Preparation of Diffusion Couples for Irradiation and High Temperature Testing of Representative TRISO PyC/SiC

Tyler J. Gerczak
Anne A. Campbell
Xunxiang Hu
John D. Hunn
Brian C. Jolly
Rachel L. Seibert
Austin T. Schumacher

**Approved for public release.
Distribution is unlimited.**

September 2018

OAK RIDGE NATIONAL LABORATORY
MANAGED BY UT-BATTELLE FOR THE US DEPARTMENT OF ENERGY

Fusion and Materials for Nuclear Systems Division

PREPARATION OF DIFFUSION COUPLES FOR IRRADIATION AND HIGH TEMPERATURE TESTING OF REPRESENTATIVE TRISO PYC/SIC

Tyler J. Gerczak
Anne A. Campbell
Xunxiang Hu
John D. Hunn
Brian C. Jolly
Rachel L. Seibert
Austin T. Schumacher

Date Published: September 2018

CONTENTS

LIST OF FIGURES

LIST OF TABLES

ACRONYMS

AGR	Advanced Gas Reactor (Fuel Development and Qualification Program)
AGR-1	First AGR fuel irradiation experiment
AGR-2	Second AGR fuel irradiation experiment
C_2H_2	Acetylene
C_3H_6	Propylene
CGF	Coating gas fraction
dpa	Displacements per atom
EBSD	Electron backscatter diffraction
EOL	End-of-life
FB-CVD	Fluidized bed chemical vapor deposition
GD-OES	Glow discharge optical emission spectroscopy
HFIR	High Flux Isotope Reactor
HTGR	High temperature gas-cooled reactor
IPyC	Inner pyrolytic carbon
MS	Methylsilane
MTS	Methyltrichlorosilane
OPyC	Outer pyrolytic carbon
PyC	Pyrolytic carbon or pyrocarbon
S-PyC	Support pyrocarbon
sccm	Standard cubic centimeters per minute
SiC	Silicon carbide (TRISO layer)
TGF	Total gas flow
TRISO	Tristructural-isotropic (coated particles)
UCO	mixed uranium carbide/uranium oxide (kernels)
UO_2	Uranium dioxide

ACKNOWLEDGMENTS

ABSTRACT

Understanding the release of fission products from intact tristructural-isotropic (TRISO) coated particle fuel during normal and off-normal service is necessary to ensuring safe and efficient reactor operation. Planar diffusion couples have been fabricated to determine the diffusion kinetics of select fission product species (Ag, Ag+Pd, Eu, and Sr) in pyrocarbon (PyC) and silicon carbide (SiC) materials which are representative of TRISO fuel. Obtaining accurate diffusion coefficients for these systems in representative materials will allow for higher fidelity inputs for fuel performance models. Three different diffusion couple variants have been produced which include a Baseline, PyC, and SiC variant. The Baseline variant serves as an example of representative PyC and SiC layers as the layer properties mimic those found in TRISO fuel from the second Advanced Gas Reactor Fuel Qualification and Development Program. The PyC and SiC variants include variation in the respective layer properties to understand the impact of PyC density and SiC grain size on fission product diffusion. The diffusion couples were designed to allow for exploration of neutron irradiation on diffusion reflecting in reactor behavior as well as high temperature thermal diffusion reflecting diffusive transport during off-normal conditions. The methodology for selecting the diffusion couple design, refinement of the individual variant layer properties, and the complete process for diffusion couple construction are summarized in this report.

1. INTRODUCTION

1.1 MOTIVATION: FISSION PRODUCT RELEASE FROM TRISO FUEL

Tristructural-isotropic (TRISO) coated particle fuel is being considered for multiple advanced reactor concepts. The fuel concept was first identified for application in high temperature gas-cooled reactors (HTGR). The development of TRISO fuel has centered around HTGR deployment [1,2] but recently the concept has been considered as a fuel form for molten salt reactors [3] and as an accident tolerant fuel concept in light water reactors [4].

