SUMMARY OF PIE ON AGR-1 COMPACT 3-2-2

Post-irradiation examination (PIE) is in progress on coated particle fuel compacts from the first Advanced Gas Reactor irradiation experiment (AGR-1). PIE has been completed on six compacts at the Oak Ridge National Laboratory (ORNL). Three compacts (Compacts 6-1-1, 4-4-2, and 5-2-3) were examined in the as-irradiated condition and three compacts (Compacts 6-4-3, 3-3-2, and 3-2-2) were subjected to safety testing at 1600°C, followed by post-safety test examination similar to the PIE performed on the as-irradiated compacts. All compacts were subjected to a standard set of analyses that included the following: (1) detection of exposed fission products by Deconsolidation-Leach-Burn-Leach (DLBL), (2) measurement of gamma-emitting fission product inventory using the Irradiated Microsphere Gamma Analyzer (IMGA), and (3) microstructural examination by x-ray tomography and materialography. The equipment and methods used are reported in detail in ORNL/TM-2012/233, *AGR-1 Irradiated Compact 6-1-1 PIE Report*. PIE on the first five compacts was summarized in ORNL/LTR-2012/397, *PIE on Five Irradiated AGR-1 Compacts*. Provided below is a brief summary of the completed PIE on Compact 3-2-2. Preliminary trends are discussed in this report, but final conclusions will require the support of additional data and further analysis. A separate report is being generated for each AGR-1 compact after PIE is complete that describes in detail the examinations performed and fully documents the data obtained. A final AGR-1 PIE summary report will compile all available data and provide a more comprehensive analysis of the AGR-1 fuel performance.

Compact 3-2-2 (AGR-1 Baseline fuel) was subjected to safety testing at 1600°C in flowing helium for 300 hours in the ORNL Core Conduction Cooldown Test Facility (CCCTF) to evaluate the effect of elevated temperature on the fuel microstructure and fission product retention. During the test period, condensable fission products (metals) were collected by the CCCTF in-furnace cold finger and gaseous fission products were collected from the helium sweep gas as it passed through liquid nitrogen-cooled cold traps. Deposition cups attached to the in-furnace cold finger were periodically removed and analyzed by gamma spectrometry and the sweep gas traps were constantly monitored for gamma activity throughout each run.

The safety test on Compact 3-2-2 began on November 2, 2011, and was interrupted by a power supply failure that occurred just as the compact reached 1600°C. This resulted in the furnace temperature being cycled back down to room temperature before the furnace was restarted. As observed in the previous Compact 3-3-2 safety test (ORNL/LTR-2012/397), additional silver appeared to be released by the unplanned thermal cycling. The final heating profile and overall time-dependent results of the safety test on Compact 3-2-2 are shown in Figure 1. The plotted fractional release values are the cumulative amount of each fission product collected on the deposition cups, adjusted for radioactive decay and average deposition cup collection efficiency, and divided by the predicted compact inventory for each fission product at the end of the irradiation. The average deposition cup collection efficiency was determined for each fission product using the combined analysis of all the deposition cups from the Compact 3-3-2 and 3-2-2 tests, both graphite holders, and the single Ta can used for the two sequential tests.

Table 1 lists the total releases for each detected fission product. Overall, Compact 3-2-2 continued to retain fission products generated during the three-year irradiation test, as designed. No significant gaseous ^{85}Kr release was detected by the sweep gas analysis system. Krypton release would be indicative of failure of all three outer layers of the tristructural isotropic (TRISO) coating, and is the primary indicator for catastrophic particle failure during the heating test. However, some fission products were released from the compact during the safety test. The main fission products detected on the deposition cups were silver and europium, with smaller amounts of strontium. Only trace amounts of cesium were released, indicating that the SiC layers remained intact.

