Local atomic structure of Pd and Ag in the SiC containment layer of TRISO fuel particles fissioned to 20% burn-up

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ABSTRACT

The structure and speciation of fission products within the SiC barrier layer of tristructural-isotropic (TRISO) fuel particles irradiated to 19.6% fissions per initial metal atom (FIMA) burnup in the Advanced Test Reactor (ATR) at Idaho National Laboratory (INL) was investigated. As-irradiated fuel particles, as well as those subjected to simulated accident scenarios, were examined. The TRISO particles were characterized using synchrotron X-ray absorption fine-structure spectroscopy (XAFS) at the Materials Research Collaborative Access Team (MRCAT) beamline at the Advanced Photon Source. The TRISO particles were produced at Oak Ridge National Laboratory under the Advanced Gas Reactor Fuel Development and Qualification Program and sent to the ATR for irradiation. XAFS measurements on the palladium and silver K-edges were collected using the MRCAT undulator beamline. Analysis of the Pd edge indicated the formation of palladium silicides of the form PdxSi (2 ≤ x ≤ 3). In contrast, Ag was found to be metallic within the SiC shell safety tested to 1700 °C. To the best of our knowledge, this is the first result demonstrating metallic bonding of silver from fissioned samples. Knowledge of these reaction pathways will allow for better simulations of radionuclide transport in the various coating layers of TRISO fuels for next generation nuclear reactors. They may also suggest different ways to modify TRISO particles to improve their fuel performance and to mitigate potential fission product release under both normal operation and accident conditions.

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1. Introduction

Tristructural-isotropic (TRISO) encapsulated fuel particles are an established technology used in high-temperature gas-cooled nuclear reactors (HTGRs) [1,2]. Fuel performance envelopes are
limited by the potential release of metallic fission products from the TRISO containment under normal operation [3] or high-temperature accident scenarios [1,4]. The current TRISO particle design (Fig. 1) at its core consists of a UO₂ or a two phase mixture of UO₂+UC₂-x (euphemistically termed UCO) fuel kernel with a diameter of ≤500 μm. This kernel is surrounded by a ~100 μm porous carbon buffer layer, a ~40 μm inner pyrolytic carbon (IPyC) layer, a ~35 μm high-density silicon carbide (SiC) layer, and a ~40 μm outer pyrolytic carbon (OPyC) layer [4–6].

The SiC and pyrolytic carbon coating layers in the TRISO fuel particle act as a pressure vessel to retain fission products. This is the underlying philosophy behind high temperature gas-cooled reactor design, aiming to utilize inherent barriers to the fuel for the purpose of radionuclide retention. These particles are dispersed in a graphite matrix and formed into cylindrical compacts. It is important to determine the mechanisms by which fission products interact with the SiC layer. This is necessary as the SiC provides the structural support and is the main barrier to the diffusion of metallic fission products [4,5]. A fraction of the fission products (FPs) and fission inventory migrate through the SiC shell and are released into the environment under in-pile testing or simulated accident tests [7–11]. In particular, previous laboratory examination studies have indicated the transport of Ag through seemingly intact particles, which poses maintenance and safety concerns [1,7,12–15], and the localized corrosion of the SiC due to Pd, a fission product that enhances corrosion and eventual failure of the SiC in particles where the IPyC has cracked due to the buffer not delaminating from the IPyC during irradiation [13,16–19]. Although a number of studies have been conducted computationally [20–24] and on both surrogate surfaces [25–38] and reactor irradiated fuel particles [7,12,39–43], the specifics of the Ag and Pd transport through SiC are not well understood. It has been theoretically calculated and experimentally shown that Pd forms silicides from SiC, primarily Pd₅Si (x = 2, 3) [28,38,44–46] in the form of islands that partially occupy the SiC surface or nodules at the SiC reaction site. The Pd attack on SiC is postulated to occur due to either Pd clustering or interstitial migration [47]. It has been suggested by recent studies that Ag is transported through the SiC with the assistance of Pd [14,27] or free Si [7,13] through an undetermined mechanism. Additionally, recent investigations suggest the formation of uranium silicides or a U-Pd-Si structure [39,40].

The primary motivation for this work was to provide a basis, built on experimental observations, to constrain the set of assumptions used in the transport models that aim to describe and quantify the release of Ag from TRISO fuel particles. The assumed Ag transport path in the SiC coating layer in these models has ranged through bulk SiC [23], using SiC grain boundaries [20,26,29–31,48], and via microcracks [22,24,33].

In this work, the understanding of the distribution and pathways of Ag and Pd as they arrive at, react with, and transport across the SiC coating layer is expanded upon. This was studied for the as-irradiated and safety tested fuel particles. The reaction products were determined from measurements of the coordination number, atom type, and position of neighboring atoms, which results in a comprehensive picture of the average coordination chemistry. These reactions have been probed utilizing synchrotron X-ray Absorption Fine Structure Spectroscopy (XAFS). Measurements were conducted on the same SiC fragments from irradiated TRISO fuel particles, and the local structure and dispersion of Pd and Ag was determined.

