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Preparation of Diffusion Couples (I) to Study Ag/Pd Migration in SiC

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1. Introduction

TRISO (tristructural isotropic) fuel particles are used as the fuel element for the very high temperature reactor (VHTR). TRISO-coated fuel particle has a fuel kernel 500 μm in diameter with three layers of pyrolytic carbon (buffer, inner pyrolytic carbon (IPyC) and outer pyrolytic carbon (OPyC)) and one of silicon carbide (SiC) between two layers, IPyC and OPyC. Among coated layers, SiC layer serves as the main diffusion barrier to prevent fission products (FPs) from releasing from TRISO fuel and provides structural integrity of this fuel at temperatures up to 1300°C during normal operation and 1600°C during accident conditions. Retention of FPs within the TRISO-coated fuel particle is very important to the accomplishment of the VHTR. The solid FPs, such as silver (Ag), palladium (Pd), and europium (Eu) are able to penetrate and transport in SiC layer most easily [1-3]. It has been observed in reactor experiments that although the SiC layer can retain most fission products, some species such as Ag can escape from fuel particles [4-9]. In particular, because of a strong γ-ray emitter and a long half-life of 250 days of ^{110m}Ag, the release of ^{110m}Ag from intact TRISO fuel is especially a concern as ^{110m}Ag in the primary coolant loop can plate out on the turbine system of VHTR causing safety and maintenance concerns and an increased risk of radiation exposure. Consequently, the release of this element not only has important safety implications but also significant economic and operational implications because it limits the operational temperature and burn-up of the fuel [3,4,10-16]. In order to improve reactor operation and reduce safety and maintenance concerns, there were many efforts to understand Ag diffusion mechanism and release rates [4,14,17-34].

In this study, spherical diffusion couples using surrogate TRISO particles were successfully prepared to trap Ag or/and Pd between IPyC layer and SiC layer, and SiC layers using silver nitrate, palladium nitrate hydrate, and polycarbosilane (PCS).

2. Experimental

2.1 Sample preparation

Diffusion couples were made using silver nitrate permeating/covering and thin film techniques such as fluidized bed chemical vapor deposition (FBCVD) to create the trapped Ag or/and Pd between IPyC and SiC layers and between SiC layers. These particles were prepared by FBCVD using zirconia particles with a diameter of 500 μm as the spherical substrates. A detail description of the FBCVD equipment used in this study can be found elsewhere [35-37]. There are two kinds of the diffusion couples, as shown schematically in Fig. 1. One has two coating layers, buffer and IPyC, on the kernel, and the other has three layers, buffer, IPyC and SiC. The coating layers were deposited on to the spherical surrogated kernels using FBCVD, in sequence. The buffer PyC layer was deposited by dehydrogenation of C_2H_2 at 1450°C under Ar gas flow. The inner dense PyC layer was made from a mixture of C_2H_2 and C_3H_6 at 1350°C in an Ar medium. And, SiC layer was also coated by mixture of CH_3SiCl_3 and H_2 at 1500°C under Ar gas flow. And then, in order to introduce fission products, such as Ag or/and Pd, between the host layers, the preparation of the diffusion couple is divided into 3 steps, as shown schematically in Fig. 1; substrate preparation (surrogate kernel (ZrO_2) coated buffer and IPyC and ZrO_2 coated buffer, IPyC, and SiC by FBCVD), Ag or/and Pd permeating/covering, and covering SiC transformed from PCS and then additional SiC/OPyC deposition by FBCVD. There are six kinds of samples designated from H1 to H6 as shown in Table 1. It can be divided two categories in Table 1. One (H1 to H3) has a surrogated TRISO particle with entrapped Ag, Pd, and Ag/Pd between IPyC layer and SiC layer, the other (H4 to H6) has a surrogated TRISO particle with entrapped Ag, Pd, and Ag/Pd between SiC layers.

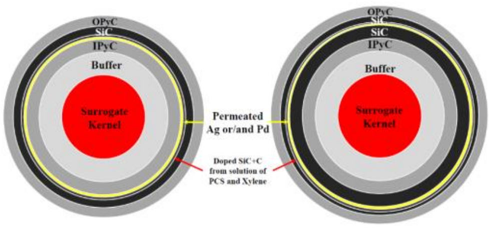

Fig. 1. Schematic illustrations of two kinds of the spherical diffusion couple.