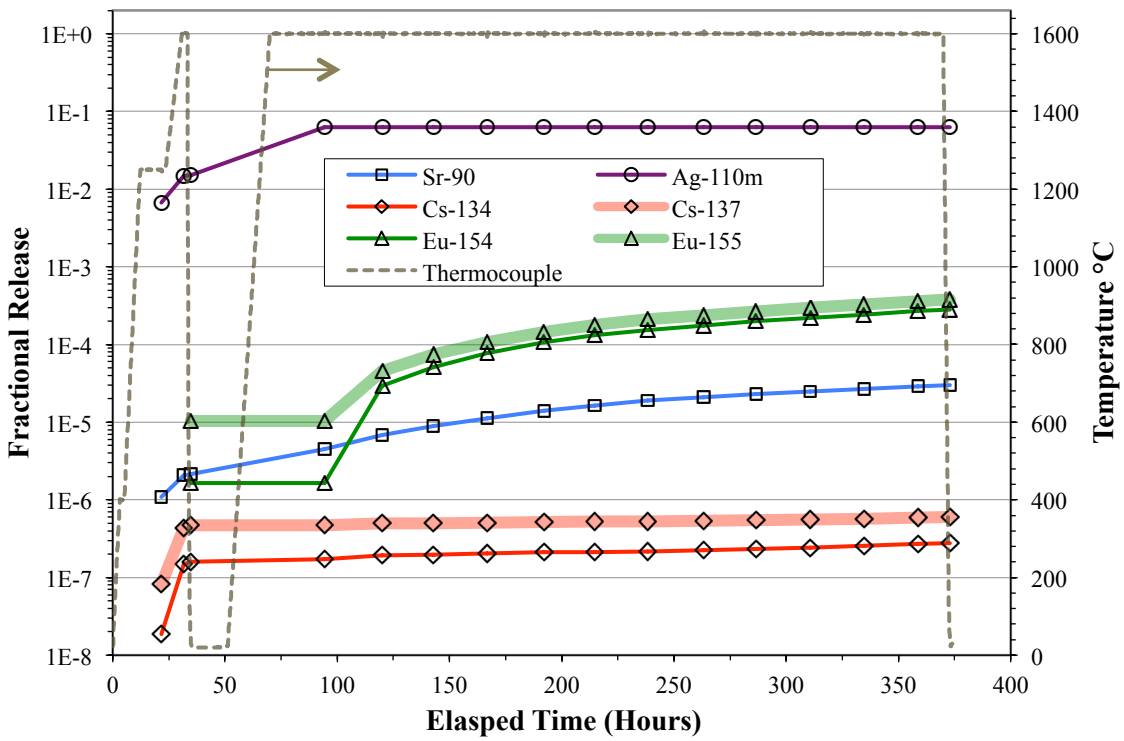

Figure 1. Release of fission products from Compact 3-2-2 during safety testing to 1600°C.

Table 1. Cumulative fission product release from Compact 3-2-2 safety test

Isotope	Fraction of Calculated Compact Inventory Released	Equivalent Particle Inventory
^{85}Kr	< 1E-06	< 4E-03
^{90}Sr	3.00×10^{-5}	0.12
^{110m}Ag	6.33×10^{-2}	262
^{134}Cs	2.79×10^{-7}	1.2E-3
^{137}Cs	6.05×10^{-7}	2.5E-3
^{154}Eu	2.80×10^{-4}	1.2
^{155}Eu	3.78×10^{-4}	1.6

Note: One particle is equivalent to a compact inventory fraction of 2.4×10^{-4}.

The observed ^{110m}Ag release was of the same order of magnitude as that observed in the DLBL analysis of other as-irradiated AGR-1 compacts, and post-safety test DLBL of Compact 3-2-2 (Table 2) showed that a significantly smaller quantity of silver remained in the compact outside the SiC than was released from the compact during the safety test. This suggests that the silver release observed at the beginning of the safety test came from silver outside the SiC, presumably released through intact SiC during irradiation. Palladium outside the SiC may have also left the compact when it was heated to 1600°C. This is suggested by the fact that palladium was typically observed in the DLBL analysis of as-irradiated compacts at levels two orders of magnitude higher than that detected by DLBL in Compact 3-2-2 after the safety test. Similar results were observed in other compacts tested at 1600°C. Analysis for palladium release in the CCCTF was not originally planned and has not yet been performed. This additional analysis is now being considered to verify that palladium is being released from outside the SiC during safety testing.

Table 2. DLBL analysis results for Compact 3-2-2.

