Journal of the European Ceramic Society 37 (2017) 3271–3284

Contents lists available at www.sciencedirect.com

Journal of the European Ceramic Society

journal homepage: www.elsevier.com/locate/jeurceramsoc

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, ID 83402, USA*
[b] *Fuel Design and Development Department, Idaho National Laboratory, Idaho Falls, ID 83415, USA*

ARTICLE INFO

Article history:
Received 18 November 2016
Received in revised form 31 March 2017
Accepted 5 April 2017
Available online 14 April 2017

Keywords:
TRISO particle
Fission product
Transport mechanism
Neutron irradiation
Electron microscopy

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.

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 (UO_2) 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 con-

---

[*] Corresponding author at: Department of Physics, Nuclear and Electrical Engineering, Idaho State University, Idaho Falls, ID 83402, USA.
E-mail address: wenhaim@isu.edu (H. Wen).

http://dx.doi.org/10.1016/j.jeurceramsoc.2017.04.012
0955-2219/Published by Elsevier Ltd.

centrations 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 release[28]. 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 1059 °C and an average fast fluence of 3.77×10^{21} n/cm^2. 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]. Fig. 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 peaks [28]. 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.

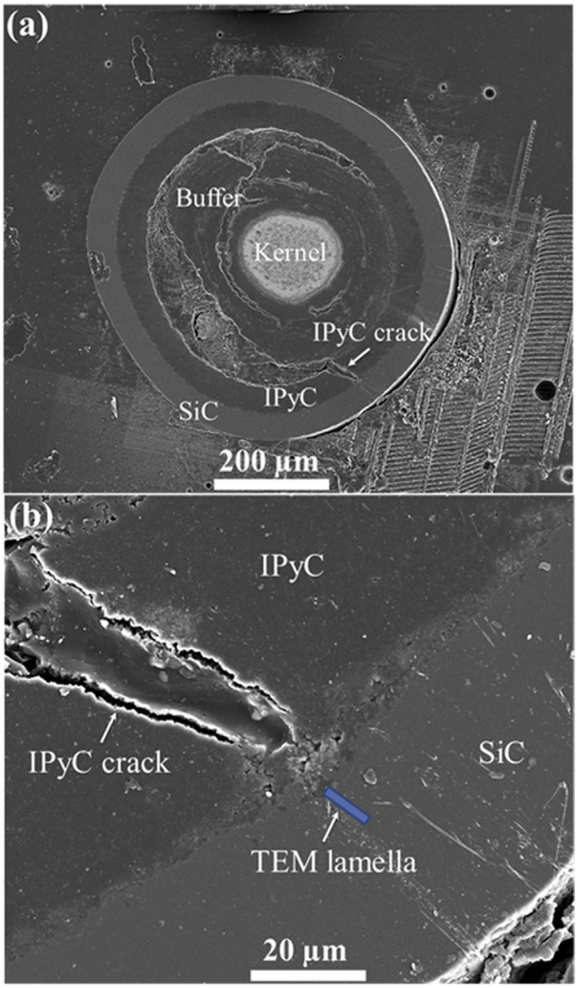

Fig. 1. SEM images of the cross section of the studied TRISO-coated particle. The TEM lamella examined was extracted from a location in the SiC layer close to the IPyC crack tip.

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 Pd_2Si or PdSi are formed [28,33]. Pd_2Si, PdSi and Pd precipitates are present in the carbon areas (note that the Si concentrations in the precipitates in the carbon areas can