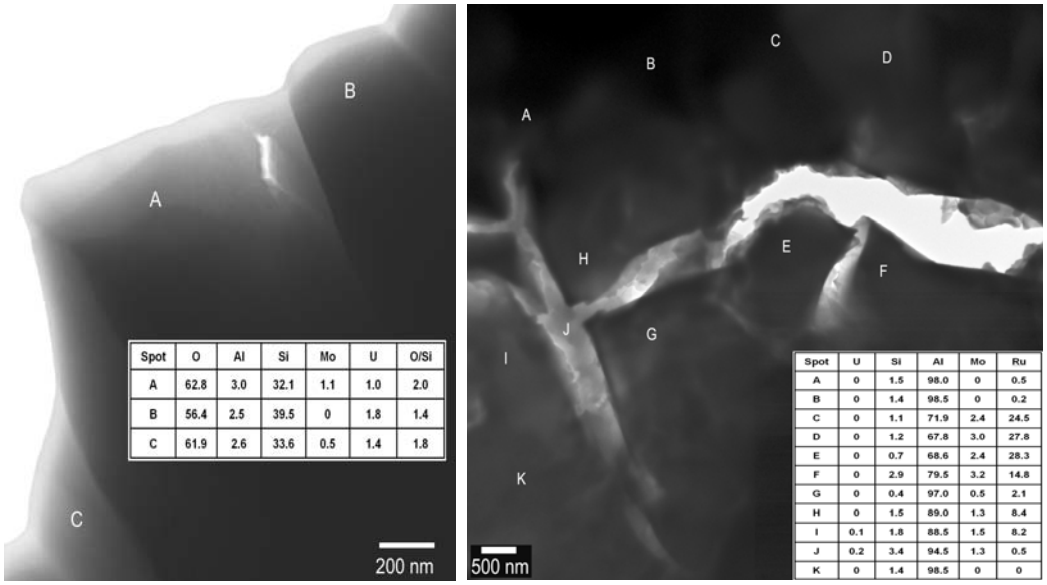


Fig 4. Fuel (left) and FMI (right)

There are areas in the fuel particle where amorphous silicon oxides, with O/Si ratio of 1.0 – 2.0, are present as shown in Figure 5 (left). These oxides were unintentionally introduced from the fuel flake fabrication. No bubbles are observed in these silicon oxides. Cluster of large Ru precipitates with size up to ~1 μm are identified in several areas with composition of 10-34 at% Ru, 59-82 at% Al, ~2 at% Si, ~3 at% Mo. Micro cracks are found in these areas containing large Ru rich precipitates as shown in Figure 5 (right).



Spot	O	Al	Si	Mo	U	O/Si
A	62.8	3.0	32.1	1.1	1.0	2.0
B	56.4	2.5	39.5	0	1.8	1.4
C	61.9	2.6	33.6	0.5	1.4	1.8

Spot	U	Si	Al	Mo	Ru
A	0	1.5	98.0	0	0.5
B	0	1.4	98.5	0	0.2
C	0	1.1	71.9	2.4	24.5
D	0	1.2	67.8	3.0	27.8
E	0	0.7	68.6	2.4	28.3
F	0	2.9	79.5	3.2	14.8
G	0	0.4	97.0	0.5	2.1
H	0	1.5	89.0	1.3	8.4
I	0.1	1.8	88.5	1.5	8.2
J	0.2	3.4	94.5	1.3	0.5
K	0	1.4	98.5	0	0

Fig 5. Silicon oxides in the fuel particle (left) and the large Ru precipitates (right).

4. DISCUSSION

Irradiation and fission of U_3Si_2/Al dispersion fuel in ATR result in the amorphisation and development of fission gas bubbles in the fuel particle and FMI. The TEM results clearly show that bubble density is higher in fuel than in FMI. The broad size distribution of bubbles shown in the Figure 1 suggests that the nucleation of these bubbles persists with fission. Bubble linkage was not observed in the fuel particles. This indicates the low mobility for fission gas atoms. Birtcher et al reported a -2.2% volume contraction for U_3Si_2 upon fully amorphisation. It is believed that this volume contraction results in a reduced free volume, therefore suppressing fission gas mobility. Finlay et al suggested that as U-235 burns, U/Si ratio decreases in U_3Si_2 fuel and the number of Si-to-Si bonds increases which is much stronger than U-to-Si bonds [6]. This may be responsible for the reduced fission gas atom mobility in solution, retention of fission gas atoms in the solution and a delay of bubble nucleation.

Unlike the irregular-shaped bubbles in U-7Mo fuel particle, all the bubbles in U_3Si_2 fuel particles are circular. This is because that U_3Si_2 fuel becomes completely amorphous at very irradiation dose of 1.13×10^{23} fissions/m^3 (T_{irr}= 30 °C) which is corresponding to the first few minutes of irradiation in the ATR [2]. Bubble takes the circular shape to reduce its surface energy in amorphous material. Note that the estimated bubble volume fraction of ~11% in the fuel particle from this work may severely underestimate the fuel particle swelling since bubbles greater than ~1 μm are not captured in TEM analysis. These large bubbles are clearly shown in the optic microscopy images where bubbles smaller than ~ 1 μm are hardly visible due to resolution limit [3].