2. Experimental details
2.1. Specimen pedigree and preparation

The TRISO fuel used in this work was produced at Oak Ridge National Laboratory (ORNL) under the Advanced Gas Reactor Fuel Development and Qualification Program and neutron irradiated in the ATR at INL. UCO fuel kernels of 19.74% 235U enrichment were coated in a 50-mm-diameter fluidized bed chemical vapor deposition coating furnace at ORNL [6] and then embedded into the cylindrical graphite matrix compacts (12.7 mm diameter and 25.4 mm height) [50]. UCO was used instead of UO₂ due in part to its ability to control CO production, which has proved detrimental to the integrity of the particles [51–54]. Limited or no CO production eliminates kernel migration in these fuel particles at high burnup [55,56]. For these studies, three different types of particles were examined as described in Table 1. All of the particles were chosen because the inner pyrocarbon, silicon carbide, and outer pyrocarbon were all intact. These particles were specifically chosen for normal, high, and low Ag retention, a variety of safety-test temperatures, and average burn-up per compact measured in fissions per initial metal atom (FIMA). Two of the particles, 611-AG59 (15% FIMA) and 331-RS43 (19% FIMA), were baseline particles, while the final particle 442-A007 (17% FIMA) was of Variant 3 [6]. The preparation of the baseline and variant 3 particles was described in detail in Lowden 2006 [6] and is briefly summarized below. The chemical vapor deposition (CVD) SiC was deposited through decomposition of methyltrichlorosilane in hydrogen using a coating bed temperature of 1500 °C. Variant 3 was produced in the same manner as the baseline particles, with the exception that the SiC was deposited at 1425 °C instead of 1500 °C with argon added to the deposition gases to improve fluidization. This created finer grain structure within the SiC coating layer.

The compacts were placed into capsules that were neutron irradiated with temperatures spanning a wide range depending on the location of the compact within the reactor. The time-average, volume-average (TAVA) temperatures for the compacts, as well as the time-average minimum and maximum temperatures, all collected at the end of the irradiation run, are given in Table 1 [57]. As these are just averages for each compact, the actual temperature of
the particles selected for this study could have been outside of these ranges. After irradiation, the fuel compacts were transferred back to ORNL and received at the Irradiated Fuels Examination Laboratory (IFEL), a hot cell facility. A selected set of compacts were annealed to higher temperatures in the Core Conduction Cooldown Test Facility (CCCTF) at IFEL for margin temperature (safety) testing to study performance under potential accident conditions [11]. Compact 3–3–1 was heated before compact deconsolidation in a controlled ramp to 1700 °C for 300 h in the CCCTF [58]. Compact 4–4–2 was deconsolidated as described next prior to loose particle safety testing to 1800 °C for 600 h [59]. The particles in the as-irradiated or safety-tested compacts were isolated via electrolytic deconsolidation of the graphite matrix in nitric acid. To determine the Ag retention in each of the approximately 4000 particles in these compacts, the Irradiated Microsphere Gamma Analyzer (IMGA) at IFEL was used [11]. After this step was complete, the particles in Table 1 were carefully chosen. The parent particles were initially crushed to break the coating layers and retrieve SiC fragments. However, the fragments could retain remnants of the fuel kernel and the C-based coating layers. Therefore, the SiC shells were isolated through a burn-leach process. This was done to reduce activity of the fragments [11] as well as the fact that the focus of this study was the state of Ag and Pd from 110mAg in the SiC fragments from particle 331-RS43, converted to its activity at 1 day after end of irradiation (Nov 7th, 2009) using its half-life, was ~2.96 kBq (8 \times 10^{-2} \mu \text{Ci}). The SiC fragments weighed on the order of 3 \times 10^{-5} g (volume of ~0.01 mm³) and were roughly 50 μm in width. Using this information, the minimum Ag concentration was calculated at 2.4 \times 10^{18} \text{cm}^{-3} (50 \text{appm}) in the SiC fragment from particle 331-RS43.

### 2.2. Synchrotron examination

The samples were then prepared for measurements at the Materials Research Collaborative Access Team (MRCAT) insertion device beamline (Sector 10) at the Advanced Photon Source [60]. Each of the SiC particles was individually mounted to kapton tape. A wire post was attached to the kapton tape at a distance of at least 10 beam diameters from the sample. Finally, the sample, kapton tape, and post were sealed in a kapton tube using epoxy so that the particle would be suitable for transport and mounting at the beamline.

