Associations of Pd, U and Ag in the SiC Layer of Neutron-Irradiated TRISO Fuel

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Abstract

Knowledge of the associations and composition of fission products in the neutron irradiated SiC layer of high-temperature gas reactor TRISO fuel is important to the understanding of various aspects of fuel performance that presently are not well understood. Recently, advanced characterization techniques have been used to examine fuel particles from the Idaho National Laboratory's AGR-1 experiment. Nano-sized Ag and Pd precipitates were previously identified in grain boundaries and triple points in the SiC layer of irradiated TRISO nuclear fuel. Continuation of this initial research is reported in this paper and consists of the characterization of a relatively large number of nano-sized precipitates in three areas of the SiC layer of a single irradiated TRISO nuclear fuel particle using standardless EDS analysis on focused ion beam-prepared transmission electron microscopy samples. Composition and distribution analyses of these precipitates, which were located on grain boundaries, triple junctions and intragranular precipitates, revealed low levels, generally <10 atomic %, of palladium, silver and/or uranium with palladium being the most common element found. Palladium by itself, or associated with either silver or uranium, was found throughout the SiC layer. A small number of precipitates on grain boundaries and triple junctions were found to contain only silver or silver in association with palladium while uranium was always associated with palladium but never found by itself or in association with silver. Intergranular precipitates containing uranium were found to have migrated ~23 μm along a radial direction through the 35 μm thick SiC coating during the AGR-1 experiment while silver-containing intergranular precipitates were found at depths up to ~24 μm in the SiC layer. Also, Pd-rich, nano-precipitates (~10 nm in diameter), without evidence for the presence of either Ag or U, were revealed in intragranular regions throughout the SiC layer. Because not all grain boundaries and triple junctions contained precipitates with fission products and/or uranium, along with the differences in migration behavior between Pd, Ag and U, it was concluded that crystallographic grain boundary and triple junction parameters likely influence migration behavior.

Keywords: SiC, TRISO, STEM, EDS, Ag transport mechanism, Pd

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1. Introduction

Although various transport mechanism hypotheses were determined from out- of- pile experimentation over the last number of decades, speculation still surrounds the mechanism of fission product and transuranic migration through the silicon carbide (SiC) layer of tri-structural isotropic (TRISO) coated nuclear fuels. A large number of out-of-pile experiments have sought to measure the diffusion rate and identify the specific method of migration. (For recent reviews see [1,2].) In the case of silver, these studies have resulted in diffusion coefficients that span three orders of magnitude and have resulted in a variety of proposed mechanisms, all of which are supported by the data generated in those studies. Unfortunately, those experiments generally do not accurately reproduce the SiC microstructure and operational conditions of actual TRISO coated nuclear fuel particles. To date, definitive proof in support of any of the proposed mechanisms in the SiC layer of TRISO fuel has not been obtained.

The availability of actual neutron-irradiated, TRISO coated particles from the AGR-1 experiment of Idaho National Laboratory [3,4], in concert with the availability of advanced characterization techniques, facilities equipped to handle irradiated materials, along with the innovative integration of these factors and experimental methods, resulted in a breakthrough by the first direct measurement of silver-containing intergranular precipitates in the SiC layer of irradiated TRISO coated nuclear fuel [5]. Z-contrast imaging in the scanning transmission electron microscope (STEM) using a high angle annular detector as well as the generation of extremely small electron probe sizes (<1 nm) in the STEM mode, was crucial for identifying the nano-sized, fission product-containing intergranular and intragranular precipitates. These combined capabilities allowed researchers to identify small precipitates with differing elemental composition and collect compositional information from these small precipitates using energy dispersive x-ray spectroscopy. This methodology was demonstrated for the first time in previous work to identify intergranular silver-containing precipitates in the SiC layer of irradiated TRISO coated nuclear fuel [5]. This work utilizes this methodology to gain a better understanding of the behavior of fission products and transuranic elements throughout the SiC layer in irradiated TRISO coated nuclear fuel particles.

The authors of this paper hypothesize that the migration of silver is enabled through Pd-assisted migration, as proposed by [6] and [7], along grain boundaries with specific crystallographic parameters, essentially adding a grain boundary-dependence on silver migration. This study is expected to provide information to evaluate this theory, as well as other proposed theories of fission product migration, that will be discussed in a future publication.