Fission Product	Compact 3-2-2		
	Pre-burn	Post burn	Total
^{90}Sr	7.4E-5 (0.31)	9.5E-4 (3.9)	1.0E-3 (4.2)
^{105}Pd	n.d.	1.3E-4 (0.53)	1.3E-4 (0.53)
^{110m}Ag	9.2E-5 (0.38)	n.d.	9.2E-5 (0.38)
^{134}Cs	n.d.	3.3E-4 (1.4)	3.3E-4 (1.4)
^{137}Cs	4.6E-7 (0.002)	4.3E-4 (1.8)	4.3E-4 (1.8)
^{144}Ce	1.2E-5 (0.05)	1.0E-3 (4.2)	1.0E-3 (4.3)
^{152}Sm	1.8E-4 (0.73)	2.7E-3 (11.3)	2.9E-3 (12.0)
^{154}Eu	3.6E-4 (1.5)	1.6E-3 (6.8)	2.0E-3 (8.3)
^{155}Eu	4.5E-4 (1.9)	1.6E-3 (6.8)	2.1E-3 (8.7)
^{235}U	5.8E-7 (0.002)	1.1E-3 (4.4)	1.1E-3 (4.4)
^{239}Pu	7.9E-6 (0.03)	8.7E-4 (3.6)	8.7E-4 (3.6)

Release values are reported as the fraction of compact inventory and the equivalent number of exposed kernels (in parentheses). "n.d." indicates a value was not determined because the measure values were below the detection threshold.

Comparison of Table 1 and Table 2 shows that more europium and strontium remained in the compact than were released by the 1600°C safety test. It cannot be determined if any additional europium or strontium were released from the particles, but it is possible that they may just be migrating out of the compact matrix during the safety test, similar to what has been suggested for silver. The total amount of europium detected outside the SiC in Compact 3-2-2 (sum of DLBL and CCCTF results) is of the same order of magnitude as that detected by DLBL in as-irradiated compacts. Additional heating tests on individual particles would be useful for determining if these elements are retained by the particles under safety test conditions.

Compact 3-2-2 was the first compact examined at ORNL where particles were not separated from the matrix residue after the deconsolidation leach for IMGA survey prior to removal of exposed carbon by the burn-leach process. For this compact, DLBL was carried through to completion, followed by IMGA examination of a small random subset of 56 particles. Given the low release values for krypton and cesium during the safety test, and the similarly low values for cesium, cerium, and uranium in the pre-burn leach, it was determined that gamma spectrometry on every particle using IMGA was not necessary. A full IMGA survey is typically used to detect particles with a below average cesium to cerium ratio (indicating defective SiC) or with a below average cerium content (indicating that the particle either had a lower fissile mass prior to irradiation or that material was lost from the kernel).

After completion of electrolytic deconsolidation and two leaches in the Soxhlet extractor, particles were transferred from the Soxhlet thimble to the acid flask and a pot boil was performed, which is typically done to finish cleaning matrix off of the OPyC prior to sieving particles for transfer to IMGA. Because the full IMGA survey was not required, the pot boil acid was distilled off to dry the matrix residue and particles prior to the burn step. Post-burn leach analysis (Table 2) shows that this distillation process

apparently resulted in coating damage. Uranium, plutonium, cerium, and strontium were all detected after the burn at levels equivalent to approximately four exposed kernels. These kernels were not exposed prior to the burn. The cesium and krypton releases in the CCCTF indicate that there were no particles with defective SiC or exposed kernels during the test, and the pre-burn leaches did not show significant quantities of these elements. Normally, distillation is done only on the acid and matrix residue, where particle damage is not an issue. For future compacts, particles will be kept in the Soxhlet thimble until a determination is made as to whether particles will be separated out for IMGA examination or whether the DLBL will be completed without interruption. This will allow use of the standard procedure for uninterrupted DLBL, which is to burn the particles and matrix residue in the Soxhlet thimble so that no acid distillation or decanting is required.

Table 2 shows that europium and samarium were detected at levels equivalent to more than the inventory expected from four particles. It is not unusual for europium and samarium to be observed at these levels and the post burn leach values are typically higher than the pre-burn leach values, as observed here. In contrast, some of the isotopes analyzed in the post-burn leach were below the equivalent inventory for four kernels. The low post-burn leach result for cesium can be explained by the fact that it is volatile at the 750°C burn temperature. The low values for palladium and silver are more puzzling. Some possible hypotheses include the following:

1) Palladium and silver may have been preferentially lost from these four particles during the safety test due to enhanced transport through partially defective SiC, which later failed during acid distillation or during the 750°C burn.

