Distribution of fission products palladium, silver, cerium and cesium in the un-corroded areas of the locally corroded SiC layer of a neutron irradiated TRISO fuel particle

Haiming Wen ^{a,b,*}, Isabella J. van Rooyen ^b

^a. Department of Physics, Nuclear and Electrical Engineering, Idaho State University, Idaho Falls, Idaho 83402, USA

^b. Fuel Design and Development Department, Idaho National Laboratory, Idaho Falls, Idaho 83415, USA

* Corresponding author. E-mail address: wenhaim@isu.edu

Abstract

Detailed electron microscopy studies were performed to investigate distribution and composition of fission products in the SiC layer of a tristructural-isotropic-coated particle exhibiting localized corrosion. Previous studies on this particle indicated that pure carbon areas in the SiC layer, resulting from localized corrosion of SiC by Pd, provide pathways for Ag, Cd, and Cs migration. This study reveals the presence of Ag- and/or Cd-containing precipitates in un-corroded SiC areas. Ag and Cd may exist by themselves or coexist with Pd. Ag and Cd mainly transport along SiC grain boundaries. An Ag-Pd-Cd precipitate was identified at a stacking fault inside a SiC grain, suggesting that intragranular transport of Ag and Cd is possible. Ce is present with Pd or Pd-U in some precipitates. U and Ce frequently coexist, whereas Ag and Cd usually do not coexist with U or Ce. No Cs was detected in any precipitates in the areas examined.

Keywords: TRISO particle; fission product; transport mechanism; neutron irradiation; electron microscopy

1. Introduction

Tristructural-isotropic (TRISO)-coated fuel particles have been designed for use in high temperature gas reactors (HTGR)^[1-3]. The fuel kernel is uranium oxide (UO₂) or uranium oxy-carbide (UCO), and the TRISO coating consists of four layers, including a porous carbon (C) buffer layer, a relatively dense inner pyrolytic carbon (IPyC) layer, a SiC layer, and an outer pyrolytic carbon (OPyC) layer^[1-3]. The SiC layer is the primary barrier for fission product (FP) transport. FP retention is a key property of TRISO coated particles^[4, 5].

Both historical in-reactor experiments^[6-8] and the first Advanced Gas Reactor experiment (AGR-1) at Idaho National Laboratory (INL)^[4, 5] indicated release of certain metallic FPs (e.g., Ag and Pd) across intact TRISO coatings. It is very important to understand the transport mechanisms of metallic FPs across the TRISO coating layers, since the release of radioactive FPs (especially ^{110m}Ag) is a potential worker safety concern. Grain boundary (GB) diffusion, Pd-assisted transport, neutron-enhanced diffusion and vapor-phase migration have been suggested as possible transport mechanisms for Ag, based on numerous studies in the past four decades^[9-13]. However, the Ag transport mechanisms remain unclear. Out-of-reactor experiments used experimental conditions or materials that are very different from real TRISO-coated particles^[14-17]. In simulations, the simulated materials and conditions are significantly different from the real ones^[18-22]. For reactor experiments, the concentrations of FPs are usually low and the sizes of FP precipitates can be extremely small, imposing significant challenges on experimental characterization^[23, 24]. However, the first direct identification of Ag-containing precipitates at SiC GBs of neutron-irradiated TRISO coated particles from the AGR-1 experiment has provided a benchmark to identify Ag in real irradiated TRISO-coated particles and potentially understand Ag transport mechanisms^[23, 24].

Pd is also an important metallic FP in TRISO-coated particles. In historical in-reactor experiments, SiC corrosion by Pd was postulated to be a failure mechanism in TRISO fuels^[25-27]. However, detailed post-irradiation examination (PIE) in AGR-1 indicated that locally elevated Pd concentration (which was induced by a crack in the IPyC layer) is a necessary condition for chemical reaction between Pd and SiC, and that without this condition, Pd migrates in the SiC layer via diffusion without chemically reacting with SiC^[28]. In addition, based on results from out-of-pile experiments, it was concluded that Pd assists Ag transport in SiC^[17, 29, 30]. However, these out-of-reactor experiments utilized Pd and Ag concentrations far greater than those in an actual TRISO particle. Thus, it is important to further study the role of Pd in Ag transport and the mechanism of Pd-assisted Ag transport in neutron-irradiated TRISO particles.

The current study follows a recent study that investigated FPs in carbon areas in the locally corroded SiC layer of a neutron-irradiated TRISO particle exhibiting high Ag and Cs release²⁸. This study is focused on FPs in the un-corroded SiC areas, with two primary objectives: first, to study the FP distribution in the SiC layer; second, to study FP transport mechanisms in the SiC layer, specifically in intact SiC areas, paying careful attention to possible relations among FPs. Transmission electron microscopy (TEM), and scanning transmission electron microscopy (STEM) coupled with energy dispersive X-ray spectroscopy (EDS) were used to carefully investigate the distribution, composition and structure of FPs (especially Pd and Ag).

2. Experimental Procedure

A TRISO-coated particle from Compact 5-2-3 of the AGR-1 experiment was studied. This compact was irradiated at Advanced Test Reactor at INL to an average burnup of 17.42% fissions per initial metal atom, with a time-averaged, volume-averaged temperature of 1,059°C

and an average fast fluence of 3.77×10^{21} n/cm². During PIE, gamma-activity measurements indicated that the fractional Cs and Ag releases for the selected TRISO particle were ~30% and ~85%, respectively^[31]. X-ray tomography performed on this particle revealed that there is a crack across the buffer layer and the IPyC layer; there is also degradation in the SiC layer, localized to one specific region connected to the IPyC crack tip^[31-33]. The TRISO particle was mounted in epoxy, then ground and polished to reveal the IPyC crack and the SiC-degraded region^[31, 32]. Scanning electron microscopy (SEM) confirmed the presence of the crack across the buffer layer and the IPyC layer that terminates at the IPyC-SiC interface^[31-33]. Pd accumulation is present at the crack tip at the IPyC-SiC interface, and a C-rich degraded region (corroded region) was identified in the SiC layer connected to the IPyC crack tip. More details about the TRISO particle can be found in references^[31-33].

TEM lamellae were sectioned via the focused ion beam (FIB) technique from the cross-section of the TRISO particle at different locations, both close to and far away from the IPyC crack^[33]. Figure 1 shows the cross-section of the TRISO particle and the location from which the TEM lamella examined in this study was extracted (the lamella was sectioned from a location in the SiC layer close to the IPyC crack tip). More details about the preparation of the TEM lamellae and the electron microscopy methods used in this study were described previously^[28, 33]. TEM, STEM, and EDS were conducted to study distribution, composition, and structure of FPs using an FEI Tecnai G2 TF30-FEG STwin microscope operating at 300 kV at the Center for Advanced Energy Studies (CAES) at the Idaho National Laboratory. The characteristic L-lines of Pd, K-lines of Ag, and L-lines of U were used in the compositional analysis by EDS to avoid the problem of overlapped peaks²⁸. 0.2 at.% is taken as the detection limit for Pd, Ag, Ce and Cs, and 0.1 at.% for U, which is consistent with other reports in the literature^[17, 24]. Only elements