Measurements of X-ray fluorescence (XRF) and XAFS were performed using a 200 μm by 200 μm X-ray beam. A cryo-cooled Si(111) double-crystal monochromator was used to select the x-ray energies within a range of 4.8 keV–30 keV. Higher harmonics were rejected from the monochromator using a platinum mirror for both the Ag and Pd K-edges, 25,514 eV and 24,350 eV, respectively. The carbon edge was not measured due to energy limitations on the synchrotron beamline. The photon energy was calibrated using a Pd foil and an Ag foil measured in transmission mode with ionization chambers filled with incident 90% N₂ and 10% Ar gases and transmitted 100% Ar gas. The TRISO samples were measured in fluorescence geometry using a solid state Vortex detector (Hitachi) placed perpendicular to the incident beam and at an angle of 45° with respect to the sample normal. The Vortex detector is an energy dispersive detector and was utilized for both XAFS and XRF measurements.

X-ray absorption spectroscopy has been previously used to provide valuable information on irradiated nuclear structures [63–65]. XAFS probes the local atomic structure of a specific absorbing atom by making use of the interference between a primary outgoing electron wave and the scattered waves off neighboring atoms. XAFS is particularly useful due to the fact that long-range order is unnecessary when probing the local structure [66]. As a function of photon energy, oscillations are observed in the XAFS spectrum due to the constructive and destructive interference of the outgoing photoelectron wave and returning wave scattered from near-neighbors. The strength of the oscillations is related to the number of scattering atoms at a given distance. For longer scattering lengths, the frequency of oscillations is higher than for shorter scattering lengths.

The XAFS data analysis was completed using the Demeter program package [67] with the Athena and Artemis interfaces for IFEFFIT software [68]. Scattering paths were generated in Artemis using known crystallographic data in for the model structures. FEFF [69,70] paths based upon the model for each structure were created and used to fit the calculated XAFS,

\[
\chi(k) = \sum_{i} N_{Si} S_{Si}(F_{i}(k)e^{-2k^{2}r_{i}^{2}}/kr_{i}^{2}) \sin[2kr_{i} + \delta _{i}(k)]
\]  

(1)

to the measured \(\chi(k)\). In Eq. (1), \(k\) is the electron momentum, \(\lambda\) is the mean-free-path of the photoelectron, \(F_{i}(k)\) is the scattering amplitude, and \(\delta _{i}(k)\) is a phase-shift factor. The latter two depend on the atomic number \(Z\) of the scattering atom in the \(i\)th path. A best fit was determined using a non-linear least squares fit over each scattering path with the amplitude of each path, \(N_{i}\), the scattering half-path length \(r_{i}\), and the Debye-Waller factor \(\sigma_{i}^{2}\), which accounts for both structural and thermal disorder in the material [65], being allowed to vary. A single energy shift, \(\Delta E_{0}\), was utilized for all paths in the fit. In addition, the full XAFS spectra from metallic silver was calculated using JFEFF and FEFF9.0 [71–73].

### 3. Results

#### 3.1. X-ray fluorescence

Fig. 2 shows an XRF spectrum from each of the three particles.

<table>
<thead>
<tr>
<th>Parent Particle</th>
<th>Safety Testing</th>
<th>Average FIMA in Compact</th>
<th>Ag Retention</th>
<th>Time Average Volume Average (TAVA) Temperature</th>
<th>Time Average Temperature Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>611-AG59</td>
<td>None</td>
<td>15%</td>
<td>15%</td>
<td>1111 °C</td>
<td>969 °C–1194 °C</td>
</tr>
<tr>
<td>331-RS43</td>
<td>300 h at 1700 °C</td>
<td>19%</td>
<td>100% post-safety testing</td>
<td>1051 °C</td>
<td>897 °C–1145 °C</td>
</tr>
<tr>
<td>442-A007</td>
<td>600 h at 1800 °C</td>
<td>17%</td>
<td>Undetectable post-safety testing</td>
<td>1024 °C</td>
<td>866 °C–1139 °C</td>
</tr>
</tbody>
</table>
The fluorescence was excited by photons with energy of 28,000 eV. The XRF data allowed us to determine an inventory of the elements found within the SiC shell of TRISO particles. All fluorescence measurements were collected in identical geometries as described above. The measurements were for a total time of 300 s on all samples. Both metallic fission products (Pd, Rh, Ru, Ag, Zr, Eu) and actinides (U, Pu) were observed in the SiC layer from all three samples. This work will focus on the Pd and Ag found within the SiC layer.

The XRF measurements performed here probed the entire thickness of the SiC fragment from the irradiated TRISO particles so the observed spectra are an average over the spatial extent of the fragment. TEM measurements [39–41] indicated that neither the Pd nor the Ag was uniformly distributed along grain boundaries within the SiC layer. The Ag content in the SiC layer was very low. The highest Ag concentration was observed in the particle annealed to 1700 °C for 300 h, as shown in the inset of Fig. 2 and consistent with the results of gamma spectroscopy. The absolute amount of Ag and Pd in the SiC was determined by comparing the XRF signal from the particles with the signal from thin film reference standards.