2) Palladium and silver may have been lost during the 750°C burn, or they may not have been fully leached by the acid. Loss during the burn is unlikely given that both these metals should be stable at this temperature. Burn-leach of crushed particles for burnup analysis at INL has indicated that palladium recovery by this method may be less than 25%, but silver should have be leached with sufficient efficiency to be detected.

3) Palladium inventory in all the particles may be much lower than calculated. This is not a viable explanation for silver given IMGA results discussed below, where all analyzed particles retained appreciable silver.

Further analysis is required to understand the low palladium and silver values that were observed in the DLBL analysis. Additional particle crushing followed by leach-burn-leach could address hypotheses 2 and 3. Investigation into the possible presence of pre-existing SiC defects would require that the defective particle be recovered from the post-DLBL sample. Initial inspection has revealed some SiC fragments in that sample, and analysis of these fragments is being considered.

After completion of DLBL, a random sample of 56 particles was examined by IMGA. Particles were loaded into individual vials and gamma scanned using a 6-hour scan time. Figure 2 through Figure 4 show the results of the IMGA examination. The narrow ^{144}Ce distribution shown in Figure 2 indicates cerium was well retained in the particles. Europium results shown in Figure 3 are similar, except that the ratio of the measured versus the calculated inventory is shifted down to around 0.85; this is common for all AGR-1 compacts and is apparently due to an over-prediction in the calculated europium inventory. In contrast, silver content in the particles was more broadly distributed, with a small population that had lost measurably more silver (Figure 4); these results are similar to as-irradiated compacts, and it cannot be concluded that the silver distribution is a result of the safety test. The main peak in the silver distribution was centered around a measured versus calculated inventory ratio of 1.0, indicating that the majority of the particles may be retaining most of their silver. Those that had noticeably lower silver inventories still retained about half their calculated inventory.

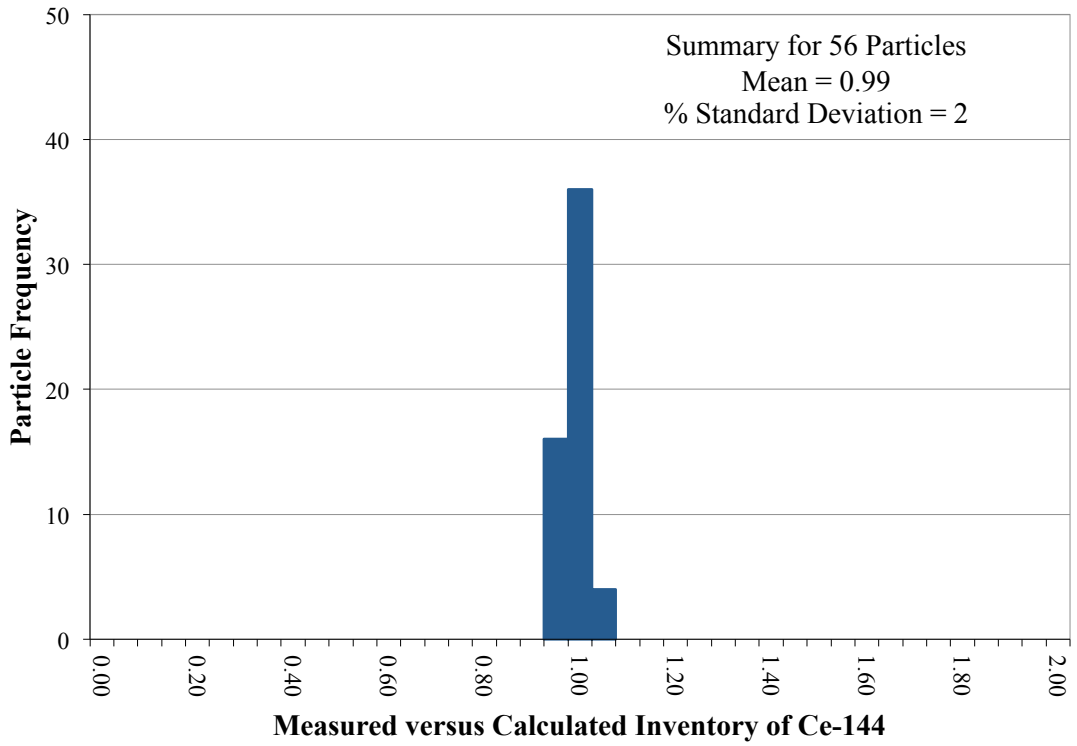

Figure 2. Ratio of ^{144}Ce retained in 56 particles from Compact 3-2-2 versus the calculated inventory, adjusted for variation in fissile material and burnup using the ^{137}Cs activity.