with measured concentrations above these detection limit are reported in this study. For precipitates in the SiC layer, the exact Si concentrations in the precipitates cannot be determined because of the significant contribution of the SiC matrix to the measured EDS spectra of the precipitates. It should be noted that this study is only intended to establish whether Si is present in the precipitates, rather than to determine the exact Si content in them. A rough estimate of the Si concentration in the precipitates in the SiC layer can be obtained by subtracting the C concentration from the Si concentration in the EDS result, assuming that Si and C concentrations contributed by the SiC matrix to the EDS result are exactly identical; if the Si concentration is equal to or smaller than the C concentration in the EDS result, it can be interpreted that no Si exists in the precipitate. However, all the compositions presented in this article are raw data from EDS results, without the subtraction described above. Due to the limitations of the STEM-EDS technique utilized and the small sizes (usually <50 nm) of precipitates studied, the SiC matrix contribution to the EDS results of the precipitates in the SiC layer cannot be excluded. The definite presence or absence of Si in the precipitates needs to be verified by more accurate experimental techniques in composition measurement, such as atom probe tomography, which is an area of ongoing work being done by the authors. However, STEM-EDS has been widely utilized as a valid and useful semi-quantitative technique for composition measurement, and the STEM-EDS results obtained on the FP precipitates, as well as the conclusions based on the results, are believed to shed light on the compositions of FPs in the SiC layer of TRISO-coated particles.

Our previous STEM-EDS study identified pure carbon areas in the SiC layer in one localized region connected to the IPyC crack tip^[28, 33]. The pure carbon areas in the SiC layer result from a localized chemical reaction between Pd and SiC that is induced by localized

accumulation of Pd^[28]. During the reaction between Pd and SiC, pure carbon areas and Pd₂Si or PdSi are formed^[28, 33]. Pd₂Si, PdSi and Pd precipitates are present in the carbon areas (note that the Si concentrations in the precipitates in the carbon areas can be accurately determined due to absence of interference from SiC), and Ag and/or Cd were frequently identified in these precipitates^[28]. The reacted areas in the SiC layer are connected to the IPyC crack tip and provide pathways for Ag, Cd, and Cs migration^[28, 33]. The present study is focused on precipitates in the unreacted SiC areas in the SiC layer; note that these areas are also connected to the IPyC crack tip.

3. Results

3.1 Precipitates at SiC Grain Boundaries

Precipitates were frequently identified at GBs in the unreacted SiC areas. These precipitates may have different chemical compositions, even compared with precipitates located at the same or interconnecting GBs. Figures 2–5 demonstrate the distribution and compositions of the different types of precipitates located at SiC GBs in the unreacted SiC areas, and the relations among precipitates.

Figure 2 shows examples of precipitates at SiC GBs in the unreacted areas in the SiC layer that are connected to the IPyC crack tip. Figure 2(a) is a low-magnification STEM image showing the general distribution of precipitates; the yellow, black, red, and green rectangular areas in (a) are magnified in (b), (c), (d), and (e), respectively. Note that these areas are within ~1-2 μm from a pure carbon area, as indicated in (a). Figure 2(f) is a further magnification of the black rectangular area in (e). Precipitates indicated with arrows and numbered were subjected to

EDS point scan analyses, and the quantified compositions corresponding to the point scans are displayed in Table 1.

Ag/Cd containing precipitates include Precipitates 1 (Ag-Cd), 2 (Ag-Cd-Pd), 3 (Pd-Cd), 4 (Ag-Pd-Cd), 8 (Ag-Cd-Pd-Si), 11 (Pd-Ag), 22 (Pd-Si-Cd), and 23 (Pd-Si-Cd). These precipitate compositions indicate that Ag and/or Cd may be present with Pd, and that Ag-Cd may exist by themselves without Pd, as in Precipitate 1. The highest Ag concentration is 8.0 at.%, found in Precipitate 4, and the highest Cd concentration is 1.3 at.%, identified in Precipitate 23. There is a variation in Ag concentration even among interconnected precipitates. For example, Precipitates 8, 9, 10, and 11 are interconnected and located at the same GB; Precipitate 8 has a significant Ag concentration (4.2 at.%), and there is only a very low Ag concentration in Precipitate 11 (0.2 at.%), whereas Precipitates 9 and 10 have no Ag. Interconnected precipitates (e.g., Precipitates 22 and 23) may also have different Cd concentrations. The GB where Precipitates 1, 2, and 3 are located (hereafter referred to as GB A) has significant concentrations of Ag and Cd, suggesting that this GB may be beneficial for Ag and Cd diffusion. In contrast, the GB where Precipitate 5 and 6 are located (hereafter referred to as GB B) has no Ag or Cd, despite the fact that it intersects with GB A. GB B probably has different characteristics from GB A and is not beneficial for Ag or Cd transport. Precipitates that do not contain Ag or Cd are identified as Pd-Si, Pd, Pd-Si-U and Pd-U. The U concentrations in the majority of Pd-Si-U and Pd-U precipitates are much lower than the Pd concentrations. Precipitate 12 (Pd-U-Ce) has a U concentration (5.9 at.%) similar to the Pd concentration, representing the highest U concentration observed in precipitates in the present study. In addition, Precipitates 7 and 12 (both are Pd-U-Ce) have low concentrations of Ce (0.4 at.%). Note that the extremely small dark spots in Figure 2(f) are nano-

cavities in the SiC, introduced by neutron irradiation^[34, 35], which were not investigated in detail in this study.

Figure 3 shows more precipitates located at SiC GBs. Figure 3(a) is a low-magnification STEM image, and the red, yellow, white, and black rectangular areas in (a) are magnified in (b), (c), (f), and (g), respectively. The green and blue rectangular areas in (c) are further magnified in (d) and (e), respectively. Figure 3(h) is a further magnification of the purple rectangular area in (g). EDS point scan analyses were performed on precipitates indicated with arrows and numbered, with the corresponding quantified compositions displayed in Table 2.

Most precipitates are identified as Pd-U, Pd, and Pd-Si. Ag and/or Cd are observed in some Pd and Pd-Si precipitates, and precipitates primarily rich in Ag/Cd are also found. Ag/Cd-containing precipitates include the following ones: 1 (Cd-Pd), 4 (Cd-Pd), 5 (Pd-Cd), 7 (Pd-Cd-Ag), 8 (Pd-Cd-Ag), 9 (Pd-Cd), 10 (Pd-Cd-Ag), 11-12 (Cd-Pd-Ag), 24-26 (Pd-Cd), and 33 (Ag-Pd). Among these precipitates, Precipitate 33 is primarily rich in Ag, and Precipitates 1, 4, 11, and 12 are primarily rich in Cd. The highest Ag concentration is 5.5 at.% found in precipitate 33 (Ag-Pd), and the highest Cd concentration is 17.7 at.%, identified in Precipitate 11 (Cd-Pd-Ag). Notably, there is variation in Ag and Cd concentration, even among interconnected precipitates (e.g., Precipitates 7, 8, 9, and 10). All the Ag/Cd-containing precipitates are located at SiC GBs. Note that nine Ag/Cd-containing precipitates (Precipitates 1, 4, 5, and 7–12) are along connected GBs; these GBs have the highest frequency for finding Ag/Cd-containing precipitates. It is likely that these GB segments possess structures and properties that are beneficial for Ag/Cd transport. In all these Ag/Cd-containing precipitates, Ag/Cd coexist with Pd, and the Ag/Cd concentrations may be significantly higher than Pd concentrations (e.g., in Precipitates 4, 11, 12, and 33 [see Table 2]). Note that there is a small dark area adjacent to Precipitate 33, which has been

