

Preparation of Diffusion Couples (II) to investigate Ag/Pd Migration in ZrC/SiC

B.G. Kim*, S. Yeo, Y.-K. Kim, W.-J. Kim, Y.J. Kim, H.M. Kim and M.S. Cho

Korea Atomic Energy Research Institute, Daedeok-daero 989-111, Yuseong-gu, Daejeon, 34057, Korea

*Corresponding author: bgkim1@kaeri.re.kr

1. Introduction

Zirconium carbide (ZrC) is one of attractive materials for use in high temperature nuclear application to take advantage of its favorable thermal and mechanical properties. Attractive properties for ZrC as a nuclear fuel material include high melting point in excess of 3500 K (for near-stoichiometric compositions), generally good resistance to fission products attack, high thermal conductivity at very high temperatures, and low neutron absorption cross-sections. ZrC, in particular, is being considered as a structural and fission product barrier coating material for TRISO (tristructural isotropic) coated nuclear fuel used in high temperature reactors (HTR's) and very high temperature reactor (VHTR), replacing or in addition to the currently used silicon carbide (SiC) [1–7]. ZrC has been considered as a promising alternative to the SiC fission product barrier of the TRISO-coated fuel particles since the 1970s, since the peak fuel temperature permissible under normal operating and accident conditions would increase while still retaining a very high degree of passive safety [8-15]. It has been demonstrated that the ZrC-coated TRISO fuel possesses much greater high temperature stability than that coated with SiC [11]. Up to now, there were few irradiation tests of ZrC-coated TRISO fuel [3,11,13,16,17]. So far, the retention properties of ZrC at operating and accident temperature of the VHTR especially for silver (Ag) have not been adequately studied. There is only one single study that explored Ag diffusivity in ZrC to investigate the diffusion behavior of Ag in ZrC (C/Zr unknown) coating layer over a wide range of temperatures (1730-2230°C) [17]. Recently a new diffusion experimental technique, called the encapsulating source method, has been developed to construct and diffusion anneal a constant source diffusion couple composed of ZrC and Ag vapor originated from Zr-8.1 wt% Ag solid solution, and the impurity diffusion coefficient of Ag in single crystalline $ZrC_{0.84}$ at 1500°C was experimentally determined to be about $2.8(\pm 1.2) \times 10^{-17} \text{ m}^2/\text{s}$ [18]. Reaction of ZrC with palladium (Pd) at temperatures up to 1500°C was examined using ZrC/Pd composite, Pd/ZrC-coated TRISO particles, and Pd/ZrC bulk diffusion couples experiments. And then, the reaction kinetics parameters, i.e., the activation energy (208.2-266.5 kJ/mol) and the reaction order (3.38-3.78) for Pd attacking through a ZrC coating in TRISO particles were determined based on both the DSC curves and the growth of the Pd_3Zr layer [19].

In this study, spherical diffusion couples of ZrC/SiC (including SiC transformed from PCS)- and ZrC/SiC (transformed from polycarbosilane (PCS))/ZrC-coated particles were prepared to carry out heating treatments at operating and accident temperature of VHTR. Ag or/and Pd, as source of fission products, was successfully entrapped between ZrC layer and SiC layer, and ZrC/SiC (transformed from PCS)/ZrC by using silver nitrate or/and palladium nitrate hydrate [20]. And then, the diffusive behavior of Ag or/and Pd in the ZrC layer and SiC layer will be investigated.

2. Experimental

2.1 Preparation of ZrC-coated particles and diffusion couples

The surrogate kernels (ZrO_2 spherical particles with approximately 530 μm in average diameter) were used as a simulant kernel. 14 g of ZrO_2 per batch were loaded into the graphite nozzle. Then, three layers consisting of a porous buffer layer, an inner PyC (IPyC) layer, and a ZrC layer were sequentially deposited. Each layer of TRISO coated particles was deposited on a spherical particle by a fluidized bed chemical vapor deposition (FBCVD) method as shown in Fig. 1 [21]. The buffer layer was deposited by dehydrogenation of C_2H_2 at 1350°C under Ar gas flow. The IPyC layer was made from a mixture of C_2H_2 and C_3H_6 at 1300°C in an Ar medium. And, ZrC layer was coated by mixture of $ZrCl_4$ and CH_4 at 1500°C for 2 hr under gas flow of Ar and H_2 as carrier and dilution gases.

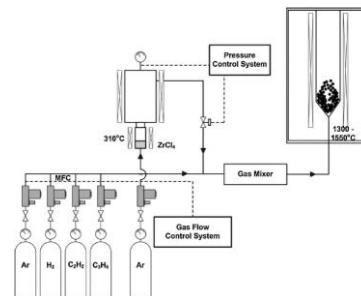


Fig. 1. Schematic diagram of FBCVD system for TRISO-coated particles with a ZrC layer [21].