2. Experimental

TRISO coated nuclear fuel was fabricated under standard conditions and subjected to irradiation under the AGR-1 experimental program in the Advanced Test Reactor at INL [8]. The irradiation conditions are summarized in Table 1. After irradiation, compacts consisting of approximately 4100 TRISO coated fuel particles were deconsolidated and randomly-selected TRISO particles evaluated for Ag-110m retention. The particles of Compact 6-3-2 were found to contain an average of only about 50% of the predicted Ag inventory, indicating a significant loss of silver from the coated particles in this compact [8]. The specific TRISO coated fuel particle studied here was coated particle 35 (CP 35) from Compact 6-3-2 which was found to retain approximately 80% of its predicted Ag inventory and was one of the TRISO particles exhibiting a higher fraction of Ag retention [8]. TEM lamellae were prepared from the SiC layer of this particle by standard focused ion beam (FIB) techniques. More information on the particle selection process and sample preparation can be found in [5] and [9].

The chosen particle, CP 35, was mounted in an epoxy resin and polished to the mid-plane of the particle, exposing the various coating layers and fuel kernel of the TRISO particle. The SiC layer was found previously to have a mean thickness of 35.3 ± 1.3 nm [5]. Since this distance was too great to be spanned by a single FIB-prepared TEM lamella, three samples that collectively spanned the entire thickness of the SiC layer were prepared. The locations of these TEM lamellae in the SiC layer are shown in Fig. 1. The sample designated “IE” was located at the inner edge of the SiC layer and included the interface between the inner pyrolytic carbon (IPyC) and the SiC layer. The sample designated “OE” was taken from the outer edge of the SiC layer nearest the outer pyrolytic carbon (OPyC) layer. The sample designated “Ctr” was taken from the center of the SiC layer and overlapped both the IE and OE samples to some extent. The plane of each TEM sample was perpendicular to the polished surface. It should be noted that the plane of the sample made an angle with the radial direction in the SiC of approximately 22° , as shown in Fig. 1.

Fission products and transuranic elements in each sample were revealed using z-contrast imaging in scanning transmission electron microscopy (STEM) using a high angle annular darkfield (HAADF) imaging. The composition of both intergranular and intragranular precipitates were then analyzed using a

fine electron probe size (<1 nm) (Tecnai TF30-FEG STwin, operating at 300 kV, at the Center for Advanced Energy Studies) and energy dispersive spectroscopy (EDS). Generally, a linescan was performed across the feature of interest with an EDS data collection time of 20 seconds at each point. The EDS spectrum at each point was analyzed using standardless analysis. The characteristic K-lines of palladium and silver were used in the standardless compositional analysis as was the characteristic L-lines of uranium. The choice of these characteristic lines avoided the severe peak overlap of the Pd and Ag characteristic L-lines and the U characteristic M-lines, typically encountered in EDS analyses using a scanning electron microscope. This avoided the errors associated with deconvolution of these peaks.

Generation and detection of characteristic x-rays is a statistical process and standardless EDS analysis requires sufficient collection time to yield an accurate representation of the composition. Based on considerations of this aspect and the EDS data collection time of 20 second per spectrum, the limit-of-detection for each of these elements was thought to be on the order of 0.2 at%, which is in line with other work in literature [6]. Therefore, any element in an EDS compositional analysis that was below 0.2 at% was deemed unreliable and was not considered to be present. It should be noted that even at the small electron probe sizes used in this study, compositional information of the matrix was undoubtedly included in the EDS spectra of both intergranular and intragranular precipitates. Therefore, the elemental compositions reported here may not accurately reflect the actual composition of the precipitates but merely indicate the presence or absence of Pd, Ag or U.