identified by Point Scans 27 and 28 as essentially carbon. This nanometer-sized carbon area was created by localized chemical reaction between Pd and SiC^[28, 33]. In addition, Ce-containing precipitates have been identified, with Ce concentrations between 0.3 and 1.0 at.%, including Precipitates 2, 6, 22, 23, and 34 that are all Pd-U-Ce, Precipitates 13 and 20 that are Pd-Ce-U, and Precipitate 31 that is Pd-Si-Ce. Therefore, Ce is associated with Pd-U or Pd, and Ce frequently coexists with U. That is, Ce has an affinity for U. In contrast, Ag/Cd does not coexist with U or Ce (i.e., U/Ce repels Ag/Cd). For the majority of precipitates containing Pd and U (Precipitates 2, 3, 6, 13, 20, 22, 23, 30, and 34), the U concentrations are much lower than the Pd concentrations. However, in Precipitates 2, 23, and 30, the U concentrations are close to or higher than half of the Pd concentrations, and in Precipitate 22, the U concentration is even higher than the Pd concentration. Furthermore, Precipitates 14–18 and 21 contain only Pd, without any Ag/Cd or U/Ce.

More precipitates located at SiC GBs are shown in Figure 4. Figure 4(a) is a low-magnification STEM image, and the yellow rectangular area in (a) is magnified in (b). The green and white rectangular areas in (b) are further magnified in (c) and (d), respectively. Precipitates indicated with arrows and numbered were subjected to EDS point scan analyses, and the corresponding quantified compositions are displayed in Table 3. Precipitate 1 is identified as Pd-U-Ce, with 2.7 at.% U and 0.5 at.% Ce. This precipitate is large, with a diameter of ~200 nm, and is located at a GB that has bright linear feature along the GB. According to EDS Point Scan 2 and an EDS line scan across the GB, the bright linear feature is Pd. More Ag/Cd-containing precipitates were identified. Precipitate 3 is Ag-Pd-Cd, with 9.1 at.% Ag and extremely low Pd and Cd concentrations. Note that both Precipitates 5 and 6 have low Ag concentrations; however, they contain only Ag. The low measured Ag concentrations may be due to the fact that these two

precipitates are very small and the SiC matrix contributes dominantly to the measured EDS compositions. The results indicated in Figure 4 further confirm that Ag and Cd may exist by themselves or coexist with Pd. It should be noted that EDS results on precipitates in all areas indicate that Ag and Cd mostly coexist with Pd, rather than existing by themselves.

Figure 5 displays more examples of precipitates located at SiC GBs. Figure 5(a) is a low-magnification STEM image, and the green, red, and white rectangular area in (a) are magnified in (b), (c), and (e), respectively. The yellow rectangular area in (b) is further magnified in (d). EDS point scan analyses were performed on precipitates indicated with arrows and numbered, with the corresponding quantified compositions displayed in Table 4. Ag/Cd-containing precipitates include Precipitates 3 (Cd-Pd-Ag), 7 (Pd-Cd-Ag), 8 (Pd-Cd), 9 (Pd-Cd), 14 (Pd-Cd), 20 (Pd-Si-Cd), and 21 (Pd-Cd-Ag). In all these Ag/Cd-containing precipitates, Ag and Cd coexist with Pd or Pd-Si. The highest Cd concentration is 9.9 at.%, found in Precipitate 3, which is Cd-Pd-Ag, and the highest Ag concentration is 2.6 at.%, also found in Precipitate 3. There is variation in Ag/Cd concentration in interconnected precipitates (e.g, Precipitates 7, 8, 9, and 10). It is evident that from Precipitate 7 to 10, the Ag/Cd concentrations monotonically decrease. Precipitates 20 and 21 are located at the same GB, suggesting that the GB may have characteristics that facilitate Ag/Cd transport. In addition, Ce-containing precipitates are identified, with Ce concentrations between 0.3 and 1.4 at.%, including Precipitates 1 (Pd-U-Ce), 4 (Pd-U-Ce), 5 (Pd-Ce-U), 6 (Pd-U-Ce), 11-13 (Pd-U-Ce), 17 (Pd-U-Ce), and 19 (Pd-Si-Ce-U). All these Ce-containing precipitates contain U. For U-containing precipitates, in addition to the Ce- and U-containing precipitates just described, there is one precipitate that contains U but not Ce, which is Precipitate 15 (Pd-U). Hence, U and Ce usually coexist with each other. Note that no precipitates that contain only U or Ce have been identified. Ce is associated with Pd-U or Pd,

and U is associated with Pd-Ce or Pd. The U- and/or Ce-containing precipitates (e.g., Precipitates 1, 2, 4, 11–13, and 17) are relatively large. Note that there is also variation in U/Ce concentration in interconnected precipitates (e.g., Precipitates 17 and 18; Precipitate 17 contains U and Ce, whereas Precipitate 18 contains only Pd without U or Ce). Overall, for precipitates at SiC GBs studied in Figure 5, Pd seldom exists by itself; instead, Pd frequently coexists with U and other FPs, such as Ce or Ag/Cd. Furthermore, from results shown in Figure 5, it is also concluded that Ag/Cd do not coexist with U or Ce.

3.2 Precipitates Inside SiC Grain Interiors

3.2.1 Pure Pd Precipitates Inside SiC Grain Interiors

Examples of intragranular precipitates studied are shown in Figure 6. A low-magnification STEM image is shown in (a), and the red, black, and green rectangular areas in (a) are magnified in (b), (d), and (e), respectively. The yellow rectangular area in (b) is further magnified in (c), and the white rectangular area in (e) is further magnified in (f). EDS point scan analyses were executed on precipitates indicated with arrows and numbered, with the corresponding quantified compositions shown in Table 5. The intragranular precipitates tend to be equiaxed, with diameters of <20 nm, and typically only a few nanometers. It was identified by EDS that all these intragranular precipitates are pure Pd. Some of them (e.g., Precipitates 1, 3, and 4) are located at stacking faults in the grain; others (e.g., Precipitates 9, 11, and 12) are located at twin boundaries in the grain. It should be noted that almost all precipitates inside SiC grain interiors are pure Pd, based on a large number of intragranular precipitates investigated. An exception is shown in Section 3.2.2. In addition, Figure 6 shows a high-number density of cavities with diameters of <5 nm are present inside the grain interiors. Some cavities align along numerous

stacking faults, as is evident in (b) and (c). However, some other cavities inside grain interiors do not align along stacking faults and are in random distribution, as seen in (d) and (e).