For calibration of the Ag and Pd content in the particles, Ag/SiC(111) and Pd/SiC(111) thin films were synthesized with varying Ag/Pd thickness using the Pulsed Laser Deposition system at the Illinois Institute of Technology. This system has been described in detail elsewhere [74]. A Si(111) substrate was etched using NH₄F to remove native oxide layers [75,76] prior to deposition of a SiC layer. After cleaning, 50 nm of SiC was deposited onto the Si(111) substrate at a temperature of 700 °C. The growth of all films was monitored using reflection high energy electron diffraction (RHEED) [77].

Ag films of thickness 2, 5, and 50 monolayers were deposited at room temperature on the SiC/Si(111) surfaces. The Ag reference films had $1.35 \times 10^{12}$, $3.38 \times 10^{12}$, and $3.38 \times 10^{13}$ atoms in the probed volume, respectively. These values were calculated using the FCC lattice constant of Ag ($a = 4.09 \angstrom$) verified by RHEED measurements. Similarly, Pd films of thickness 2, 5, and 50 monolayers were also deposited at room temperature on the SiC/Si(111) surfaces. The Pd reference films had $1.73 \times 10^{12}$, $4.32 \times 10^{12}$, and $4.32 \times 10^{13}$ atoms in the probed volume, respectively, using the FCC Pd lattice constant of $a = 3.89 \angstrom$ verified by RHEED.

The reference films were then transported to MRCAT for XRF measurements. Quantitative measurements utilized the Ag Kα fluorescence line (22,163 eV) and Pd Kα fluorescence line (21,177 eV). The ratio of XRF peak intensities between the thin films and the signal from each TRISO SiC fragment were calculated and used to determine the number of atoms and atomic concentration listed in Table 2. Ag concentration appears above the lower limit determined by gamma spectroscopy. We were unable to calculate Ag concentration in the 1800 °C safety-tested particle because the quantity was so low that we couldn’t be certain about the quantification above background.

### 3.2. X-ray absorption

The content of Ag was inhomogeneous across the set of samples. The particle annealed to 1700 °C for 300 h, the particle of highest Ag retention, was the only sample with enough Ag from which an XAFS spectrum could be measured. The Ag K-edge XAFS spectrum (25,514 eV) [78] from the 1700 °C particle is shown in Fig. 3 along with the spectrum from a reference Ag metal foil. The edge position of the data from both the foil and the sample are aligned at 25,514 eV and 25,517 eV, respectively, and the oscillation peaks after the edge are aligned, as detailed in Table 3.

Fig. 4 shows the normalized Pd K-edge (24,350 eV) [78] absorption spectra for the irradiated TRISO specimen. The edge positions from the irradiated samples are shifted in the range of 3–4 eV to higher binding energy (larger photon excitation energy) relative to that of Pd metal, as shown in Table 3. The direction of this shift is consistent with the magnitude and direction of the silicide shifts observed at the L₂ and L₃ edges of Pd [79]. Their observation of a larger contribution to the XAFS from the first Pd-Si shell is also consistent with the data.

Fig. 5 shows the $k^2$-weighted XAFS data, and Figs. 6–8 show their Fourier transforms in real space. $\chi(k)$ depicts the oscillations in the absorption spectrum as a function of wavenumber. The R-space functions are related to the radial distribution of atoms but shifted from the absolute position due to the strong interaction between the electron and the scattering potential. The fitting parameters are summarized for each fit in Tables 4–6. The FEFF model
Table 2
Measured quantity of Ag and Pd in the SiC layer of the 200 μm by 200 μm probed region of each sample, as well as the extrapolated atomic density of the selected element assuming a uniform distribution.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Silver (Ag)</th>
<th>Palladium (Pd)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Total atoms in probed region</td>
<td>Atoms/cm²</td>
</tr>
<tr>
<td>611-AG59 (As-irradiated)</td>
<td>$1.6 \times 10^{12} \pm 0.8 \times 10^{12}$</td>
<td>$8.1 \times 10^{17} \pm 2.4 \times 10^{17}$</td>
</tr>
<tr>
<td>331-R543 (1700 °C)</td>
<td>$2.8 \times 10^{12} \pm 0.8 \times 10^{12}$</td>
<td>$1.4 \times 10^{18} \pm 0.4 \times 10^{18}$</td>
</tr>
<tr>
<td>442-A007 (1800 °C)</td>
<td>Below Quantifiable Limit</td>
<td>Below Quantifiable Limit</td>
</tr>
</tbody>
</table>

Fig. 3. The Ag K-edge (25,514 eV) XANES from the particle safety tested to 1700 °C for 300 h compared to an Ag foil. The edge positions are clearly aligned, as are the near-edge peaks in the spectrum, indicating the Ag in the SiC particle is of metallic nature.