3. Results

The FIB-prepared TEM samples were initially surveyed in the conventional TEM mode. The SiC layer appeared to be completely intact. Material defects in the SiC layer of the irradiated TRISO particle, e.g. micro cracks, nano cracks or micro pipes, which others have suggested are responsible for fission product migration [6, 10-12], were not observed in these three samples. Numerous precipitates in various areas on each sample were analyzed using energy dispersive x-ray analysis. The areas containing precipitates with fission products that were analyzed have been identified in the images in Fig. 2. Generally, precipitates containing fission products in each of these areas were prominent when imaging with the HAADF in the STEM mode and were associated with either grain boundaries, triple junctions, intergranular or intragranular particles. (See Fig. 3.) However, not all grain boundaries and triple junctions had significant quantities of any of the elements of interest, i.e., Pd, Ag and/or U. (Only these elements were found at levels above the limits of detection). The form of these elements, whether existing as a relatively pure element or compounded/alloyed with other elements, could not be determined. The precipitates generally did not extend completely through the sample, and x-ray information from the SiC matrix could not be excluded during data collection, preventing definitive determination of the composition of the minor phases present. However, previous work suggests that some of the intergranular precipitates in the SiC layer of similarly irradiated TRISO fuel may, indeed, be silicides of Pd [13] and/or Pd & U, e.g. $\text{Pd}_x\text{U}_y\text{Si}_z$ [9], while work involving out-of-pile testing indicates the presence of a Pd-Ag-Si solution [7] or Pd_2Si containing small amounts of Ag (Ag: Pd on the order of 1:30) [6].

In general, grain size increased radially from the inner to outer regions of the SiC layer, a common characteristic of coatings produced by chemical vapor deposition (CVD) methods, and previously reported by both [14] and [15]. The increasing grain size resulted in fewer grain boundaries in the Ctr and OE samples compared to sample IE. The number of intergranular precipitates exhibiting fission products (area density) also significantly decreased from the inner to the outer regions of the SiC layer. Table 2 shows the breakdown of the number of each type of precipitate analyzed on each of the three samples. The presence of each element or elements in each precipitate is summarized below.

Grain Boundaries – Intergranular precipitates on grain boundaries showed levels of Pd, U and/or Ag above the limits of detection (~0.2 at %). No other fission products (e.g. Ce, Sr, Cs) or transuranic elements (e.g. Pu) above the limits of detection were found in any of the EDS spectra. Grain boundary precipitates with exclusive concentrations of Pd were quite prevalent, for example, Fig. 4a found in sample OE, Area A. Precipitates on some grain boundaries in both IE and Ctr samples contained both Pd and U in significant quantities, for example, Fig. 4b, though relatively few in number. Some grain boundaries in the IE sample exhibiting concentrations of both Pd and Ag above the limits of detection were also found (see Fig. 4c). A significant number of grain boundaries that exhibited concentrations of only Ag (see Fig. 4d), were found in the IE and Ctr samples. Ag and U, whether alone or in combination with other elements, were not found in any grain boundaries analyzed in the outer sample, OE. Also, no grain boundaries with measurable concentrations of Pd, U and Ag together were found in any grain boundary in the three samples.

These observations on the distribution of Pd, U, Ag and the combinations of these elements in grain boundaries across the irradiated SiC layer are quantitatively summarized in Fig. 5. In all three samples, grain boundary precipitates exhibiting only Pd were most prevalent. Grain boundary precipitates with Pd and Ag associated together were found in the IE sample but not in the Ctr or OE samples. However, grain boundary precipitates exhibiting only the presence of Ag were found in both IE and Ctr samples but not in grain boundaries of the OE sample. U was found with Pd in grain boundary precipitates of the IE and Ctr samples but never found alone or associated with Ag in any of the samples.

Triple Junctions – As with grain boundaries, not all triple junctions had fission products and transuranic elements associated with them. Triple junctions with precipitates exhibited segregation behavior of fission products and uranium similar to that of grain boundaries. Again, triple junctions exhibited significant concentrations of either Pd, Pd + U, Pd + Ag or Ag, as in the observations on grain boundaries. Typical compositional line profiles observed for each type of segregation behavior is given in Fig. 6, while the relative fraction of each type of segregation is summarized in Fig. 7. A relatively high fraction of triple junction precipitates in all three samples (IE, Ctr and OE) exhibit the presence of only Pd with no indication of either U or Ag (see Fig. 6a and Fig. 7). A somewhat smaller fraction of triple junction precipitates in the IE and Ctr samples showed elevated concentrations of both Pd and U (see Fig. 6b and Fig. 7). Also, a significant fraction of triple junction precipitates in the IE and Ctr samples were found to contain both Pd and Ag (see Fig. 6c and Fig. 7). Only two triple junctions in the IE sample were found that exhibited only Ag without significant concentrations of either Pd or U (see Fig. 6d). Triple junction precipitates containing only U, Ag+U or Ag+U+Pd were not found in any of the areas analyzed on the three samples.