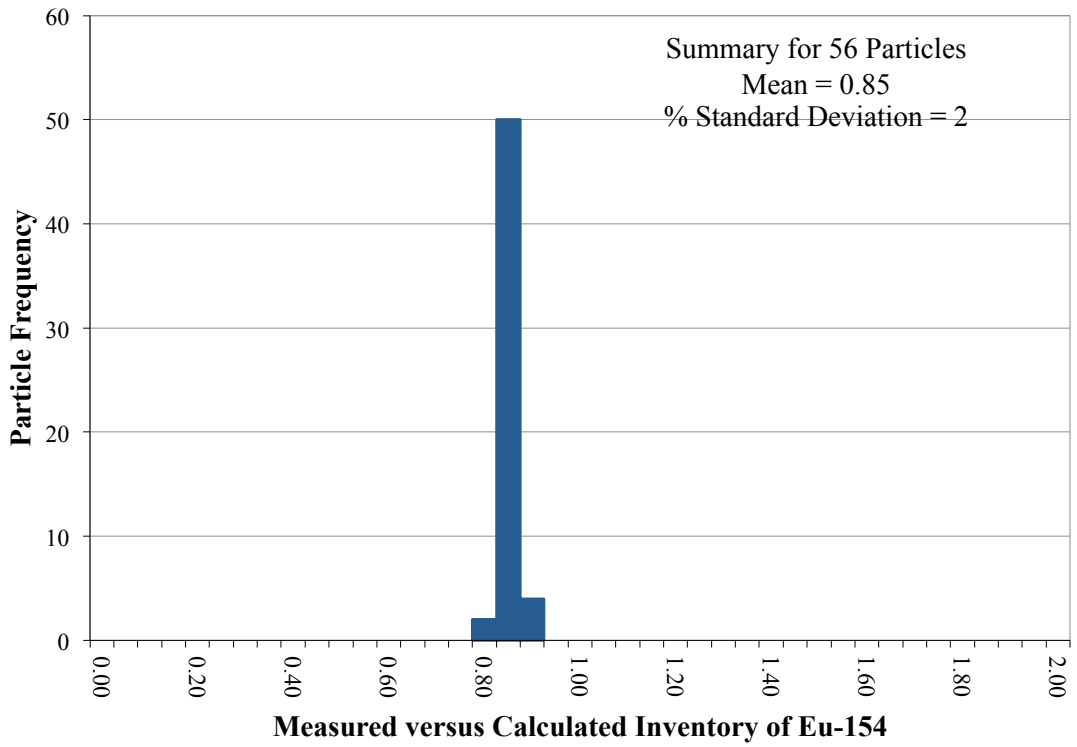

Figure 3. Ratio of ^{154}Eu retained in 56 particles from Compact 3-2-2 versus the calculated inventory, adjusted for variation in fissile material and burnup using the ^{137}Cs activity.