Table 3
The experimentally observed Pd and Ag K-edge peak positions of the XAFS spectra from the irradiated TRISO samples are detailed below. Only the 1700 °C safety tested sample had enough Ag for quantitative measurement.

<table>
<thead>
<tr>
<th>Spectrum</th>
<th>Palladium K-edge</th>
<th>Silver K-edge</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Derivative Peak (keV)</td>
<td>XANES Maximum (keV)</td>
</tr>
<tr>
<td>As-Irradiated</td>
<td>24.353</td>
<td>24.381</td>
</tr>
<tr>
<td>1700 °C, 300 h</td>
<td>24.353</td>
<td>24.384</td>
</tr>
<tr>
<td>1800 °C, 600 h</td>
<td>24.354</td>
<td>24.382</td>
</tr>
</tbody>
</table>

Fig. 4. The Pd K-edge (24,350 eV) energy spectra from all three SiC particles is shown. The post-edge oscillations have variations between the three structures, with the as-irradiated structure and the particle annealed to 1800 °C looking the most similar.
for the Pd$_2$Si structure was based on a hexagonal structure with space group P - 6 2 m with lattice parameters $a = 6.4965 \, \text{Å}$ and $c = 3.433 \, \text{Å}^{[80]}$, while the Pd$_3$Si structure was orthorhombic, space group P n m a, with lattice parameters $a = 5.735 \, \text{Å}$, $b = 7.555 \, \text{Å}$, and $c = 5.260 \, \text{Å}^{[80]}$.

The as-irradiated particle demonstrates Pd$_x$Si characteristics, where $x = 2, 3$, but due to radiation damage does not fit to a complete crystal structure. Specifically, two Pd-Si paths were observed at distances of $2.31 \pm 0.02 \, \text{Å}$ and $2.47 \pm 0.02 \, \text{Å}$ with coordinations of $2.2 \pm 0.2$ and $3.0 \pm 0.4$, respectively. Additionally, two Pd-Pd paths were fit from the Pd$_2$Si structure at $2.78 \pm 0.02 \, \text{Å}$ and $3.39 \pm 0.02 \, \text{Å}$, with coordinations of $1.8 \pm 0.2$ and $3.0 \pm 0.5$, respectively. All fitting parameters are detailed in Table 4. The interatomic spacings are consistent with both Pd$_2$Si and Pd$_3$Si. The coordination numbers are intermediate between the two structures. Less coordination was observed of the longer Pd-Pd bonds than predicted by the crystal structure.

For the 1700 °C safety tested particle, the data fits well to a Pd$_3$Si crystal structure with the potential presence of a small amount of Pd$_2$Si. A Pd-Si path was fit at $2.26 \pm 0.02 \, \text{Å}$ with a coordination of $2.2 \pm 0.2$.

![K-space plot](image)

**Fig. 5.** K-space plot of the datasets from all three particles and their corresponding fits in the dashed lines. The K-space in each particle has similar features, as they are all silicides.

![R-space plot](image)

**Fig. 6.** The R-space plot of the fit for the as-irradiated particle. This particle was fit to a combination of Pd$_2$Si and Pd$_3$Si, with the silicide paths coming from the Pd$_3$Si structure and the palladium paths from the Pd$_2$Si.
Fig. 7. The R-space fit of the particle irradiated to 1700 °C. This particle was fit to a Pd$_3$Si structure.

Fig. 8. The R-space fit of the 1800 °C particle. This particle was fit to a Pd$_2$Si structure.

Table 4
Summary of fitting parameters for the as-irradiated (AI) particle. The as-irradiated particle was fit to two palladium paths from Pd$_2$Si and two silicon paths from Pd$_3$Si. The coordination number of the fit was different than the perfect crystal (PC), and the sigma-squared parameters varied greatly between the fits from the AI, the 1700 °C (Table 5), and the 1800 °C (Table 6) indicating a large amount of disorder within the materials.