The design of the TRISO fuel particle consists of a fissile fuel kernel surrounded by four successive layers of low-density carbon buffer, pyrolytic carbon (PyC), silicon carbide (SiC), and a final PyC layer, Figure 1. The kernel material for TRISO fuel produced for the Advanced Gas Reactor Fuel Qualification and Development Program (AGR) is a two phase uranium dioxide (UO_2) and uranium carbide material (UCO), however, UO_2 fuel has also been investigated [2,5]. The first pyrolytic carbon layer is termed the "inner" pyrolytic carbon (IPyC), while the second layer is termed the "outer" pyrolytic carbon (OPyC). The individual particles are overcoated with a graphite and resin binder and compacted into a final fuel geometry. Typical final geometries include pebble or prismatic concepts. During service each layer in the TRISO construction provides a specific purpose. In particular, the IPyC layer provides a barrier to the release of gaseous fission products and SiC layer provides a barrier to the release of metallic fission products not retained in the kernel. Figure 1 shows a cross-section of an as-fabricated TRISO particle from the first AGR irradiation (AGR-1) along with an X-ray radiograph of a prismatic compact from the second AGR irradiation (AGR-2) showing the distribution of particles within the prismatic compact.
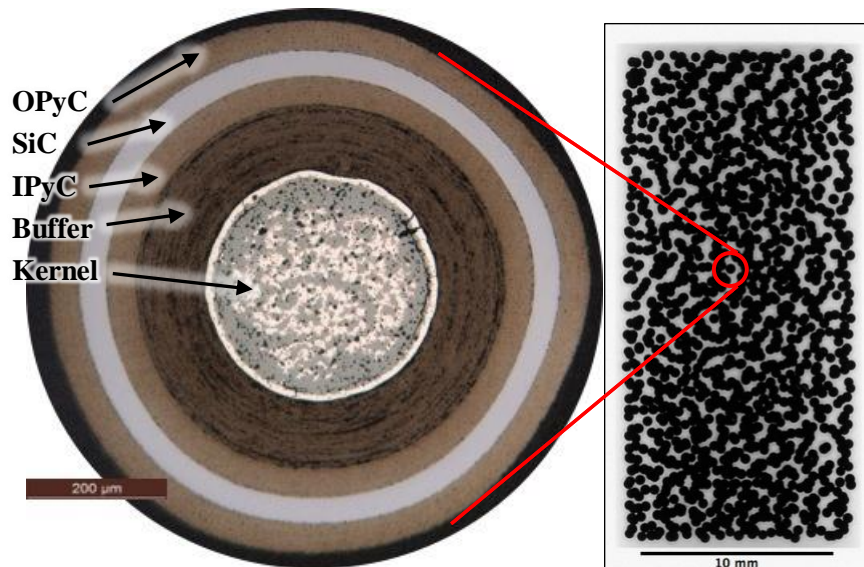
Figure 1. AGR-1 particle cross-section and x-ray radiography of a prismatic compact from AGR-2.

The TRISO fuel design is defined by its all refractory construction which enables high temperature operation and passive safety benefits in HTGR reactor designs. At elevated temperatures, associated with both normal operation and accident and margin conditions, diffusive release of select fission products from the TRISO fuel system becomes relevant [6,7]. An understanding of the release kinetics and factors

impacting release are required to provide fuel performance models with accurate data to ensure high fidelity simulations and safe and efficient reactor operation.

Historically, [110m]Ag release has garnered much attention due to its notable release relative to other fission products and lack of consensus regarding the release mechanism [8–10]. Concerning silver release, there is a reported discrepancy between the diffusion kinetics reported from in-pile release experiments, out-of-pile release experiments, surrogate experiments, and computational modeling efforts [11–26]. The reported in-pile release is more rapid than out-of-pile release and surrogate experiments. This variation highlights the motivation to understand the impact of neutron irradiation on silver transport. Microstructural effects have also been observed to impact release, necessitating the investigation of diffusion in representative materials to yield accurate diffusion kinetics. Another factor that is postulated to impact silver release is the complexity of the diffusion system, where it is speculated that palladium may increase silver transport through the system [11,12]. At elevated irradiation temperatures and during safety testing at margin temperatures (1800 ℃), ^{90}Sr and [154]Eu have also been observed to be released [6]. Here, ^{90}Sr is a biologically relevant isotope relevant to reactor safety while [154]Eu is a radiologically relevant isotope for qualifying fuel performance. Limited insight exists concerning the diffusion kinetics of strontium and europium in TRISO materials relative to silver [1].

To determine diffusion coefficients of silver, strontium and europium in representative TRISO materials a planar diffusion couple system was developed. The diffusion couple design includes both PyC and SiC materials as the release pathway from TRISO fuel is across the IPyC into the SiC layer. The nature of the IPyC/SiC interface is speculated to impact behavior of fission products interacting with the SiC layer [27]. The diffusion couples are fabricated using the same fluidized bed chemical vapor deposition (FB-CVD) system used to produce TRISO coated particle fuel for the AGR-1 irradiation. Thus, the PyC/SiC construction represents the integral release pathway through representative PyC/SiC materials to understand transport.

Three different materials systems are being investigated to understand the impact of different layer properties on diffusive transport of four separate fission product systems (Ag, Ag+Pd, Eu, and Sr). The different material systems include a Baseline variant, PyC variant, and SiC variant. The Baseline sample is intended to be representative of the AGR-2 TRISO fuel material system. The PyC variant focuses on a higher density PyC layer to modify the PyC/SiC interface while the SiC variant includes a larger grain size microstructure. The planar design was sought to utilize depth profiling techniques necessary for diffusion analysis.