3.2.2 Ag-containing Precipitate at Stacking Fault Inside a SiC Grain

As described in Section 3.1, most Ag- or Cd-containing precipitates are located at SiC GBs. However, there is an exception. Figure 7 shows an Ag-Pd-Cd precipitate at a stacking fault inside a SiC grain. Figures 7(a) and (b) are STEM images showing the location of the Ag-Pd-Cd precipitate, and (b) is a magnification of the red rectangular area in (a). The composition of the precipitate was determined by EDS to be Ag-Pd-Cd; this is Precipitate 4 in Figure 2(b), and its composition is shown in Table 1. In Figure 7(b), it appears that the Ag-Pd-Cd precipitate is located at a boundary. However, in STEM, diffraction contrast is absent or very weak; accordingly, it is not easy to identify GBs, twin boundaries, or stacking faults. Consequently, the Ag-Pd-Cd precipitate needs to be investigated in TEM mode, where diffraction contrast is prevalent, to determine accurately its location relative to a possible boundary. Figure 7(c) is a TEM image of approximately the same area as Figure 7(b). From Figure 7(c), the Ag-Pd-Cd precipitate is actually located inside a SiC grain, and the GBs of the SiC grain are clearly identified. The red rectangular area in (c), enclosing the precipitate, is magnified in (d), where it appears that the precipitate is located at a stacking fault (the straight lines in [d] are stacking faults inside the SiC grain interiors). Figure 7(e) is a further magnification of the red rectangular area in (d) that encloses the Ag-Pd-Cd precipitate. It shows that the Ag-Pd-Cd precipitate is crystalline, although the lattice fringes are not evident, due to the fact that the resolution is limited and that the precipitate is not on a low-index zone axis. Figure 7(f) is a further magnification of the smaller red rectangular area in (d) where stacking faults are present; from

(d), the Ag-Pd-Cd precipitate is located at the upper-right stacking fault. Figure 7(g) is the inverse fast Fourier transform (IFFT) of the white square area in (f). In (g), the continuous lattice fringes across the stacking faults indicate absence of a GB or a twin boundary and confirm the presence of stacking faults. Therefore, it can be determined that the Ag-Pd-Cd precipitate is located at a stacking fault inside the SiC grain (see [c] and [d]).

3.3 Electron Diffraction on Large Precipitates in the SiC Layer

Limited selected-area electron diffraction (SAED) studies were performed on large precipitates to preliminarily study their structures. The diameter of the smallest selected-area aperture on the TEM microscope utilized in this study is ~190 nm. Consequently, accurate SAED can only be performed on precipitates with diameters of >190 nm, and approximate SAED results may also be obtained on precipitates with diameters slightly <190 nm. For precipitates that are significantly <190 nm, the diffraction signal from the SiC matrix significantly interferes with the diffraction patterns of the precipitates, which makes the SAED results hard to interpret. Note that most FP precipitates are too small for performing SAED.

Figure 8 shows the SAED results obtained on three large precipitates. Figure 8(a) is a low-magnification TEM image showing precipitates. The red and green rectangular areas in (a) are magnified in (b) and (c), respectively. The large precipitate displayed in (b) was identified by EDS in STEM as Pd-U with a small concentration of Ce (see EDS Point Scans 11–13 in Figure 5 and the corresponding compositions in Table 4). SAED was performed on the blue circle in Figure 8(b), and the corresponding diffraction pattern is presented in the inset. The amorphous ring in the diffraction pattern of this precipitate indicates that the precipitate is amorphous. The large precipitate in (c) was identified by EDS in STEM as Pd-Si. SAED was performed on the

blue circle, with the corresponding diffraction pattern presented in the inset. Interestingly, there are both amorphous ring and diffraction spots in the diffraction pattern of this precipitate, suggesting that the precipitate is semi-crystalline. Figure 8(d) is a TEM image of another large precipitate, which was identified by STEM-EDS as Pd-U with a small concentration of Ce (see EDS Point Scans 1 and 2 in Figure 5 and the corresponding compositions in Table 4). SAED was performed on the blue, white and red circles, and the corresponding diffraction patterns are displayed in (d1), (d2), and (d3), respectively. From the diffraction patterns, notably, the lower left part of the precipitate is amorphous, whereas the upper right part is semi-crystalline. Therefore, there is variation in structure in a single precipitate (or interconnected precipitates). This is in agreement with findings obtained using high-resolution TEM on a TRISO particle from Compact 131^[36]. It is evident that the structures of FP precipitates are complex, and that precipitates having similar or identical compositions may have different structures. These unique phenomena may be attributed to the non-equilibrium state and to the high density of defects generated during neutron irradiation.

4. Discussion

4.1 Pd Transport

The results of the present study indicate that Pd-U, Pd-Si, and Pd-Si-U precipitates are all located at SiC GBs, and that pure Pd precipitates are present at SiC GBs and inside SiC grain interiors, as shown in Figures 2–6 and associated Tables 1–5. The migration of Pd in SiC is well known^[6, 8, 13, 29, 37, 38], and the diffusion coefficient of Pd in SiC is relatively high^[39, 40]. It is likely that both the lattice diffusion and GB diffusion coefficients are significant; accordingly, both lattice diffusion and GB diffusion are becoming significant for Pd transport in SiC around

1,000°C. In addition, neutron irradiation is anticipated to have significantly enhanced the diffusion, owing to high concentrations of defects generated in far excess of thermal equilibrium values^[13, 41]. It is noted that Pd precipitates at SiC GBs are usually significantly larger than those inside SiC grains (Figures 2–6 and associated Tables 1–5), possibly due to the faster GB diffusion compared with lattice diffusion^[42, 43].

In the TRISO particle investigated in this study, palladium silicides (Pd_2Si and PdSi) were previously found in the carbon “channel” in the SiC layer, created by the chemical reaction between Pd and SiC²⁸. In the regions in the SiC layer that are connected to the IPyC crack and contain the carbon “channel,” the Pd-Si observed in the unreacted SiC areas are from the Pd-Si in the pure carbon areas. For example, Figure 2 shows that Precipitates 14–20 (located in the red and green rectangular areas in Fig. 2[a]), which are identified as containing Si, are ~2 μm away from the pure carbon area (with Pd-Si in it) in the bottom of Figure 2(a). It is likely that Pd-Si have migrated from the pure carbon area to the red and green rectangular areas. In regions in the SiC layer away from the IPyC crack of this TRISO particle, or in the SiC layers of TRISO particles from other compacts, there are not significant chemical reactions between Pd and SiC in the SiC layer. Accordingly, there are no pure carbon areas or accompanying palladium silicides created in the SiC layer; however, Pd-Si was still identified^[28, 33, 44]. Limited chemical reactions between Pd and SiC may occur at the IPyC-SiC interface where Pd accumulates to some extent, creating Pd-Si. The Pd-Si created at the IPyC-SiC interface may migrate into the SiC layer; thus, Pd-Si is present in the SiC layer. The above interpretation for the presence of Pd-Si in the SiC layer is consistent with the experimental observations that the interfaces between Pd-Si and the SiC matrix are intact without any sign of a reaction layer (Figures 2–5 and associated Tables 1–4).

4.2 Ag Transport Mechanisms

Our previous study indicated that in the particular TRISO particle investigated, in the regions in the SiC layer that are connected to the IPyC crack and contain the carbon “channel,” the carbon areas provide pathways for Ag transport^[28, 33]. Ag partitions to palladium silicides and Pd in the carbon areas, and the palladium silicides and Pd may assist Ag transport through the carbon areas and across the SiC layer; in addition, Ag and Pd migrate through nanocracks in the carbon areas^[28]. The present study indicates that Ag containing precipitates are present in the unreacted SiC areas outside the carbon “channel” (Figures 2–5 and associated Tables 1–4), and that Ag also migrates through the unreacted SiC areas; the mechanisms for this migration are anticipated to be similar to those for Ag transport in the SiC layer in other TRISO particles without localized SiC corrosion, for example, grain boundary diffusion^[15-17, 19, 45-48], neutron-enhanced diffusion^[13, 41, 49], Pd-assisted transport^[17, 24, 29, 30], and vapor-phase migration^[6, 14, 21].