<table>
<thead>
<tr>
<th>Path</th>
<th>$R_{SC}$ (Å)</th>
<th>$R_{MD}$ (Å)</th>
<th>$\sigma^2$ (Å$^2$)</th>
<th>$N_{SC}$</th>
<th>$N_{MD}$</th>
<th>Theory</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd$_0$ → Si$_1$ → Pd$_0$</td>
<td>2.35</td>
<td>2.31 ± 0.02</td>
<td>0.007 ± 0.001</td>
<td>1</td>
<td>2.2 ± 0.2</td>
<td>Pd$_3$Si</td>
</tr>
<tr>
<td>Pd$_0$ → Si$_2$ → Pd$_0$</td>
<td>2.48</td>
<td>2.47 ± 0.02</td>
<td>0.010 ± 0.002</td>
<td>2</td>
<td>3.0 ± 0.4</td>
<td>Pd$_3$Si</td>
</tr>
<tr>
<td>Pd$_0$ → Pd$_1$ → Pd$_0$</td>
<td>2.84</td>
<td>2.78 ± 0.02</td>
<td>0.006 ± 0.001</td>
<td>6</td>
<td>1.8 ± 0.2</td>
<td>Pd$_3$Si</td>
</tr>
<tr>
<td>Pd$_0$ → Pd$_3$ → Pd$_0$</td>
<td>3.43</td>
<td>3.39 ± 0.02</td>
<td>0.008 ± 0.001</td>
<td>2</td>
<td>3.0 ± 0.5</td>
<td>Pd$_2$Si</td>
</tr>
</tbody>
</table>
Table 5
Summary of fitting parameters for the 1700 °C particle. This particle was fit to a Pd3Si structure. The second silicon path was likely not fit because it was merged in with the third silicon path due to their close distances.

<table>
<thead>
<tr>
<th>Path</th>
<th>Rmax (Å)</th>
<th>Rmin (Å) [1700 °C]</th>
<th>σ² (Å²) [1700 °C]</th>
<th>Nsc</th>
<th>Nsh [1700 °C]</th>
<th>Theory</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd0 → Si1 → Pd0</td>
<td>2.35</td>
<td>2.26 ± 0.02</td>
<td>0.005 ± 0.002</td>
<td>1</td>
<td>1.3 ± 0.2</td>
<td>Pd3Si</td>
</tr>
<tr>
<td>Pd0 → Si1 → Pd0</td>
<td>2.56</td>
<td>2.47 ± 0.03</td>
<td>0.007 ± 0.002</td>
<td>2</td>
<td>3.0 ± 0.3</td>
<td>Pd3Si</td>
</tr>
<tr>
<td>Pd0 → Pd4 → Pd0</td>
<td>2.85</td>
<td>2.74 ± 0.03</td>
<td>0.005 ± 0.001</td>
<td>6</td>
<td>2.5 ± 0.3</td>
<td>Pd3Si</td>
</tr>
<tr>
<td>Pd0 → Pd5 → Pd0</td>
<td>2.97</td>
<td>2.85 ± 0.03</td>
<td>0.014 ± 0.004</td>
<td>4</td>
<td>3.6 ± 0.8</td>
<td>Pd3Si</td>
</tr>
<tr>
<td>Pd0 → Pd6 → Pd0</td>
<td>3.56</td>
<td>3.42 ± 0.03</td>
<td>0.003 ± 0.003</td>
<td>1</td>
<td>1.3 ± 0.4</td>
<td>Pd3Si</td>
</tr>
</tbody>
</table>

Table 6
Summary of fitting parameters for the 1800 °C. This particle was fit to a Pd3Si structure.

<table>
<thead>
<tr>
<th>Path</th>
<th>Rmax (Å)</th>
<th>Rmin (Å) [1800 °C]</th>
<th>σ² (Å²) [1800 °C]</th>
<th>Nsc</th>
<th>Nsh [1800 °C]</th>
<th>Theory</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd0 → Si1 → Pd0</td>
<td>2.42</td>
<td>2.44 ± 0.04</td>
<td>0.008 ± 0.002</td>
<td>4</td>
<td>4.7 ± 0.7</td>
<td>Pd3Si</td>
</tr>
<tr>
<td>Pd0 → Pd1 → Pd0</td>
<td>2.84</td>
<td>2.87 ± 0.04</td>
<td>0.011 ± 0.002</td>
<td>6</td>
<td>5.9 ± 1.0</td>
<td>Pd3Si</td>
</tr>
<tr>
<td>Pd0 → Pd2 → Pd0</td>
<td>3.43</td>
<td>3.44 ± 0.06</td>
<td>0.003 ± 0.003</td>
<td>2</td>
<td>2.0 ± 0.4</td>
<td>Pd3Si</td>
</tr>
</tbody>
</table>

1.3 ± 0.2, which is within experimental error of the coordination in a perfect crystal of Pd3Si. A second Pd-Si bond was fit at 2.47 ± 0.03 Å with a coordination number of 3.0 ± 0.3. The increased coordination relative to that expected in Pd3Si is likely due to the presence of a small quantity of Pd3Si, as Pd3Si has a highly coordinated bond at a similar distance. Three Pd-Pd paths were fit at 2.74 ± 0.03 Å, 2.85 ± 0.03 Å, and 3.42 ± 0.03 Å, with coordination numbers of 2.5 ± 0.3, 3.6 ± 0.8, and 1.3 ± 0.4, respectively, as detailed in Table 5. Again, these coordination numbers are smaller than one would observe in a perfect Pd3Si crystal but do begin to approach the expected values [80]. We would expect to observe higher coordination at larger R upon heating due to recombination of defects and/or melting recrystallization, as compared with the as-irradiated material. The temperatures reached during safety-testing exceeded the melting points of Pd2Si and Pd3Si [81], so it would not be unrealistic to expect melting and recrystallization.