Line profiles showing significant amounts of both Pd and U or both Pd and Ag across triple junctions are consistent with an alloy or compound, where these elements are intimately mixed, rather than overlapping pure (or nearly pure) phases – elemental or silicides – of Pd, Ag and U. The U and Ag concentration profiles, as in Fig. 6b and Fig. 6c, tend to follow the Pd concentration profile closely with the maximum concentration of each element occurring at the same location along the analysis line. Precipitates in triple junctions that contain only Pd, U or Ag could overlap due to stereological effects and both would be illuminated by the electron beam in the TEM, giving rise to concentration line profiles containing both Pd and U or Pd and Ag. However, if such overlapping phases existed, the concentration profiles of either U or Ag would likely be shifted to the right or left with respect to the concentration profile of Pd and the location of maximum concentration of U or Ag would not coincide with the location of the maximum Pd concentration in the line profiles, at least to some degree. (The precipitates would have to be the same size and exactly aligned to produce the concentration profiles in Fig. 6b and 6c). This “out-of-phase” behavior was not observed in any of the concentration line profiles of triple junctions exhibiting the presence of both Pd and U or both Pd and Ag. Furthermore, no line profiles across triple junctions were found to

contain solely U, or U in combination with Ag, or U in combination with Ag and Pd (see Fig. 7), which would be expected from the overlap of U or Pd+U precipitate with Ag or Pd+Ag precipitates.

The distribution of Pd, U, Ag and the combinations of these elements in triple junctions across the irradiated SiC layer are summarized in Fig. 7. This plot shows that triple junctions in the IE sample (closest to the fuel kernel) contained precipitates with only Pd, Pd+U, Pd+Ag or only Ag. However, no triple junction precipitates with just U, U+Ag or Pd+U+Ag were found in this sample or in the Ctr and OE samples. In the Ctr sample, triple junction precipitates with Pd, Pd+U and Pd+Ag were found while precipitates with just Ag, just U, U+Ag or U+Ag+Pd were not. Finally, in the OE sample (furthest from the fuel kernel) all 16 triple junctions analyzed contained only Pd. No amount of Ag or U, alone or in combination with other elements, was observed above the level-of-detection in any of these triple junction precipitates.

Intragranular Precipitates - Only a small number of intragranular particles were analyzed on each sample. Although more prevalent in the IE sample, these particles were found throughout all three samples. Figure 8 shows examples of two such particles, one round and one rod-like, with the accompanying compositional profile. In both of these examples, as in all the compositional profiles obtained from intragranular particles, the only element present in significant quantities (other than Si or C) was Pd.

Extent of Pd, U and Ag Migration – The distance moved by the various elements during irradiation was determined qualitatively for comparison. (The SiC layer thickness in Fig. 1 appears to be approximately 40 μm , though it is known that the true thickness of the SiC layer should be approximately $35 \pm 1.3 \mu\text{m}$ [5]. Thus, the plane of the cross section in Fig. 1 is not located at the mid-point of the spherical particle. Based on an apparent SiC layer thickness of 40 μm , trigonometry can be used to estimate that the planar cross section in Fig. 1 is approximately 165 μm from the actual mid-point of the TRISO particle. This would result in an apparent thickness of the SiC layer of 40 μm . Therefore, the distances measured in the TEM photographs and reported here will be greater than the actual values measured along a true radial direction by up to ~16%. For a discussion of errors in the distances measured on these samples see reference [16].) Figure 5 and Figure 7 qualitatively indicate the extent of the movement Pd, U and Ag through the SiC layer along grain boundaries and triple junctions during irradiation. As mentioned above, Pd was found in all three samples and the furthest analysis point where Pd was detected was found to be in Area G of the OE sample (see Fig. 2c). Palladium was prevalent in both triple junctions and grain boundaries in this area; see examples in Fig. 9. Area G on the OE sample is on the order of 39 μm from the IPyC/SiC interface, when measured in a radial direction in the SiC layer (see Fig. 1). Pd likely would have been found at the OPyC/SiC interface had analyses been performed there. So it can be concluded that Pd migrated completely through the SiC layer during the irradiation experiment which is also supported by the finding of Pd in the OPyC layer of the irradiated TRISO particles after deconsolidation and leach-burn-leach (DLBL) compositional analyses [3].