In this study, Cd is found to frequently coexist with Ag (Figures 2–5 and associated Tables 1–4). Cd is also a direct fission product, and can also be from Ag decay^[12]. Of the Ag/Cd-containing precipitates identified in this study, >90% contain Pd. That is, Ag and Cd usually coexist with Pd, although they can exist by themselves (e.g. Precipitate 1 in Table 1, and Precipitates 5 and 6 in Table 3). This phenomenon suggests that Pd assists Ag/Cd transport. Previous studies have reported that Pd may assist Ag transport^[17, 29]. The diffusivity of Pd in SiC is higher than that of Ag^[39, 40], and by partitioning to Pd, the diffusion of Ag may be enhanced. Ag and Pd have identical fcc crystal structure, and the lattice constants are very similar. From the Pd-Ag phase diagram, Ag can be dissolved in Pd at ~1,000°C, forming a Pd-Ag solid solution^[50]. During diffusion, an Ag atom may be bound with a Pd atom, which then migrates in the form of

Pd-Ag atom pair, and the diffusion of the Pd-Ag pair may be more rapid than that of Ag alone. However, this speculation needs to be confirmed with atomic-scale modeling and simulation.

The results of this study indicate that Ag containing precipitates are predominantly observed at GBs (Figures 2–5 and associated Tables 1–4), and that GB diffusion is an operative mechanism for Ag transport. In addition, different GBs (even adjacent or intersecting GBs) behave differently in Ag transport (Figures 2–3 and associated Tables 1–2), probably due to their different crystallographic characteristics, although the GB characteristics are not investigated in the present study. Furthermore, the presence of an Ag-Pd-Cd precipitate at a stacking fault inside a SiC grain (Figure 7) suggests that intragranular transport of Ag is also a possible mechanism for Ag transport, although the intragranular migration rarely occurs. It is likely that the lattice diffusivity of Ag in SiC is distinctly lower than the GB diffusivity^[15, 19, 48], and accordingly, GB diffusion is predominant. However, the neutron irradiation creates high concentrations of defects in the lattice, which significantly enhance the lattice diffusion^[13, 41]. Hence, the lattice diffusivity of Ag in SiC may become significant. Note that the Ag-containing precipitate inside the SiC grain also contains Pd, suggesting that Pd may also have played a role in enabling Ag intragranular transport. Furthermore, the intragranular Ag-Pd-Cd precipitate is located at a stacking fault, suggesting that intragranular transport of Ag occurs via relatively high-energy pathways, as stacking faults have higher energy than lattice sites and high-energy pathways have lower activation energy for diffusion^[42, 43].

4.3 Ce Transport

The diffusivity of Ce in SiC is anticipated to be low, based on the very low release of Ce from TRISO fuels^[4, 5]. Note that even for this TRISO particle with local SiC corrosion, there was

no detectable Ce release^[31, 32]. Our previous study²⁸ indicated that very small Ce concentrations are found in some palladium silicides, in the pure carbon areas in the SiC layer, and therefore, the palladium silicides may also assist Ce transport. In addition, Ce and U usually coexist in palladium silicides in the pure carbon areas, and U and Ce both have small concentrations in all U/Ce-containing palladium silicides. Furthermore, Ag and Cd usually do not coexist with U or Ce. The present study indicates that Ce-containing precipitates with low Ce concentrations (usually <1 at.%; e.g., Precipitates 7 and 12 in Table 1, and Precipitates 2, 6, 13, 20, 23, and 34 in Table 2) are present in the unreacted SiC areas outside the carbon “channel” . These precipitates are anticipated to be from the carbon “channel.” All Ce-containing precipitates in the unreacted SiC areas are primarily rich in Pd, and no precipitates containing only Ce were observed. Hence, Ce does not migrate alone in the unreacted SiC areas, and it has to partition to FP precipitates primarily rich in Pd, migrating with the assistance of Pd. In addition, only a very small concentration of Ce appears to be able to partition to an individual FP precipitate. Ce in the unreacted SiC areas also frequently coexists with U, whereas Ce/U does not coexist with Ag/Cd. The mechanisms for these two observations are unknown.

4.4 U Transport

U-containing precipitates, including Pd-Si-U and Pd-U, are identified in the unreacted SiC areas (Figures 2–5 and associated Tables 1–4). For the majority of Pd-Si-U and Pd-U precipitates, the U concentrations are much lower than the Pd concentrations. In our previous study, Pd-Si-U precipitates were identified in the IPyC layer in areas that are close to the IPyC-SiC interface, and the U concentrations in the precipitates are <20% of Pd concentrations^[28, 33]. Pd₂Si₂U precipitates were reported to be present at the IPyC-SiC interface and in the IPyC layer in a TRISO particle from Compact 6-3-2^[10, 23]. The U to Pd ratio observed for Pd-Si-U

precipitates in the IPyC and SiC layers in the TRISO particle investigated in the present study is usually much smaller than the U to Pd ratio (1:2) in $\text{Pd}_2\text{Si}_2\text{U}$; therefore, these Pd-Si-U precipitates do not appear to be $\text{Pd}_2\text{Si}_2\text{U}$.

The mechanisms for the presence of Pd-U and Pd-Si-U precipitates in the SiC layer were not understood, despite the fact that such precipitates were reported in a previous study^[44]. The U is anticipated to be from the fuel kernel, where a mixture of UC and UO_2 is located. From STEM-EDS results on TEM lamella sectioned from the buffer layer (not shown here), an extremely high number density of U-rich precipitates is present in the buffer layer, suggesting that U from the fuel kernel can significantly migrate to the buffer layer. The U-rich precipitates in the buffer layer migrate further into IPyC layer. STEM-EDS results on TEM lamellae cut from the IPyC layer indicate that precipitates beyond several microns away from the IPyC-SiC interface are rich in U, whereas precipitates close to the IPyC-SiC interface are mostly Pd-Si or Pd-Si-U with small concentrations of U^[28, 33]. Since SiC is a much stronger barrier to U diffusion compared with carbon, the migration of U is slowed down when reaching the IPyC-SiC interface; accordingly, there is an accumulation, and therefore, increased concentration of U at the interface. It appears that Pd and U at the IPyC-SiC interface react with SiC to form Pd-Si-U, and the created Pd-Si-U precipitates migrate toward the SiC layer or toward the IPyC layer. Hence, Pd-Si-U precipitates are present in the SiC layer. Not all U at the IPyC-SiC interface reacts with Pd and SiC to form Pd-Si-U precipitates, leaving some U available to directly migrate into the SiC layer. Since the U diffusivity in SiC is anticipated to be much smaller than the Pd diffusivity based on the large atomic radius of U (U diffusivity in SiC is not available in the literature), U may partition to Pd, and migrate in the form of a Pd-U atom-pair or complex, which has enhanced diffusivity compared with U alone. From the Pd-U phase diagram^[51], small

concentration of U can be dissolved in Pd. That is, Pd-U is formed, and Pd assists the transport of U. Note that Pd-U is not observed in the IPyC layer^[28, 33], possibly because the diffusivity of U in carbon is not dramatically lower than that of Pd and accordingly U migrates in carbon without assistance of Pd.

