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Original Article

Electron microscopy study of Pd, Ag, and Cs in carbon areas in the locally corroded SiC layer in a neutron-irradiated TRISO fuel particle

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ABSTRACT

A detailed electron microscopy study was performed on focused ion beam-prepared lamellae from different locations relative to a crack across the inner pyrolytic carbon layer of a neutron-irradiated tristructural isotropic-coated particle. The distribution and composition of fission products across the inner pyrolytic carbon and silicon carbide (SiC) layers were studied. Previously, this crack was identified in the particle that released significant inventory fractions of cesium and silver during irradiation and displayed localized palladium pileup with SiC degradation. In this study, carbon areas were found in the SiC layer close to the crack tip and they had precipitates that consisted mostly of palladium silicides or palladium, with silver and/or cadmium frequently identified. Results confirmed that areas in the SiC layer close to the crack tip with localized accumulation of palladium were corroded by palladium, forming pure carbon areas and palladium silicide that provided pathways for silver, cadmium and cesium migration.

1. Introduction

Tristructural-isotropic (TRISO)-coated fuel particles are designed as nuclear fuel for high-temperature gas reactors [1–3]. Typical TRISO fuel consists of either a uranium oxide (UO_2) or mixed uranium carbide/uranium oxide (UCO) fuel kernel and successive coating layers of a porous carbon (C) buffer, relatively dense inner pyrolytic carbon (IPyC), high-strength silicon carbide (SiC), and outer pyrolytic carbon [1–3]. The TRISO coating acts as a containment system for fission products (FP) produced in the kernel. The SiC layer of the TRISO coating is the primary barrier for metallic FPs released from the kernel and also serves as the principal structural layer. One of the key design features for TRISO-coated fuel particles is that most radioactive FPs must be retained in the particles to avoid contamination of the coolant and the turbine structures [4,5].

Release of certain metallic FPs (e.g., silver [Ag] and palladium [Pd]) across intact TRISO coatings has been observed for decades [6–8] and in the first Advanced Gas Reactor (AGR-1) experiment at Idaho National Laboratory [4,5]. Release of radioactive FPs (especially $^{110\,\mathrm{m}}$Ag) constitutes a potential worker safety concern due to their plate-out on the cooler metallic parts of the reactor. Hence, it is important to identify the transport mechanisms of metallic FPs across the TRISO coating layers to assist in identifying mitigation solutions. During the past four decades, numerous studies, including reactor experiments, out-of-reactor experiments, and simulations, have been performed to investigate transport behavior and mechanisms of FPs (especially Ag) [6–41]. Grain boundary diffusion [11,14,15,17,18,22,24,35], irradiation-enhanced diffusion [9,23,26,37,40,41], Pd-assisted transport [24,27,33,38], and vapor-phase migration [6,13,25] have all been suggested as possible governing transport mechanisms for Ag. Despite the large number of studies, the Ag transport mechanisms remain poorly understood.

Pd is another metallic FP of interest in TRISO-coated particles. Pd was observed to coalesce at the IPyC-SiC interface and to chemically interact with the SiC layer in irradiated TRISO-coated particles with UO_2, UC_2, or UCO fuel kernels, thereby potentially reducing the effectiveness of the SiC layer as a FP transport barrier [42,43]. Therefore, SiC corrosion by Pd has been postulated to be a potential failure mechanism in low-enriched uranium TRISO fuels when the irradiation temperature exceeds 1100 °C [42–45]. In addition, diffusion-couple experiments also indicated the occurrence of chemical reaction between SiC and Pd [27,45,46]. However, AGR-1 post-irradiation examination results generally showed no significant chemical attack of SiC by Pd for TRISO-coated particles with UCO fuel kernel [29]. Therefore, the driving factors for corrosion by Pd in the SiC layer of neutron-irradiated, TRISO-coated particles remain unclear.