In the 1800 °C particle, the data fits well to Pd3Si. Pd-Si bonds at 2.44 ± 0.04 Å with coordination of 4.7 ± 0.7 are observed, with the coordination being slightly larger likely due to disorder. Pd-Pd bonds are observed at 2.87 ± 0.04 Å and 3.44 ± 0.06 Å, with coordinations of 5.9 ± 1.0 and 2.0 ± 0.4, respectively, as in Table 6. These coordination numbers and bond distances match well with theoretical values [80].

4. Discussion

4.1. Silver

The higher concentration of Ag observed via XRF in the 1700 °C safety-tested particle compared to the as-irradiated particle is expected, as the particle had high Ag retention post-irradiation due to gamma spectroscopy results. The comparison between the Ag foil and the Ag spectrum from the 1700 °C particle indicates that the Ag in the SiC fragment is of metallic character. The absorption edges of the Ag foil and Ag spectrum are aligned, as are the peaks after the absorption edge. If the Ag were to substitute for Si in the SiC lattice, it would be surrounded by four tetrahedral C atoms and therefore a carbon signature would be observed in both the edge position and post-edge oscillations. This has previously been observed in studies conducted on gallium implanted SiC [82]. On the other hand, it has been observed through a study on Pt-Ag/C nanoparticles that when Ag does not interact with C, it has a metallic signature with the foil and sample edges aligning [83]. Supplemental calculations using JFEFF and FEFF9 [71–73] for XAFS calculations based on ab-initio, self-consistent real-space multiple scattering theory, have been completed to further show the difference between metallic and non-metallic Ag XAFS spectra, shown in Fig. 9. Calculations were completed for an fcc Ag crystal to compare to experimental data to demonstrate the accuracy of the calculation. A second XAFS spectrum was calculated for a crystal with Ag substituted into a Si site in cubic 3C-SiC, where Ag would be interacting with four tetrahedral carbon atoms. There is a clear edge shift and change in post-edge oscillations observed in the calculated spectrum when Ag substitutes for Si within the SiC lattice, while the oscillations from the model fcc Ag crystal, the Ag in the SiC layer from the TRISO particle and the Ag foil were nearly identical. Both the experimental measurements and the calculated spectra clearly indicate that the experimental Ag spectrum is metallic rather than substitutional in the SiC layer.

It is possible to utilize XAFS to determine if the Ag in the sample is elemental or present in an alloy if the bond spacing changes according to Vegard’s Law [84–86]. In Fig. 3, it is clear that there are no observable changes in the spectrum until further out in energy. Because of the low Ag concentration, sufficient signal to noise ratio was not attainable at energies high enough above the edge to observe changes consistent with Vegard’s Law [85,86]. Therefore, it was not possible to determine if the Ag in the sample was elemental or an alloy with Pd. This information does not confirm the formation of a Pd/Ag alloy, which has previously been described as a potential diffusion mechanism in which Pd assists in the transport of Ag across the SiC layer [14,25,27]. The metallic character of the Ag does imply that Ag is not dissolved as atomic species inside the SiC lattice. To the best of our knowledge, metallic bonding of Ag has not previously been directly observed in the SiC layer of irradiated TRISO particles.

4.2. Palladium

The XRF data confirms the observed in-reactor performance of the SiC boundary layer of the TRISO fuels. The XRF data indicated the presence of fission products, actinides, and impurity species in the SiC layer of all three particles, even at the elevated temperatures used in safety testing. The sample heated to 1800 °C had less Pd than in the as-irradiated sample and the sample safety tested to 1700 °C. It is not clear if this represents an overall trend towards decreasing concentration of Pd or if this is representative of only these three specific samples. It would require further experimentation to be certain. However, it would not be surprising if this were a trend correlated with diffusion of Pd in SiC [8,58] or the formation of Pd-Si compounds. Their melting point is well below this temperature, and may affect how much Pd remains inside the SiC layer.

The Pd K-edge XAFS indicated the formation of silicides with
increasing temperature, specifically Pd2Si (in the 1800 °C particle) and Pd3Si (in the 1700 °C particle). The observed formation of silicides in all three samples supports a number of previous ex-situ experiment studies, which hypothesize that the reaction occurring between SiC and Pd is one of the following:

\[2\text{Pd} + \text{SiC} \rightarrow \text{Pd}_2\text{Si} + \text{C} \quad [18,28,46].\]

\[3\text{Pd} + \text{SiC} \rightarrow \text{Pd}_3\text{Si} + \text{C} \quad [28].\]

It is possible that this excess carbon is then picked up by the uranium to form uranium carbides. A carbon XAFS spectrum was not collected due to energy limitations of the beamline used in this study. However, results from the U L3-edge indicate uranium-carbide formation [87].