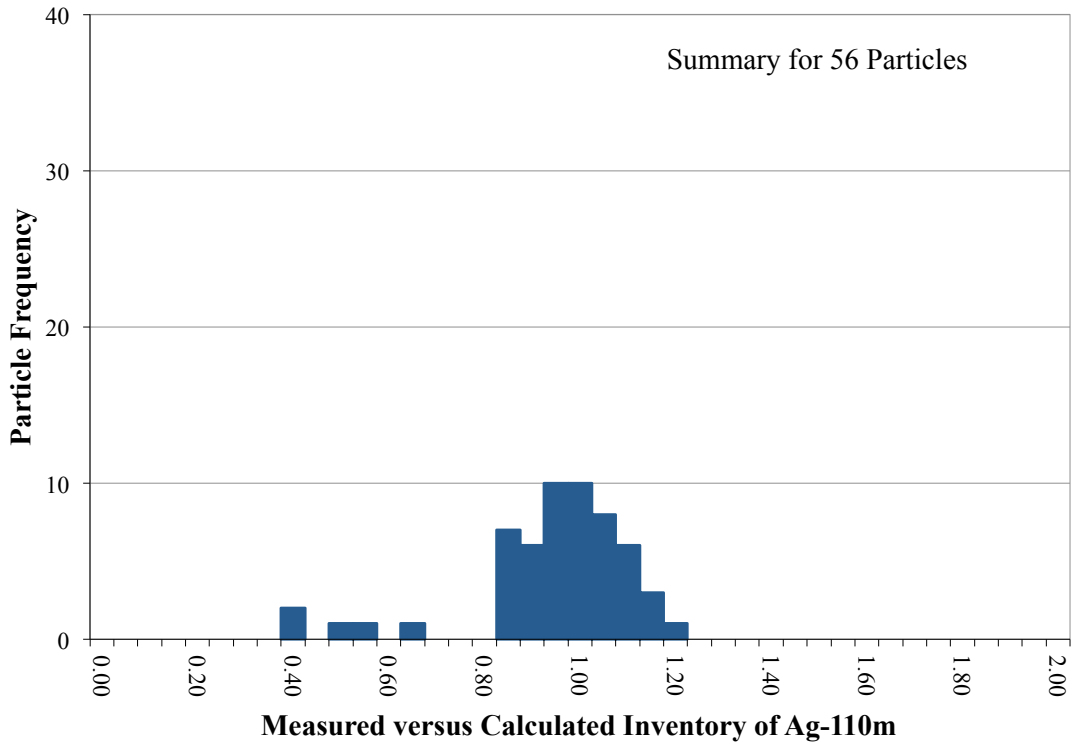

Figure 4. Ratio of ^{110m}Ag retained in 56 particles from Compact 3-2-2 versus the calculated inventory, adjusted for variation in fissile material and burnup using the ^{137}Cs activity.

The four particles with the lowest ^{110m}Ag content (Figure 4) were analyzed by x-ray tomography or materialography (two particles each) and compared to five other particles with average silver retention. There was no apparent correlation between the silver retention and the particle microstructure that could be observed by x-ray or optical microscopy. Figure 5 shows examples of two x-ray tomographs from particles with different silver retention. Both show typical buffer shrinkage and buffer/IPyC separation, with one region where the layers are still attached.

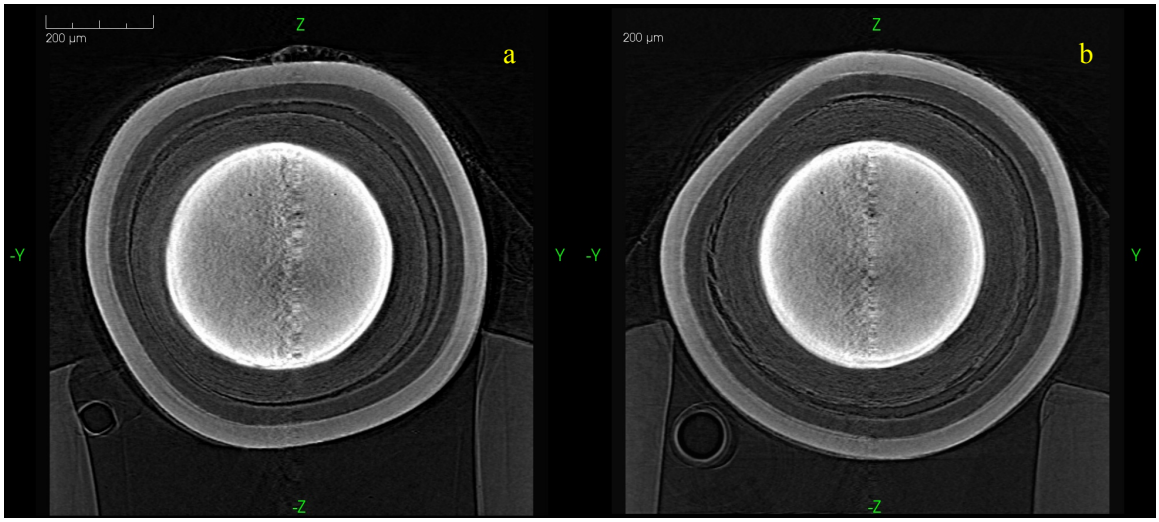

Figure 5. X-ray tomographs of a particle that exhibited lower silver retention (a), and a particle that exhibited average silver retention (b). A gap is evident between the buffer and IPyC, and there is no OPyC layer remaining after the burn.