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; substrate preparation (surrogate kernel (ZrO_2) coated buffer, IPyC and ZrC by FBCVD as shown in Fig. 1, Ag or/and

Pd permeating/covering, covering SiC transformed from PCS and then additional ZrC coating by using FBCVD as shown in Fig. 1, or additional SiC/OPyC deposition by another FBCVD equipment for SiC coating [20]. There are two kinds of the diffusion couples, as shown schematically in Fig. 2. One has two additional layers, such as SiC and OPyC layers, and the other has only an additional ZrC layer under on-going.

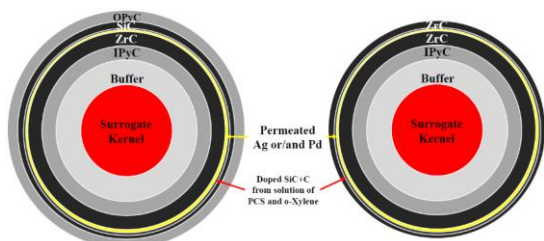


Fig. 2. Schematic illustrations of two kinds of the diffusion couple for surrogate TRISO particle

2.2 Sample Characterization

After permeating/covering of Ag or/and Pd, covering SiC transformed from PCS on the particles, the surface of particles was examined using a scanning electron microscope (SEM) coupled with an energy-dispersive X-ray spectrometer (EDX). And, after depositing of additional SiC/OPyC layers or ZrC layer by FBCVD, 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).

3. Results and Discussions

Fig. 3 and 4 shows SEM images and EDX analyses of cross section of ZrC-coated particle after heat-treating to decompose silver or/and palladium nitrates at 110 in air and 440°C under Ar gas flow at 2L/min or/and then transforming SiC from PCS at 200°C for 2 hrs in air and 950°C for 0.5 hr under Ar gas flow at 2L/min and coating additional SiC and OPyC layers at 1500°C and 1350°C by FBCVD, respectively. As shown in Fig. 4 (f) and (g), Ag and Pd were successfully trapped between SiC layer and ZrC layer. However, as shown in Fig. 3 (f), it is hard whether Ag would be successfully trapped between SiC layer and ZrC layer due to melting away or sublimation of Ag during coating of additional SiC and OPyC layers.

4. Future Works

Although the work detailed in this study provides another step forward in understanding Ag/Pd transport in silicon carbide and zirconium carbide, much further work remains to be done using the heat treatments. For instance, after heat treatments at operating and accident temperature (1150°C, 1200°C, 1600°C) for 50, 100, 200 hrs under Ar gas flow at 2L/min, the Ag or/and Pd diffusivity or/and the diffusion mechanism for Ag or/and Pd transport in SiC and ZrC should be investigated.

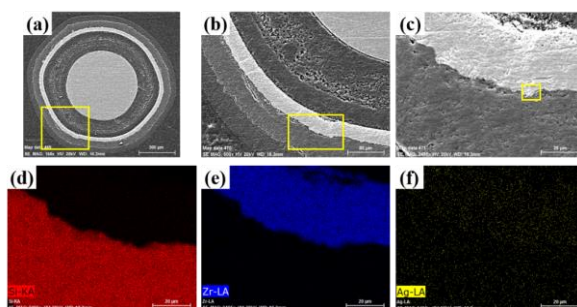


Fig. 3. SEM images and EDX analyses of cross-section of ZrC-coated particle and coated additional SiC and OPyC layers; (a) overview; (b) and (c) enlarged views of rectangular area (yellow color) in Fig. 3 (a) and (b); (d), (e) and (f) element map for Si, Zr and Ag using EDX on SEM in Fig. 3 (c).

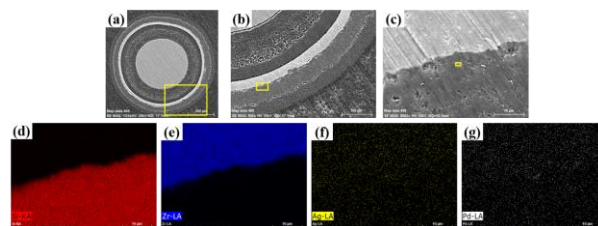


Fig. 4. SEM images and EDX analyses of cross-section of ZrC-coated particle and coated additional SiC and OPyC layers; (a) overview; (b) and (c) enlarged views of rectangular area (yellow color) in Fig. 4 (a) and (b); (d), (e), (f) and (g) element map for Si, Zr, Ag and Pd using EDX on SEM in Fig. 4 (c).

5. Conclusions

Multi-layer diffusion couples were prepared to study the migration of fission products (FPs), such as Ag or/and Pd, in SiC layer and ZrC layer. Ag or/and Pd was successfully trapped between two layers, SiC layer and ZrC layer, and ZrC 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 ZrC and the role of the Pd for Ag migration in these layers.

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