The movement of U and Ag was not as extensive as that of Pd in the samples taken from this one particle. Figure 10 shows a triple junction containing a small amount of U, with Pd present also, in Area C and D of the Center sample (see Fig. 2b) and is the furthest grain boundary or triple junction from the IPyC/SiC interface in which U was found. This triple junction is at a distance of approximately 23 μm , measured in a direction perpendicular to the IPyC/SiC interface in Fig. 1. The grain boundary furthest from the IPyC/SiC interface that exhibited a significant Ag concentration (see Fig. 11a and 11b) was also found in Area C and D of the Ctr sample (see Fig. 2b), at a distance of approximately 24 μm .

4. Discussion

In this work, the compositional characteristics of a substantial number of intergranular precipitates have been analyzed and reported. Information on the nano-level, important to the further understanding on the movement of fission products and uranium through the SiC layer in neutron irradiated TRISO fuel, has been revealed. However, even with the large number of observations, some limitations on the conclusions, as discussed below, are warranted.

Migration of Pd and Ag - The preceding results show different behavior in the movement of Pd, U and Ag through the SiC layer during this irradiation experiment. The movement of Pd away from the fuel kernel, to the IPyC/SiC interface and into the SiC layer appears to be accelerated compared to the behavior of Ag (and U), which also originates in the fuel kernel. This may be a direct consequence of the higher yield of Pd versus Ag from fission of the AGR-1 fuel over the course of the irradiation experiment. Calculations show the ratio of Pd to Ag atoms produced is on the order of 13 [17]. Ultimately, a greater concentration (and concentration gradient) of Pd will develop at the IPyC/SiC interface due to the higher rate of Pd production compared to Ag. However, the possibility of an Ag diffusion coefficient significantly smaller than that for Pd cannot be ruled out at this point.

The presence of Pd-rich, Ag-rich and Pd+Ag triple junction and grain boundary precipitates is consistent with out-of-pile experiments performed by [6] and [7]. In their work, both Pd and Ag were in contact with polycrystalline 3C-SiC at temperatures similar to this work but at much higher concentrations. The resulting liquid was able to penetrate the SiC and form precipitates on grain boundaries and triple junction that were Pd-rich, Ag-rich and either Ag-rich with minor amounts of Pd or Pd-rich with minor amounts of Ag, - similar to the intergranular precipitates found in this study. Researchers also observed that Ag, without the presence of Pd, was incapable of migrating into and through polycrystalline SiC. They concluded that Pd was essential in forming a Pd silicide phase that was capable of migrating along the SiC grain boundaries. Ag, they concluded, displaced some Pd within the Pd silicide phase to develop Pd+Ag phases containing variable amounts of Ag. In this way, Ag is carried along with the Pd silicide as it migrates through the SiC layer. Furthermore, they found that if the Ag concentration becomes high enough, all the Pd can be displaced from the Pd silicide to form a Si-Ag liquid. Upon cooling, the Si and Ag separate since there is no solubility of Ag in Si [18] to form an Ag-rich phase. As mentioned, the fission yield of Ag is relatively small compared to Pd [17] and therefore the concentration of Ag and the number of Ag-rich intergranular precipitates can be expected to be relatively small compared to Pd. One would also expect more Ag-rich intergranular precipitates closer to the IPyC/SiC interface, where the Ag concentration is the highest during irradiation, compared to areas closer to the OPyC. This is qualitatively confirmed in this work where no Ag-containing intergranular precipitates were observed in the outer sample (OE), furthest from the source of Ag, as shown in Fig. 5 and Fig. 7. However, the total area studied here is only a very small fraction of the TRISO fuel particle and additional analyses on other areas of the irradiated SiC layer are needed to verify the observed trends. At this point, all observations on intergranular precipitates in this work on the SiC layer of irradiated TRISO fuel appear to be consistent with the Pd-assisted Ag migration mechanism put forth by [6], [7], and [14], although their work was done with concentrations of these elements much higher than those found in TRISO coated fuels under actual operating conditions, potentially enabling an alternative dominant mechanism, such as liquid formation and penetration along grain boundaries.