Figure 6 shows polished cross sections of two particles that had lower silver retention, and Figure 7 shows two particles with average silver retention. Three of the particles exhibited typical buffer densification, where the buffer detached and shrank away from the IPyC layer, as is often observed in AGR-1 irradiated particles. The cross section of the fourth particle showed incomplete delamination of the buffer from the IPyC and complex buffer fracture. The reduced constraint on kernel swelling resulted in larger pores and regions where the kernel protruded into the buffer gaps. This buffer/kernel behavior has been observed in about 25% of the AGR-1 particles analyzed from multiple compacts, and does not appear to impact the silver retention.

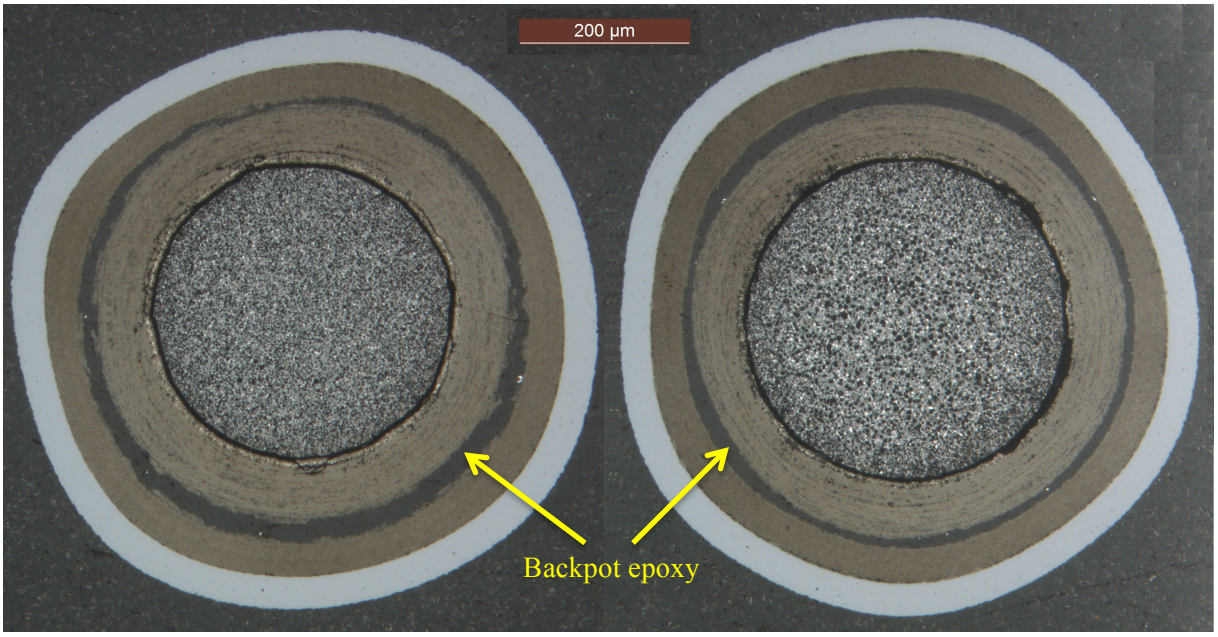

Figure 6. Optical micrographs of polished cross sections of two particles with lower silver retention.