As described above, the Pd found in the SiC is not perfectly crystalline, and has some change in the number of each species of atom surrounding the Pd. This fall off in coordination is likely due to radiation damage or addition of fission product precipitates, resulting in smaller grains of perfect crystallinity in the material. This is commonly observed in XAFS on irradiated materials. High temperature heating during safety testing removes radiation damage and promotes crystalline precipitate structures. Furthermore, liquid phase formation in the Pd-Si-C ternary system [88] is expected during the 1700 °C and 1800 °C heating tests, that should result in new precipitates after solidification. Heating to 1800 °C is above the melting temperature of fission products, so upon cooling the precipitates have nearly completely recrystallized into Pd2Si, and thermal exposure has likely removed all vestiges of radiation damage in the Pd2Si.

Despite the reduced coordination and the observed decrease in radiation damage upon heating, it is clear that these three samples have palladium-silicides forming within the SiC matrix. From ongoing experimental studies, grain boundary diffusion of fission products is likely and indicate a non-uniform distribution of Pd and Ag within the SiC material. The heated specimen are much closer to predicted crystal structures than the as-irradiated particle. The as-irradiated particle showed the greatest amount of radiation damage. It has significant attenuation of all the expected peaks at high-R value. The as-irradiated particle also indicates the presence of both Pd2Si and Pd3Si. The Pd2Si and Pd3Si structures used to fit the Pd K-edges are the most stable -silicide phases due to the lower enthalpy of formation values, with ΔH (kJ/mol) of around −64.2 and −57.9, respectively [89]. Most prior simulation studies found the formation of Pd2Si or the combination of Pd2Si and Pd3Si, which is further supported by the Pd-Si-C phase diagram. It must be noted that the as-irradiated particle can also be fit to a U-Pd-Si [90,91] structure with an extra Pd-Si path. XAFS fitting indicates this is less likely than a palladium-silicide structure, but cannot completely be ruled out from the data. It has also been observed in the form UPd2Si2, UPd3Si2, or U-Pd-Ag in recent TEM studies [39–41].

Upon heating, the changing ratio of Pd2Si to Pd3Si with increasing temperature could be accounted for by a number of factors. The shift from one to the other may be due to microstructure or temperature. The melting point (1331 °C for Pd2Si and 1045 °C for Pd3Si) of the palladium silicides [81] are lower than the heating temperatures used in this study. Therefore, it is likely that localized melting occurred and recrystallization effects may play a role. The information obtained in this study has reconfirmed previous experimental observations [13,16–18] and theoretical predictions [46] on irradiated TRISO particles. In addition, the evolution of the material upon high temperature heating was studied. The knowledge that palladium silicides are formed, rather than carbides, is useful in determining the exact diffusion mechanism of Pd through SiC in TRISO particles at these elevated temperatures.

The speciation of Pd and Ag is now being used to help determine the transport of these metallic fission products in the SiC layer of TRISO fuels. Ag does not react with the silicon carbide barrier layer except for its known dissolution mechanism (Ag + 10 at% Si) [7,92]. This increases the likelihood that it will diffuse across the SiC because it is not greatly slowed by any physical or chemical bonding processes. Palladium forms palladium silicides, leaving behind free carbon. This interaction has been shown to reduce the integrity of the SiC by aiding in SiC degradation.

5. Conclusions

XAFS results indicate the formation of palladium silicides. The formation of palladium-silicides, in particular Pd2Si, was expected.  

Fig. 9. Plot of the FEFF9 calculation results of an Ag foil (purple line) compared to experimental data on an Ag foil (blue) and the calculated spectrum of Ag substituted into an Si lattice site in cubic SiC (green). The XAFS from the particle irradiated to 1700°C is included for reference (orange). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)
Ag was found in very low quantities and was only measurable in one sample. The data from this sample indicates the presence of metallic Ag, with no strong chemical bonding with either the silicon or carbon in the SiC layer of the TRISO particles. It is not clear from this work how the formation of these reaction products affects the structural integrity of the TRISO particles. However, fission product retention is observed in the particles heated to higher temperatures. At high temperatures, it appears defects are annealed out of the Pd$_3$Si. These measurements have provided key information on the fission product reactivity in the SiC layer of reactor fissioned TRISO fuels. Knowledge of these reaction pathways will allow for better simulation of the long-term behavior of TRISO fuels and may also suggest ways to modify TRISO particles to improve fuel performance.

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