Additionally, this work seems to suggest that the transport capabilities of triple junctions may be different than those of grain boundaries. Figure 5 and Figure 7 show that triple junctions consistently contain Pd that may have either Ag or U associated with it. It seems more likely to find grain boundaries that only contain Ag compared to triple junctions. Conversely, U is more likely to be found in triple junctions rather than grain boundaries. The root cause of this behavior is not understood at this time but may be due to the strong influence of crystallography on the free volume at grain boundaries that can affect the mobility of various atomic species in them [19]. Generally, the free volume at triple junctions can be

expected to be greater than that of grain boundaries and influenced less by the crystallographic relationships between the grain boundaries comprising the triple junction, allowing greater mobility of various atomic species along them. Although it is difficult to rationalize the preference for Ag to be associated with grain boundaries rather than triple junctions.

The presence of nano-sized, intragranular, Pd-rich precipitates, reported in prior characterization work on this compact [5], [20] and [21], also has been mentioned recently in neutron irradiated 3C-SiC but was not analyzed in detail in that work [14]. Intragranular nano-precipitates have not been reported in out-of-pile studies. One of the differences between the irradiated SiC in this work and that of out-of-pile tests is the enhanced generation of lattice defects, especially vacancies and voids, due to irradiation damage [9, 14]. Although the mechanism for the formation of these intragranular Pd particles is not obvious from this study, one scenario does seem plausible; namely, grain boundaries and triple junctions will act as the dominant “sink” for these lattice defects. As they diffuse to the grain boundaries and triple junctions, a flux of atoms, including fission product atoms, will diffuse away from these microstructural features, carrying them into the SiC grains. Bulk SiC has no solubility for Ag, does not form silicides and it has been shown in many studies, e.g., [11], [19] and [22], that bulk Ag diffusion in SiC is insignificant. Conversely, even though the solubility of Pd in SiC is negligible, it does form various silicides, potentially allowing it to move into the SiC grains under the action of a flux of carbon vacancies— at the grain boundary a Pd atom exchanges with a carbon vacancy, forming a Pd silicide that can move through the lattice, presumably similar to how Pd moves in the grain boundary. The necessary carbon vacancy flux is plausible since irradiation tends to produce more carbon vacancies (3-4 times) than Si vacancies [23]. Ag does not form stable silicides and, therefore, cannot enter the SiC lattice in this manner. For Ag to move with the Pd silicide, a di-vacancy or higher order vacancy would be required. The concentration of these divacancies and higher order vacancies decreases rapidly with increasing order [24]. In this case, incorporation of Ag into intragranular particles would be rare, resulting in very low Ag concentrations, though, [6] reports Ag-containing Pd_2Si with an Ag:Pd ratio of 1:30. If this is the case in these nano-intragranular precipitates, the Ag content would be well below the limits-of-detection for this study.

Migration and behavior of U in the SiC layer - The source of U in the SiC layer is not clear but undoubtedly comes from the UCO kernel – possibly released by the high temperature, reducing conditions produced by the IPyC layer surrounding the UCO fuel or due to contamination during the CVD fabrication process [25]. The migration behavior of U through 3C-SiC has not been addressed in out-of-pile experiments. In this work, U is never found alone or in conjunction with Ag. It is, however, always associated with Pd. Uranium does form silicides and the concentration profiles in Fig. 4b and Fig. 6b are consistent with U substitution for Pd in Pd silicides and the observations of [9]. Excess free volume associated with grain boundaries and triple junctions may lessen the effects of uranium’s larger atomic radius and allow its migration with Pd through the SiC layer via these microstructural features. However, U was not found in the intragranular particles and factors other than silicide-forming ability, such as its larger atomic radius, may prevent U from entering the lattice and being incorporated into the intragranular particles. Finally, the lack of association of U with Ag remains unexplained. The chemical behavior and atomic radius of Pd and Ag are quite similar and one would expect U to associate with Ag in a manner similar to Pd but this was not observed in this study.