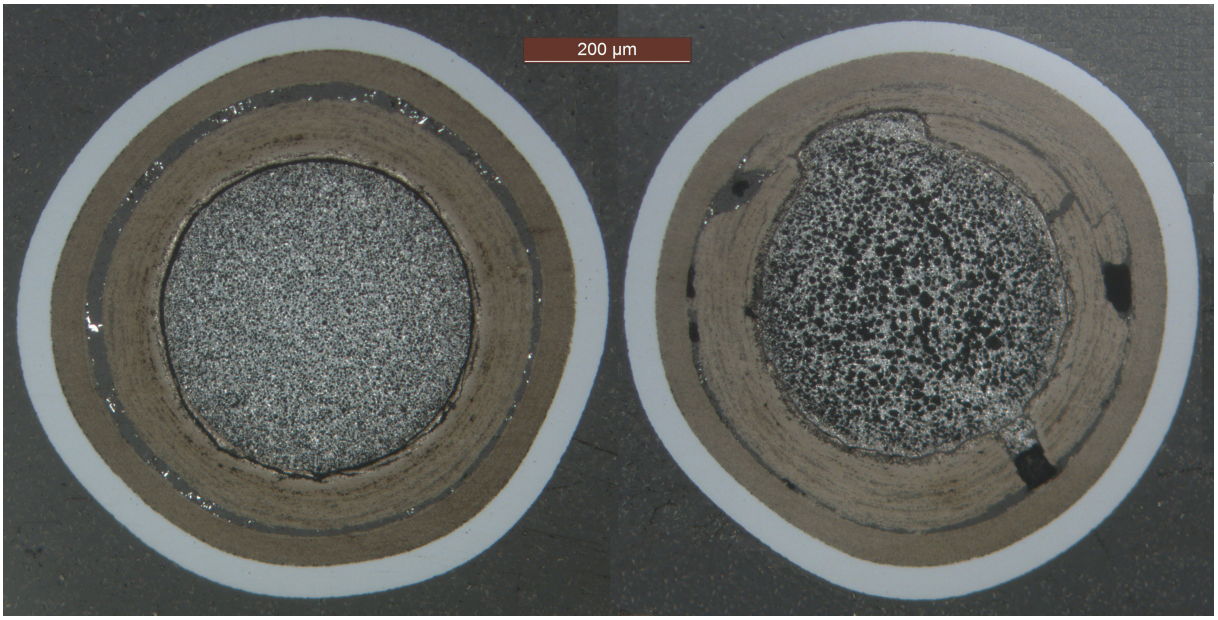

Figure 7. Optical micrographs of polished cross sections of two particles with average silver retention.

Conclusion

All planned PIE on AGR-1 Compact 3-2-2 was successfully completed. The compact was subjected to 1600°C safety testing followed by acid leaching, gamma spectroscopy, x-ray tomography, and materialographic inspection. This was the sixth compact from the AGR-1 irradiation experiment examined at ORNL, three with safety testing performed prior to the other PIE. Data obtained on fission product retention and radiation-induced microstructural changes have provided new insights into TRISO particle fuel performance and suggested additional areas for future investigation.

The general mechanism for silver release and the additional effect of thermal cycling need to be studied further. X-ray tomography and optical microscopy of mechanical cross sections has not shown any obvious relationship between silver release and the irradiation-induced changes in the buffer or kernel. Scanning electron microscopy with elemental analysis may provide additional data on why silver retention varies, but thermal history may also play a key role. Furnace testing of individual particles using various thermal profiles would help provide additional understanding of the effect that maximum temperature and temperature gradient could have on silver retention. Individual particle furnace testing, where fission product inventory before and after heating could be measured by IMGA, would also provide data on whether europium is released through intact SiC at the elevated safety testing temperatures.

The possible role of palladium in silver migration through intact SiC also requires further attention. Palladium release from intact SiC is higher than expected and needs to be quantified better. Although significant palladium has been detected outside of the SiC, and palladium has been observed clustered inside the SiC, palladium corrosion has not been observed, with the possible exception of a few select particles. Analysis for palladium release during the irradiation or during safety testing was not part of the original PIE plan. Analysis of irradiation capsule components and safety test furnace internals is needed for complete understanding of the palladium redistribution. The efficiency of the DLBL analysis to detect palladium is also a concern. Leach-burn-leach of crushed particles could be performed to study the collection efficiency for palladium, as well as various other fission products.

Four particles with exposed kernels were observed after DLBL of Compact 3-2-2. This may have been an artifact of the unusual procedure used to dry and burn off the exposed carbon. Alternately, the exposed kernels may be related to failure of already defective SiC, where the defects did not completely penetrate the layer. The absence of silver in the four exposed kernels suggests the latter scenario. If the particles had through-wall defects in the SiC, cesium would have been released during the safety test. However, if there were defects that only penetrated a significant fraction of the SiC layer, silver and palladium release could have been enhanced, and these weakened layers may have been more susceptible to damage during handling between the pre- and post-burn leaching.

Acknowledgment

This work was supported by the U.S. Department of Energy, Office of Nuclear Energy, under the Very High Temperature Reactor Technology Development Office/Advanced Gas Reactor Fuel Development and Qualification Program.