The migration distance of Pd-Si-U or Pd-U precipitates in the SiC layer is usually limited due to the limited diffusivity, and the number of Pd-Si-U or Pd-U precipitates decreases with increasing distance from the IPyC-SiC interface^[44]. All Pd-Si-U and Pd-U precipitates in the SiC layer are observed at GBs (Figures 2–5 and associated Tables 1–4). The lattice diffusivity of U in SiC is anticipated to be dramatically lower than the GB diffusivity, and even with the assistance of Pd, the lattice diffusivity of Pd-Si-U and Pd-U in SiC is still expected to be low. Hence, GB diffusion of Pd-Si-U and Pd-U precipitates in the SiC layer is anticipated to be predominant over lattice diffusion. It is noted that in some cases, Pd-U or even U alone is found almost across the entire SiC layer^[44], suggesting that the diffusivity of U in the SiC is enhanced by the specific irradiation condition or certain microstructural characteristics of SiC.

5. Summary and Conclusions

In this study, detailed TEM and STEM-EDS were performed to investigate the distribution and composition of FP precipitates in the un-corroded SiC areas in the locally corroded SiC layer with a carbon “channel” of a neutron-irradiated TRISO-coated particle. The study was focused on U and FPs Ag, Pd, Cd, and Ce. The following conclusions have been drawn:

- Ag- and/or Cd-containing precipitates are present in the un-corroded SiC areas that are close to the corroded SiC areas. Ag/Cd also migrates through the un-corroded SiC areas. Ag/Cd may exist by themselves or coexist with Pd.

- Most of the Ag/Cd-containing precipitates contain Pd. That is, Ag/Cd usually co-exist with Pd, and Pd assists Ag/Cd transport.
- Most Ag/Cd-containing precipitates are located at SiC GBs, indicating that Ag/Cd predominantly transports along GBs. Different GBs behave differently in Ag/Cd transport.
- An Ag-Pd-Cd precipitate was identified at a stacking fault inside a SiC grain, indicating that intragranular transport of Ag/Cd is also a possible transport mechanism, although the intragranular migration rarely occurs.
- Precipitates in the SiC layer are mostly Pd, Pd-Si, Pd-U, and Pd-Si-U. Pd precipitates are present at both SiC GBs and inside SiC grain interiors, and Pd precipitates at SiC GBs are usually significantly larger than those inside SiC grains. Pd-Si, Pd-U, and Pd-Si-U precipitates are all located at SiC GBs. Pd-Si in the unreacted SiC areas are from the Pd-Si created in the carbon “channel” or at the IPyC-SiC interface.
- For a majority of Pd-Si-U and Pd-U precipitates, the U concentrations are much lower than the Pd concentrations. Pd-Si-U precipitates in the un-corroded SiC areas are from Pd-Si-U created at the IPyC-SiC interface, where Pd and U with locally elevated concentrations react with SiC to form Pd-Si-U. Unreacted U at the IPyC-SiC interface migrates into the SiC layer together with Pd. That is, Pd assists the transport of U. All Pd-Si-U and Pd-U precipitates in the SiC layer are observed at GBs.
- Some of the Pd-rich precipitates (especially large ones) contain small concentrations of Ce. Ce frequently coexists with U in Pd-rich precipitates. No precipitates containing only Ce were observed. Ce migrates in the unreacted SiC areas only with the assistance of Pd.
- Ag/Cd do not coexist with U or Ce.

- FP precipitates in the SiC layer can be crystalline, semi-crystalline, amorphous, or partly amorphous and partly semi-crystalline, owing to the non-equilibrium state and to the high density of defects generated during neutron irradiation.
- No Cs was detected in any precipitates in the areas examined.

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Figure Captions

Figure 1. SEM images of the cross section of the studied TRISO-coated particle. The TEM lamella examined was extracted from a location in the SiC layer close to the IPyC crack tip.

Figure 2. Precipitates at SiC grain boundaries in unreacted SiC areas. EDS point scans were performed on spots indicated by arrows and circles, and the quantified compositions corresponding to the point scans are displayed in Table 1. Precipitates are mostly identified as Pd-Si-U, Pd-Si, Pd-U, and Pd. Ag and/or Cd are observed in some Pd and Pd-Si. Precipitates primarily rich in Ag are found (Precipitates 1, 2, 4, and 8). Ag and Cd can also exist by themselves.

Figure 3. Precipitates at SiC grain boundaries in unreacted SiC areas. EDS point scans were performed on spots indicated by arrows and circles, and the quantified compositions corresponding to the point scans are displayed in Table 2. Precipitates are mostly identified as Pd-U, Pd, and Pd-Si. Ag and/or Cd are observed in some Pd and Pd-Si. Precipitates primarily rich in Cd are found (Precipitates 1, 4, 11, and 12). Ce is found in some Pd-U and one Pd-Si precipitate. Ce is mostly associated with Pd and U. Ag/Cd do not coexist with U or Ce.

Figure 4. Precipitates at SiC grain boundaries in unreacted SiC areas. EDS point scans were performed on spots indicated by arrows and circles, and the quantified compositions corresponding to the point scans are displayed in Table 3. Precipitate 3 is primarily rich in Ag, with small Pd and Cd concentrations. Ag can exist by itself (Precipitates 5 and 6), or coexist with Pd (Precipitate 3).

Figure 5. Precipitates at SiC grain boundaries in unreacted SiC areas. EDS point scans were performed on spots indicated by arrows and circles, and the quantified compositions corresponding to the point scans are displayed in Table 4. Precipitates are mostly identified as Pd-U, Pd, and Pd-Si. Ag and/or Cd are observed in some Pd and Pd-Si. Precipitates primarily rich in Cd are found (Precipitate 1). Ce is found in most Pd-U and one Pd-Si precipitates. All Ce is associated with Pd and U. Ag/Cd do not coexist with U or Ce.

Figure 6. Precipitates inside SiC grain interiors in unreacted SiC areas. EDS point scans were performed on spots indicated by arrows and circles, and the quantified compositions corresponding to the point scans are displayed in Table 5. Precipitates are all identified as Pd.

Figure 7. An Ag-Pd-Cd precipitate at a stacking fault inside a SiC grain. (a and b) STEM image showing the location of the Ag-Pd-Cd precipitate, the composition of which was determined by EDS; (c) TEM image corresponding to (b); (d) a magnification of the red rectangle in (c); (e) a magnification of the red rectangle in (d) where the Ag-Pd-Cd precipitate is located; (f) a magnification of the red rectangle in (d) where stacking faults are present; (g) inverse fast Fourier transform of the white square in (f), where the continuous lattice fringes indicate absence of grain boundary and confirm the presence of stacking faults.

Figure 8. Selected-area electron diffraction on precipitates. (a) A low-magnification TEM image; (b) a magnification of the red rectangle in (a), with diffraction performed on the blue circle and the corresponding diffraction pattern presented in the inset; (c) a magnification of the

green rectangle in (a), with diffraction performed on the blue circle and the corresponding diffraction pattern presented in the inset; (d) TEM image of another precipitate, with diffraction performed on the blue, white, and red circles and the corresponding diffraction patterns presented in (d1), (d2), and (d3), respectively. Precipitate in (b) and (d) are Pd-U with small Ce concentrations, and precipitate in (c) is Pd-Si, as determined by EDS in STEM. From the diffraction patterns, precipitate in (b) is amorphous, and precipitate in (c) is semi-crystalline; for precipitate in (d), the lower left part is amorphous, whereas the upper right part is semi-crystalline.