Grain boundary dependence of Ag migration – In this study it was evident that a relatively high fraction of grain boundaries and triple junctions did not exhibit intergranular precipitates. In fact, it was difficult to find grain boundaries and triple junctions that had intergranular precipitates as the distance from the source of fission products and uranium increased, i.e. in the Ctr and, especially, the OE samples. Precipitate-free grain boundaries are evident in Figs. 3, 4c and 6c. These boundaries are in the vicinity of grain boundaries with precipitates so it is hard to attribute the lack of precipitates on these boundaries to a lack of supply of fission products and uranium. One possible explanation is a dependence of fission

product migration/transport behavior on grain boundary character, i.e. grain boundary misorientation and grain boundary plane. These parameters are known to influence grain boundary diffusivity in metals and alloys. In SiC, these parameters can be expected to determine the relative numbers of Si and C terminations within the grain boundary plane. Since Pd and Ag do not react strongly with carbon it is likely that grain boundaries with an abundance of carbon terminations will conduct these elements to a lesser extent than a boundary with an excessive amount of Si terminations. Work is underway to understand the grain boundary character of boundaries with and without precipitates. The results of that work and the implications on the fission product migration mechanism will be reported in a future publication.

Considerations of the post-irradiation elemental distribution - It must be kept in mind that the distributions of Pd, U and Ag observed in this work may be the result of very slow cooling after completion of the high temperature, irradiation experiment. Typically, the irradiated TRISO particles require 2-3 days to cool from the test temperature, $\sim 0.6T_{MP}$, possibly allowing sufficient time for changes in the spatial distribution of the elements as well as phase separation, precipitation, compound formation, etc. Decreasing temperatures are generally associated with decreasing solubility and segregation of insoluble elements to defects, such as grain boundaries, triple junctions, voids, etc. Therefore, these effects must be considered when applying the observations reported here to mechanisms of fission product migration under high temperature, operational conditions.

Final Considerations-Although the number of intergranular precipitates interrogated in this work is relatively large, the results still only represent a rather small fraction of the SiC layer in a single TRISO particle. The volume of SiC interrogated in this study is extremely small in comparison to the total volume of the SiC layer surrounding the fuel kernel (on the order of $1 \times 10^{-6} V_{tot}^{SiC}$), leaving open the possibility that not all types of fission product-containing precipitates have been found. The microstructure and distribution of fission products may vary significantly on a local level. Furthermore, each fuel compact typically contains over 4100 TRISO fuel particles and thus each TRISO fuel particle experiences slightly different operating conditions, including thermal gradients and irradiation conditions, which may explain the relatively large release of Ag from the TRISO coated fuel particles in this compact during irradiation.

It must also be kept in mind that the results reported here may *or may not* have implications on the dominant transport mechanism(s) in the release of fission products from irradiated TRISO fuel. One must consider the dominant transport mechanism(s) may be sufficiently fast and, when coupled with low fission product production rates, especially in the case of Ag [7], fission products may never accumulate to the extent that they exceed the minimum levels of detection for EDS analyses and are thus not detected in this analysis. Therefore, the grain boundaries and triple junctions that exhibit precipitates containing fission products and uranium may simply represent slower transport paths that allow for the accumulation of the fission products to levels exceeding the limits of detection. However, either scenario suggests fission product transport (and uranium transport) appears to be dependent on the specific properties of individual grain boundaries and triple junctions. Crystallographic information on grain boundaries and triple junctions with and without precipitates containing fission products, along with modeling and simulation studies on transport in these two types of grain boundaries and triple junctions, will be required to fully elucidate the dominant transport mechanism through SiC. Some work has seemed to indicate that grain boundary character has a strong influence on at least silver migration in SiC [26]. INL started studies in 2012 on actual irradiated TRISO coated particles to determine the effect of grain boundary characteristics and, as mentioned, will be reported elsewhere.

Finally, it needs to be mentioned that the results presented here seemingly contradict those reported by O'Connell, et al. [14] on Ag migration in neutron-irradiated SiC, where they saw very little migration at

similar temperatures and irradiation conditions. However, a number of experimental differences exist between that work and the results presented here. Silver migration in O’Connell’s study [14] was characterized following a 24 hour anneal at 1000°C on samples that were created by depositing thin layers of Pd and Ag on *previously* neutron irradiated CVD-SiC. The source of Pd and Ag in this study, though much lower in concentration, was present at the SiC layer throughout the duration of the neutron irradiation, which was over 600 times greater than in the O’Connell work. Additionally, the temperature at which Ag migration took place in this work was also slightly higher, ~1100°C versus 1000°C for the O’Connell work. The differences in behavior observed here can reasonably be attributed to these differences in experimental conditions and are in no-way contradictory to those obtained by O’Connell. There is no reason to believe that their conclusions of the strong influence of neutron irradiation fluence and irradiation temperature on Ag migration behavior do not apply.