2.2 Sample Characterization

At each stage of the process of sample preparation, the surface and the fractography of particles was examined using a scanning electron microscope (SEM) coupled with an energy-dispersive X-ray spectrometer (EDX). All the embedded samples in epoxy resin were polished to a cross section by standard metallographic polishing procedures, then cleaned ultrasonically in distilled water, and subsequently dried with hot air. The cross section of particles were also examined using SEM and EDX. All SEM images of cross-section presented in this paper were taken in the as-polished condition without etching. And, X-ray image of particle was taken by using X-Ray CT system (160 kV Micro X-ray System, Cheetah, YXLON).

Table 1. Six kinds of samples presented in this study

Sample ID	Initial layers	Entrapped elements
H1	Surrogate kernel/buffer/IPyC	Ag
H2	Surrogate kernel/buffer/IPyC	Pd
H3	Surrogate kernel/buffer/IPyC	Ag+Pd
H4	Surrogate kernel/buffer/IPyC/SiC	Ag
H5	Surrogate kernel/buffer/IPyC/SiC	Pd
H6	Surrogate kernel/buffer/IPyC/SiC	Ag+Pd

3. Results and Discussions

Fig. 2 show the SEM images and EDX analyses of a cross-section of H5 particles after coating of additional SiC and OPyC layers at 1500°C and 1350 °C, respectively. Average thicknesses of additional SiC and OPyC are about 65 μm (SiC), 38 μm (OPyC), respectively. As shown in Fig. 2 (f), Pd was successfully trapped between SiC layers. However, in case of H1 particle, it is hard whether Ag would be successfully trapped between IPyC layer and SiC layer due to melting away or sublimation of Ag during coating of additional SiC and OPyC layers. In case of H4 particle, it was also shown a similar tendency to H1 particle. Fig. 3 shows the two-dimensional X-ray micro-tomography images showing the presence of Pd trapped between the SiC layers in a H5 coated fuel particle, and shows the distribution of pockets of Pd around the particle. These images show that Pd can be trapped inside the particle by the new methodology.

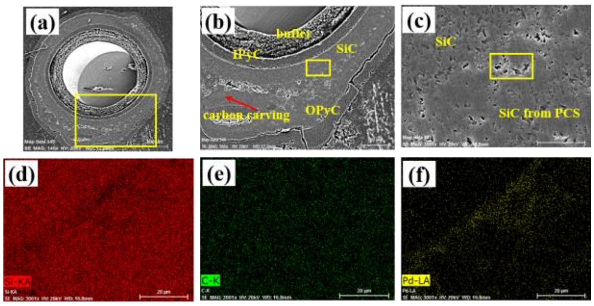

Fig. 2. SEM images and EDX analyses of cross-section of H5 particle coated additional SiC and OPyC layers; (a) overview; (b) and (c) enlarged views of rectangular area (yellow color) in Fig. 2 (a) and (b); (d), (e) and (f) element map for Si, C and Pd using EDX on SEM in Fig. 2 (c).

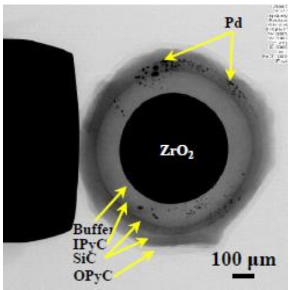

Fig. 3. X-ray micro-tomography images showing of the presence of palladium between two layers of SiC and the distribution of pockets of palladium in a H5 particle.

4. Future Works

Although the work detailed in this study provides another step forward in understanding Ag or/and Pd transport in silicon carbide, much further work remains to be done using the heat treatments. For instance, after heat treatments at 1150°C, 1200°C, 1600°C for 50, 100, 200 hrs under Ar gas flow at 2L/min, the Ag or/and Pd diffusivity in SiC should be determined. And the diffusion mechanism for Ag or/and Pd transport in SiC should be investigated and due to the presence of Pd, which can be react with SiC and form palladium silicides along grain boundaries of SiC, the migration of Ag in SiC might be facilitated.

5. Conclusions

Using surrogate TRISO-coated particles, multi-layer diffusion couples were prepared to study the migration of fission products (FPs), such as Ag or/and Pd, in SiC layer. Ag or/and Pd was successfully trapped between two layers of IPyC and SiC, and SiC layers. These diffusion couples will provide the opportunity to investigate diffusion mechanism and to determine diffusion coefficients of Ag or/and Pd as FPs in SiC and the role of the Pd for Ag migration in SiC layer.

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