Table 1. Quantified compositions corresponding to the EDS point scans in Figure 2.

Concentration (at.%)	C	O	Si	U	Pd	Cs	Ce	Ag	Cd	I	Sr	Precipitate Identification
Point Scan 1	47.3	0.8	49.5	—	—	—	—	1.8	0.4	—	—	Ag-Cd
Point Scan 2	46.0	—	51.0	—	0.8	—	—	1.5	0.4	—	—	Ag-Cd-Pd
Point Scan 3	49.8	0.7	47.4	—	1.4	—	—	—	0.7	—	—	Pd-Cd
Point Scan 4	41.3	0.8	47.3	—	2.0	—	—	8.0	0.6	—	—	Ag-Pd-Cd
Point Scan 5	48.0	0.5	46.6	—	4.5	—	—	—	—	—	0.4	Pd
Point Scan 6	46.3	0.6	43.8	0.1	9.0	—	—	—	—	—	—	Pd-U
Point Scan 7	56.3	0.5	29.1	3.8	9.8	—	0.4	—	—	—	—	Pd-U-Ce
Point Scan 8	34.8	0.8	59.1	—	0.9	—	—	4.2	0.2	—	—	Ag-Cd-Pd-Si
Point Scan 9	34.5	—	56.0	—	8.7	—	—	—	—	—	0.3	Pd-Si
Point Scan 10	40.0	—	49.5	—	10.1	—	—	—	—	—	—	Pd-Si
Point Scan 11	43.9	—	39.0	—	16.3	—	—	0.2	—	—	—	Pd-Ag
Point Scan 12	57.7	0.5	29.3	5.9	6.1	—	0.4	—	—	—	—	Pd-U-Ce
Point Scan 13	44.9	0.7	49.1	—	5.0	—	—	—	—	—	0.2	Pd
Point Scan 14	37.9	1.6	50.6	—	9.8	—	—	—	—	—	—	Pd-Si
Point Scan 15	40.0	—	56.7	0.1	2.7	—	—	—	—	—	—	Pd-Si-U
Point Scan 16 [#]	44.4	1.2	49.3	—	5.0	—	—	—	—	—	—	Pd-Si
Point Scan 17	39.1	—	50.9	1.5	8.1	—	—	—	—	—	—	Pd-Si-U
Point Scan 18	41.8	—	51.6	—	6.2	—	—	—	—	—	—	Pd-Si
Point Scan 19	45.3	0.8	50.3	—	3.2	—	—	—	—	—	0.2	Pd-Si
Point Scan 20	41.7	—	52.2	0.3	5.2	—	—	—	—	—	—	Pd-Si-U
Point Scan 21	51.2	0.7	45.3	0.1	2.5	—	—	—	—	—	—	Pd-U
Point Scan 22	46.4	1.3	47.8	—	3.8	—	—	—	0.8	—	—	Pd-Si-Cd
Point Scan 23	41.4	—	52.5	—	4.4	—	—	—	1.3	—	—	Pd-Si-Cd

[#]Precipitate 16 is inside grain interior. All the other precipitates are at grain boundaries. 0.2 at.% is taken as the detection limit for Ag, Pd, Ce, and Cs, and 0.1 at.% is taken for U. Only elements with measured concentrations above the detection limit are reported. “—” indicates that the concentration of the element is below the detection limit.

Table 2. Quantified compositions corresponding to the EDS point scans in Figure 3.

Concentration (at.%)	C	O	Si	U	Pd	Cs	Ce	Ag	Cd	I	Sr	Te	Precipitate Identification
Point Scan 1	69.1	0.7	24.8	—	2.4	—	—	—	2.9	—	—	—	Cd-Pd
Point Scan 2	61.1	—	37.5	0.4	0.7	—	0.3	—	—	—	—	—	Pd-U-Ce
Point Scan 3	61.5	—	30.6	1.0	6.4	—	—	—	—	—	0.4	—	Pd-U
Point Scan 4	66.4	0.5	29.0	—	0.7	—	—	—	2.8	—	—	0.5	Cd-Pd
Point Scan 5	58.2	0.8	28.4	—	6.3	—	—	—	6.0	—	—	—	Pd-Cd
Point Scan 6	38.7	1.4	32.1	1.6	24.8	—	1.1	—	—	—	0.2	—	Pd-U-Ce
Point Scan 7	51.2	—	19.0	—	16.0	—	—	0.9	12.7	—	—	—	Pd-Cd-Ag
Point Scan 8	48.0	—	9.2	—	25.5	—	—	1.4	15.8	—	—	—	Pd-Cd-Ag
Point Scan 9	47.7	0.6	20.4	—	22.8	—	—	—	8.2	—	—	—	Pd-Cd
Point Scan 10	57.1	—	12.5	—	21.8	—	—	1.2	7.1	—	—	—	Pd-Cd-Ag
Point Scan 11	54.6	—	20.8	—	5.7	—	—	1.1	17.7	—	—	—	Cd-Pd-Ag
Point Scan 12	63.7	0.5	18.2	—	3.4	—	—	1.4	11.9	—	—	0.8	Cd-Pd-Ag
Point Scan 13	65.9	—	25.5	0.5	6.9	—	0.7	—	—	—	0.3	—	Pd-Ce-U
Point Scan 14	55.9	—	37.0	—	6.0	—	—	—	—	—	—	1.0	Pd
Point Scan 15	64.0	—	28.8	—	7.1	—	—	—	—	—	—	—	Pd
Point Scan 16	66.5	0.6	26.2	—	6.7	—	—	—	—	—	—	—	Pd
Point Scan 17	64.9	—	26.6	—	8.3	—	—	—	—	—	—	—	Pd
Point Scan 18	54.6	—	35.4	—	9.7	—	—	—	—	—	—	—	Pd
Point Scan 19 [#]	53.6	—	38.4	—	8.0	—	—	—	—	—	—	—	Pd
Point Scan 20	61.4	0.9	29.3	0.3	7.5	—	0.5	—	—	—	—	—	Pd-Ce-U
Point Scan 21	71.1	—	22.2	—	6.5	—	—	—	—	—	—	—	Pd
Point Scan 22	63.2	—	30.1	3.6	2.7	—	0.3	—	—	—	—	—	U-Pd-Ce
Point Scan 23	70.0	—	23.7	1.8	3.9	—	0.5	—	—	—	0.2	—	Pd-U-Ce
Point Scan 24	62.4	—	17.7	—	14.5	—	—	—	5.3	—	—	0.2	Pd-Cd
Point Scan 25	71.3	0.8	24.2	—	2.2	—	—	—	1.5	—	—	—	Pd-Cd
Point Scan 26 ^{##}	65.7	—	27.6	—	6.5	—	—	—	—	—	—	—	Pd-Cd
Point Scan 27	88.4	—	11.3	—	—	—	—	—	—	—	—	—	C
Point Scan 28	88.4	—	11.5	—	—	—	—	—	—	—	—	—	C
Point Scan 29 [#]	69.1	—	24.5	—	6.3	—	—	—	—	—	—	—	Pd
Point Scan 30	72.7	—	20.8	2.1	4.0	—	—	—	—	—	—	—	Pd-U
Point Scan 31	38.1	—	54.3	—	6.9	—	0.4	—	—	—	0.4	—	Pd-Si-Ce
Point Scan 32	19.4	1.0	68.1	0.1	10.0	—	—	—	—	0.3	—	0.8	Pd-Si
Point Scan 33	49.7	—	43.1	—	1.5	—	—	5.5	—	—	—	—	Ag-Pd
Point Scan 34	50.1	—	41.1	1.2	6.8	—	0.5	—	—	—	—	—	Pd-U-Ce

^{##}Cd peaks are present in the EDS spectrum of Precipitate 26, although the compositions automatically quantified by the EDS software do not include Cd. It is interpreted that Precipitate 26 contains Cd.