The accumulation of bubbles and fission product in a narrow zone (~ 1 μm) in FMI near the interface of Al matrix and FMI has been observed in several areas as shown in Figure 2. This is consistent with the

EPMA result for a U_3Si_2/Al fuel plate at a much lower fission density (1.3×10^{21} f/cm^3) and higher temperature (~230 °C) [4]. These bubbles are not expected to affect the fuel performance since bubble sizes remain small below the resolution limit in the optical microscopy images shown by Kim et al [3]. The ratio of (Si+Al)/U for FMI in Table 1 are in the range of 6.5-9.3. This is significant higher than that of $U_3Al_7Si_2$ reported by Leenaers et al. The discrepancy may be related to the difference in fission density which is approximately 4 times high in this work.

One of the most noticeable microstructural characteristics in the irradiated U_3Si_2/Al is inhomogeneous. The TEM image in Figure 3 capturing all the major components from Al matrix to fuel particle shows bubble accumulation in FMI near the interface of FMI and fuel particle, different from that shown in Figure 2. Although bubble size is much smaller, the accumulation of bubbles near the interface of FMI and fuel particle appears consistent with result from optical microscopy observation by Kim except that bubbles are much larger (> 1 μm) and distribute mostly in the fuel side. Again, the ratio of (Si+Al)/U for FMI listed in the Table 2 is greater than 3 for $U(Si, Al)_3$ type phase.

Note that large part of FMI layer shown in TEM image is quite clean with very low counts of visible bubbles. This is consistent with the optical microscopy images for the relevant fission density. It appears that bubbles in FMI layer tend to distribute preferentially near either side of interfaces. The details on the microstructural evolution in FMI may be obtained if TEM characterization of U_3Si_2/Al at different fission density including fresh fuel is performed. From both TEM and optical microscopy results, it appears that fuel swelling is largely driven by bubble development in the fuel particles.

The high resolution weak beam dark field image shown in Figure 4 (left) reveals a mixture of amorphous material with nano-crystalline grains in the fuel particles. The SAD patterns for most areas of the fuel particle show a single diffused amorphous ring with very weak contrast of discrete rings. It indicates very low volume fraction of these nano-grains. These nano-grains may be beneficial by acting as sinks and attracting fission gas atoms and keeping them in the solution. The presence of small gas bubbles shown in high magnification images of FMI layer suggests that bubble nucleation persists at high fission density. The role of light contrast specks in the FMI layer on fuel performance is not clear. The (Si+Al)/U ratio for this area is ~ 10. Analogy to the speck features in Al matrix, these specks in FMI layers may be related to Si rich precipitates in FMI.

There is a noticeable amount of amorphous Si-O compounds found in the fuel particles with O/Si ratio from 1.4 to 2.0. TEM micrographs of these compounds reveal no bubbles in the microstructure. It indicates that material turning to amorphous is not necessarily problematic in terms of bubble swelling. The silicon oxide compounds are believed to be introduced from the fabrication of U_3Si_2 fuel flakes. In addition to fission product detected in low concentrations of typically < 3 at% in various locations in fuel particle and FMI layer, large Ru rich precipitates (~ 1 μm) are found in several locations with its atomic concentration up to 34%. Note that each ^{235}U atom fissioning produces 200 at% of fission product. The fission yield of Ru for U-235 in a thermal spectrum reactor is relatively high (~16 at.% of fission product per ^{235}U fission). This fission product tends to form metallic inclusion near the light contrast strips in the fuel [7]. Theses strip features consisting mostly pure aluminum were also found in SEM images of the fresh silicide fuel, likely introduced from fuel fabrication.

One of the objectives in this TEM work is to compare the microstructure of FMI between U-7Mo dispersion fuel and U_3Si_2 dispersion fuel to understand their effect on fuel performance. The estimated nearest-neighbor-distance (NND) for FMI in high flux U_3Si_2/Al TEM sample in this work is approximately 0.243 ± 0.001 nm at a fission density of 5.4×10^{21} fission/cm^3. The corresponding numbers are 0.251 nm for a U-7Mo/Al-2Si TEM sample (RERTR-6 high flux) at 4.5×10^{21} fission/cm^3 [8] and 0.239 nm for a U-7Mo/Al TEM sample at 1.4×10^{21} fission/cm^3 [9]. These numbers are very close to each other. A smaller NND number at a higher fission density for U_3Si_2/Al fuel may be responsible for less bubble observed in the FMI layer comparing to that of U-7Mo/Al-2Si. Although U_3Si_2/Al and U-7Mo/Al-2Si have different fuel and matrix composition with different microstructural development in the fuel particles, the composition and the estimated NND for FMI are very similar. The deviation of (Si+Al)/U ratio from ~3 in the amorphous FMI at high fission density do not appear to be a problem for these dispersion fuels.

5. CONCLUSION

The microstructure of irradiated U_3Si_2/Al dispersion fuel consists of uniformly distributed fission gas bubbles. It is a mixture of amorphous phase with nano-crystalline grains in the fuel. For bubbles smaller than 1 μm, the average bubble diameter, volume and number density are ~94 nm, 1.1×10^6 nm^3 and 1.05×10^{20} m^{-3}, respectively. The estimated volume fraction of these bubbles in the fuel is ~11%. A narrow region (~1 μm) of high concentration bubbles is found in FMI near either interface of fuel/FMI or interface of FMI/Al matrix with the latter depleted in U and Si. No bubble linkage can be identified in fuel particle or FMI layer. Most part of the FMI remains clear with less bubble than that in U-7Mo/Al-2Si. With a 20% higher fission density, the estimated NND for FMI in U_3Si_2/Al is 3% smaller than that of U-7Mo/Al-2Si, indicating a more effective retention of fission gas atoms in the solution.

Acknowledgements

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