5. Summary and Conclusions

This work reports on the characterization of a relatively large number of nano-sized intergranular precipitates in the SiC layer of a single irradiated TRISO nuclear fuel particle using standardless EDS analysis on FIB-prepared TEM samples. Analysis of the composition and distribution of these precipitates found on grain boundaries, triple junctions, intragranular precipitates and intergranular precipitates allowed the following conclusions to be made for this particle:

1. The intergranular precipitates were found to contain palladium, silver, and/or uranium
2. Palladium was the most common element found in these intergranular precipitates
3. Often, either silver or uranium was found along with palladium in these intergranular precipitates
4. Grain boundaries were more likely to contain precipitates exhibiting only significant amounts of silver compared to triple junctions
5. Uranium was never detected when silver was present and vice versa. Also, uranium was never found alone – it was always associated with palladium.
6. Palladium was found throughout the 35 μm thick SiC layer
7. Uranium and silver were detected only 23 and 24 μm , respectively, along the radial direction into the SiC layer
8. Even though a relatively large number of precipitates were analyzed, generalized conclusions regarding the results is imprudent as they represent only a small fraction of the SiC layer volume ($\sim 1 \times 10^{-6} V_{\text{tot}}^{\text{SiC}}$) and were obtained from a single, irradiated TRISO fuel particle with a unique irradiation history
9. Not all grain boundaries and triple junctions contained precipitates, suggesting the crystallographic relationships associated with these microstructural features may be important.
10. Intragranular, nano-precipitates (~ 10 nm in diameter) were found to be Pd-rich without evidence for either Ag or U.

In general, it was found that on select grain boundaries and triple junctions Pd readily associates with either Ag or U, but never both. Furthermore, for unexplained reasons, U and Ag do not appear to associate in grain boundaries and triple junctions.

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Table 1. Irradiation Parameters for TRISO Particle

Parameter	Value
% FIMA average burnup	11.3
Time-average, volume average temperature, °C	1070
Time-average, maximum temperature, °C	1144
Approximate time-at-temperature, days	620.2
Approximate fast fluence, n/cm ²	2.38 x10 ²¹
Fuel type	Baseline

Table 2. Breakdown of intergranular and intragranular precipitates analyzed

Sample ID	Number of Precipitates on Grain Boundaries Analyzed	Number of Precipitates on Triple Junctions Analyzed	Number of Intragranular Precipitates Analyzed	Total number of Precipitates Analyzed
Inner	35	54	1	90
Center	38	14	7	59
Outer	21	17	2	40
Total	94	85	10	189

Figure 1. TEM samples were prepared by focused ion beam methods from the locations indicated in this photo— Inner (IE), Center (Ctr) and Outer (OE). Samples were oriented approximately 22° relative to the IPyC/SiC interface.

Figure 2. Low magnification images of the (a) IE, (b) Ctr and (c) OE TEM samples taken with the HAADF detector showing the areas analyzed.

Figure 3. Overview of Area B of sample IE showing fission product-containing precipitates (grain boundaries – 1, 3 and 9, triple junctions – 2, 4, 7, 8, 10 and 11, and intragranular precipitates - ppt) that were analyzed.

Figure 4. Examples of grain boundaries containing (a) only Pd, (b) Pd and U, (c) Pd and Ag and (d) Ag.

Figure 5. Summary of the distribution of elements in grain boundaries.

Figure 6. Examples of triple junctions containing (a) only Pd, (b) Pd and U, (c) Pd and Ag and (d) Ag.

Figure 7. Summary of the distribution of the elements in triple junctions

Figure 8. Examples of intragranular particles – (a) round and (c) rod-like, showing only the presence of significant amounts of Pd – (b) & (d), respectively.

Figure 9. (a) Example of triple junction in Area G and (c) a grain boundary in Area F of the OE sample (Figure 2c) showing the presence of palladium – (b) and (d), respectively.

Figure 10. (a) Triple junction in Area C and D of the Ctr sample (Fig. 2b) showing (b) a small but significant concentration of U.

Figure 11. The EDS line scan depicted at “1” in (a) of Area C and D in the Ctr sample (Fig. 2b) shows (b) significant Ag concentration.