[#]Precipitate 19 and 29 are inside grain interiors. All the other precipitates are at grain boundaries. 0.2 at.% is taken as the detection limit for Ag, Pd, Ce, and Cs, and 0.1 at.% is taken for U. Only elements with measured concentrations above the detection limit are reported. “—” indicates that the concentration of the element is below the detection limit.

Table 3. Quantified compositions corresponding to the EDS point scans in Figure 4.

Concentration (at.%)	C	O	Si	U	Pd	Cs	Ce	Ag	Cd	I	Sr	Te	Precipitate Identification
Point Scan 1	45.1	–	28.8	2.7	22.9	–	0.5	–	–	–	–	–	Pd-U-Ce
Point Scan 2	62.0	–	31.3	–	6.7	–	–	–	–	–	–	–	Pd
Point Scan 3	57.3	0.9	32.0	–	0.4	–	–	9.1	0.4	–	–	–	Ag-Pd-Cd
Point Scan 4	74.4	–	23.0	–	2.0	–	–	–	–	–	0.3	–	Pd
Point Scan 5*	90.6	–	9.0	–	–	–	–	–	–	–	–	–	Ag
Point Scan 6	66.7	0.7	31.5	–	–	–	–	0.9	–	–	–	–	Ag

*Ag peaks with high intensities are present in the EDS spectrum, although the compositions automatically quantified by the EDS software do not include Ag. It is interpreted that Precipitate 5 contains very significant Ag concentration. 0.2 at.% is taken as the detection limit for Ag, Pd, Ce, and Cs, and 0.1 at.% is taken for U. Only elements with measured concentrations above the detection limit are reported. “–” indicates that the concentration of the element is below the detection limit.

Table 4. Quantified compositions corresponding to the EDS point scans in Figure 5.

Concentration (at.%)	C	O	Si	U	Pd	Cs	Ce	Ag	Cd	I	Sr	Te	Precipitate Identification
Point Scan 1	62.9	0.5	18.7	5.9	11.7	–	0.3	–	–	–	–	–	Pd-U-Ce
Point Scan 2	68.3	–	18.2	3.7	8.7	0.4	–	–	–	–	0.2	–	Pd-U-Cs
Point Scan 3	70.5	5.4	6.7	–	4.8	–	–	2.6	9.9	–	–	–	Cd-Pd-Ag
Point Scan 4	65.9	1.6	22.1	4.2	5.4	–	0.9	–	–	–	–	–	Pd-U-Ce
Point Scan 5	11.9	–	71.7	0.2	14.4	–	1.4	–	–	–	0.5	–	Pd-Ce-U
Point Scan 6	64.0	1.5	24.2	4.4	4.7	–	1.1	–	–	–	–	–	Pd-U-Ce
Point Scan 7	58.9	–	22.8	–	11.1	–	–	1.2	5.9	–	–	–	Pd-Cd-Ag
Point Scan 8	52.4	–	20.0	–	24.5	–	–	–	2.6	–	0.4	–	Pd-Cd
Point Scan 9	51.1	–	24.8	–	23.2	–	–	–	0.3	–	0.4	–	Pd-Cd
Point Scan 10	56.1	–	24.6	–	18.8	–	–	–	–	–	0.2	–	Pd
Point Scan 11	58.3	1.2	24.9	3.4	11.5	–	0.7	–	–	–	–	–	Pd-U-Ce
Point Scan 12	41.7	1.0	24.7	4.0	27.8	–	0.7	–	–	–	–	–	Pd-U-Ce
Point Scan 13	45.5	0.9	40.4	1.2	11.4	–	0.5	–	–	–	–	–	Pd-U-Ce
Point Scan 14	54.1	2.9	30.6	–	9.5	–	–	–	2.5	–	–	–	Pd-Cd
Point Scan 15	55.0	0.5	41.2	0.3	2.3	–	–	–	–	–	0.4	–	Pd-U
Point Scan 16	56.6	1.1	37.2	–	5.1	–	–	–	–	–	–	–	Pd
Point Scan 17	40.2	1.1	27.8	2.6	27.2	–	1.0	–	–	–	–	–	Pd-U-Ce
Point Scan 18	60.7	1.7	32.3	–	5.0	–	–	–	–	–	0.2	–	Pd
Point Scan 19	40.7	1.0	47.9	0.2	9.5	–	0.4	–	–	–	0.2	–	Pd-Si-Ce-U
Point Scan 20	32.3	0.6	61.0	–	4.3	–	–	–	1.1	0.2	–	–	Pd-Si-Cd
Point Scan 21	48.2	–	34.7	–	15.2	–	–	0.4	0.9	–	–	–	Pd-Cd-Ag

0.2 at.% is taken as the detection limit for Ag, Pd, Ce, and Cs, and 0.1 at.% is taken for U. Only elements with measured concentrations above the detection limit are reported. “–” indicates that the concentration of the element is below the detection limit.

Table 5. Quantified compositions corresponding to the EDS point scans in Figure 6.

Concentration (at.%)	C	O	Si	U	Pd	Cs	Ce	Ag	Cd	I	Sr	Te	Precipitate Identification
Point Scan 1	50.6	0.7	41.9	—	6.9	—	—	—	—	—	—	—	Pd
Point Scan 2	56.3	0.6	38.7	—	4.4	—	—	—	—	—	—	—	Pd
Point Scan 3	58.3	0.8	38.2	—	2.8	—	—	—	—	—	—	—	Pd
Point Scan 4	57.5	1.1	37.8	—	3.6	—	—	—	—	—	—	—	Pd
Point Scan 5	48.9	1.1	45.1	—	4.9	—	—	—	—	—	—	—	Pd
Point Scan 6	57.9	0.7	36.7	—	4.7	—	—	—	—	—	—	—	Pd
Point Scan 7	60.4	—	36.9	—	2.4	—	—	—	—	—	—	—	Pd
Point Scan 8	55.2	0.9	40.6	—	3.3	—	—	—	—	—	—	—	Pd
Point Scan 9	57.7	1.3	35.1	—	5.9	—	—	—	—	—	—	—	Pd
Point Scan 10	57.9	0.7	38.0	—	3.4	—	—	—	—	—	—	—	Pd
Point Scan 11	56.0	0.6	40.2	—	3.2	—	—	—	—	—	—	—	Pd
Point Scan 12	58.0	0.7	36.9	—	4.3	—	—	—	—	—	—	—	Pd

0.2 at.% is taken as the detection limit for Ag, Pd, Ce, and Cs, and 0.1 at.% is taken for U. Only elements with measured concentrations above the detection limit are reported. “—” indicates that the concentration of the element is below the detection limit.