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Cesium (Cs) is yet another important FP because of the relatively high fission yield of radioactive isotopes ^{134}Cs and ^{137}Cs [26,47]. Cs is generally well retained in TRISO-coated particles [16,26]. Earlier studies reported that even when half the SiC layer thickness was corroded by Pd, its integrity and ability to retain volatile FPs such as Cs was not jeopardized [42]. The AGR-1 experiment has frequently identified release of Ag and Pd through intact TRISO coatings, with Cs generally well retained and without significant corrosion of SiC by Pd [4,5,29]. However, degraded SiC layers were identified in three TRISO particles in two compacts from the AGR-1 experiment, and these particles had relatively high releases of both Ag and Cs [48,49]. Degradation of the SiC layer was caused by chemical reaction with Pd initiated at a SiC inner surface exposed by an IPyC crack, where a higher Pd concentration existed [48–50]. The localized SiC corrosion was believed to provide pathways for Cs release [48–50]. It is important to clearly identify the mechanisms for SiC layer degradation/failure and Ag and Cs transport across the TRISO coating layers (especially the SiC layer) in the particles with degraded SiC layers.

The present study was undertaken with two primary objectives: first, to further study the observed corrosion of SiC by Pd to understand the condition under which the corrosion occurs and, second, to more clearly ascertain the role of SiC corrosion in Ag and Cs releases. A TRISO-coated particle from the AGR-1 experiment that had high Ag and Cs release with localized SiC layer degradation was selected for this study. The microstructure of the TRISO particle and the composition and distribution of FPs (especially Pd, Ag, and Cs) were investigated using transmission electron microscopy (TEM), and scanning transmission electron microscopy (STEM) coupled with energy dispersive x-ray spectroscopy (EDS). Special attention was given to correlation between FPs and the microstructural features of the coating layers.

2. Experimental

The study involved a TRISO-coated particle from Compact 5-2-3 of AGR-1. The unique compact identification number (i.e., 5-2-3) is based on the specific capsule, level, and stack number for each compact. Compact 5-2-3 refers to the compact in Capsule 5 at Level 2 of Stack 3. The capsule design and details about the AGR-1 experiment have been described previously [4]. Compact 5-2-3 was irradiated at the Advanced Test Reactor at Idaho National Laboratory to an average burnup of 17.42% fissions per initial metal atom, a time-averaged and volume-averaged temperature of 1059 °C, and an average fast fluence of 3.77×10^{25} n/m^2 with an energy of $E > 0.18$ MeV [51,52]. Compact 5-2-3 contained AGR-1 Variant 1 fuel particles, with SiC deposited at 1500 °C in a fluidizing gas containing methyltrichlorosilane and hydrogen, which produced a near-theoretical density (3.206 g/cm^3) and a low-porosity structure [53]. AGR-1 Variant 1 fuel particles are similar to AGR-1 baseline fuel particles, except that the IPyC coating layer was deposited at 1290 °C, which is 25 °C higher than the deposition temperature of the IPyC layer of baseline fuel particles [53].

During post-irradiation examination of TRISO particles from Compact 5-2-3, gamma-activity measurements identified two specific particles (out of 4088 particles deconsolidated from the compact and surveyed) with lowCs inventories indicative of particles with compromised SiC layers facilitating Cs release [48]. The fractional Cs and Ag releases were determined, by comparing the measured retained inventory to the predicted inventory for ^{134}Cs, ^{137}Cs, and $^{110\,m}$Ag. For one of the two Cs-releasing particles (i.e., Particle AGR1-523-SP01), the fractional releases of Cs and Ag were ~30% and ~85%, respectively. The particle had no detectable cerium (Ce) or europium release (i.e., measured activities were within normal distribution for measured isotopes). Non-destructive, three-dimensional, x-ray tomography performed on this particle (Fig. 1) revealed degradation/defect in the SiC layer and this degradation was localized to one specific region that was connected to a crack in the IPyC layer; the crack terminated at the IPyC-SiC interface. Buffer fractures and buffer/IPyC delamination are also evident in Fig. 1. The localized region with SiC degradation was then exposed by mounting the particle in epoxy in an optimal orientation and, subsequently, grinding and polishing it while guided by three-dimensional x-ray data. Optical microscopy analysis confirmed the SiC degradation to be co-located with the crack in the IPyC layer. Preliminary scanning electron microscopy (SEM) analysis suggested the SiC degradation contained large C-rich features and notable build-up of Pd. The SEM analysis also indicated Pd-Si features located along the IPyC crack away from the SiC layer degradation, suggesting the IPyC crack served as a pathway for Si transport away from the SiC layer [48,49]. Given these initial observations, advanced microscopy was performed during this study to further understand SiC degradation and FP transport in the SiC degradation region.

To examine the microstructure of the TRISO particle and the FPs in it, TEM lamellae were fabricated via the focused ion beam technique utilizing a dual-beam FEI Quanta 3D FEG system. Before cutting the TEM lamellae by focused ion beam, SEM images were taken to decide the locations where TEM lamellae were to be sectioned. Fig. 2(a) shows a SEM image of the cross section of the particle. The buffer layer is fractured in several places and a crack can be seen across the IPyC layer. Ten TEM lamellae were cut from different locations of the cross section of the TRISO particle (as shown in Fig. 2(a) and (b)). Lamella 4 was perpendicular to the IPyC-SiC interface. Lamella 7 was extracted from a location in the IPyC layer adjacent to the crack, Lamella 8 was right at the crack tip and approximately parallel to the IPyC-SiC interface and contains mostly IPyC, and Lamella 10 was close to the crack tip and in the SiC layer. Lamellae 5, 6, and 9 were all approximately perpendicular to the IPyC-SiC interface and were in regions slightly away from the crack. Results obtained from examining TEM Lamellae 4 through 9 are briefly summarized in this paper and results on Lamella 10 are detailed and discussed. TEM, STEM, and EDS were conducted with a FEI Tecnai G2 TF30-FEG STwin microscope operating at 300 kV at the Center for Advanced Energy Studies.

Because of the large differences in atomic numbers between the SiC matrix and the FPs and actinide elements, the distribution of these FPs and actinide elements was revealed primarily using high-angle annular dark-field (HAADF) imaging in STEM that has Z (atomic number) contrast. In HAADF STEM, fission products have bright contrast and therefore can be readily identified even when they are extremely small (e.g., a few nanometers in diameter). It is noted that the purpose of HAADF STEM is to identify the presence and distribution of FPs rather than obtain structural information. The HAADF STEM images were intentionally oversaturated so that FPs were highlighted and that the SiC or C matrix was observed simultaneously with FPs. The composition of both intergranular and intragranular FP precipitates was then analyzed using EDS with a fine electron probe size (i.e., < 1 nm) and a Si (Li) EDS detector (EDAX). Each EDS point scan was performed with a data acquisition time of ~50 s and line scans were conducted across the features of interest with an EDS data acquisition time of 10 s at each point. The FEI commercial TEM Imaging and Analysis (TIA) software was used to analyse the EDS results. EDS spectra were semi-quantified after subtracting a fitted polynomial background for the X-ray lines. Each of the elements was semi-quantified based on a standardless k-factor quantification using 300 keV and a modelled sample thickness correction inside the TIA software. Based on the provided threshold intensity over background (6:1), peaks intensities were subsequently integrated, semi-quantified, and reported. Owing to the severe overlaps among the Pd and Ag characteristic L-lines and the uranium (U) characteristic M-lines, the characteristic L-lines of Pd, K-lines of Ag, and L-lines of U were used for semi-quantification in the compositional analysis to avoid errors associated with deconvolution of overlapped peaks [54]. Because L-lines are the dominant peaks for Pd, L-lines instead of K-lines of Pd were used to obtain more accurate Pd concentrations in the FP precipitates and, accordingly, a more accurate Pd:Si ratio if Si is present in the precipitates. It is noted that all K, L, and M-lines of Pd, Ag, and U were considered by the EDS software during the