The test matrix for the diffusion couple study is shown in Table 1. The test conditions cover the three sample variants and four fission product systems. The exposure conditions are meant to investigate diffusion under irradiation and diffusion at temperatures representing accident and margin conditions. To understand the influence of neutron irradiation on diffusion, select samples have been irradiated at elevated temperature in hydraulic "rabbit" capsules in the High Flux Isotope Reactor (HFIR) to two different irradiation doses defined by the displacements per atom (dpa) of the SiC layer (Section 3.3). A thermal equivalent sample will be compared to the neutron irradiated sample to determine the impact of neutron irradiation on diffusion and solubility of the specific fission product system. The results of this study aim to provide diffusion coefficients in a baseline PyC/SiC material system while also identifying how various layer properties and neutron irradiation impacts diffusion in materials representative of the TRISO system.

Table 1. Test matrix for planar diffusion couple experiment [28].

Condition	Sample Conditions
Neutron Irradiation (0.5 dpa, 1100±50 °C)	Baseline: Ag, Ag+Pd, Eu, Sr Commercial-SiC: Ag SiC Variant: Ag, Eu, Sr
Neutron Irradiation (1.0 dpa, 1100±50 °C)	
Thermal Diffusion (Temperature & time equivalent of 0.5 dpa)	
Thermal Diffusion (Temperature & time equivalent of 1.0 capsule)	
High-Temperature Thermal Diffusion (1500 °C, two conditions)	Baseline: Ag, Ag+Pd, Eu, Sr PyC Variant: Ag, Ag+Pd SiC Variant: Ag, Eu Sr
High-Temperature Thermal Diffusion (1600 °C, two conditions)	Baseline: Ag, Ag+Pd, Eu, Sr PyC Variant: Ag, Ag+Pd SiC Variant: Ag, Eu Sr
High-Temperature Thermal Diffusion (1700 °C, two conditions)	Baseline: Ag, Ag+Pd, Eu, Sr PyC Variant: Ag, Ag+Pd SiC Variant: Ag, Eu Sr

*Excess samples will go to NEUP archive.
^The estimated neutron irradiation temperature is based on capsule design thermal analysis [29].

This report is a summary of the diffusion couple development process. In depth description of the process summarized here has been captured in a series of quarterly reports which serve to document the development process [28,30–33].

1.2 DEVELOPMENT ROUTE

1.2.1 Criteria for Design

The criteria for the diffusion couple design focused on the layer properties and system requirements. One such design requirement was a diffusion couple system which facilitated application of depth profiling techniques. This is critical for the determination of concentration profiles in the PyC and SiC layers for diffusion kinetics analysis. The sample geometry and size must be such that a FB-CVD reactor can be used to produce samples with representative PyC and SiC microstructures. The system should be closed and simulate the pathway for release from TRISO fuel, that is, diffusion through PyC to SiC. The closed system also limits loss of the diffusing "fission product" species to the environment. The concentration of "fission product" species should represent that which is present in the TRISO fuel system. The diffusion couple design must also fit within the constraints of the irradiation capsule design which limits the size and geometry of the samples. The irradiation capsule design occurred in parallel with the diffusion couple development [29].

Targeted layer properties for the PyC and SiC layers were identified based on the AGR program experience. Table 2 identifies the properties targeted for the unique layers for each variant. The Baseline properties focused on representing UCO kernel fuel from the AGR-2. This fuel represents TRISO particles produced at an industrial-scale to which there is extensive associated PIE efforts. The critical design requirements for the diffusion couple are SiC microstructure and PyC density and the baseline variant is required to fall within the measured grain size for AGR-2 UCO TRISO [34]. The PyC variant focused on a higher density PyC relative to the Baseline variant. The higher density PyC is intended to modify the PyC/SiC interface to limit interfacial stitching which is speculated to impact the interaction of fission products with the SiC layer. For the PyC variant, the SiC microstructure was constant while a PyC

density target of >1.95 g/cm^3 was identified. The SiC variant required a larger SiC grain size compared to the Baseline variant. Grain size has shown to impact release during safety testing at 1800 ℃ for [110m]Ag and [154]Eu during AGR-1 safety testing, where larger-grained SiC displayed a lower effective diffusion coefficient relative to finer-grained SiC [6,34]. The SiC variant grain size targets represent the grain size from AGR-1 large grained variants and provides a comparison for the impact on microstructure on fission product diffusion.

Table 2. Properties of AGR-2 UCO fuel variant and the three planar diffusion couple variants [33].

	PyC Density	SiC Grain Size	
	(g/cm^3)	(major axis, μm)	(minor axis, μm)
AGR-2 UCO[*] [5,34]	1.890±0.011	0.89±0.14	0.35±0.05
Baseline	1.85–1.95	0.75–1.03	0.30–0.40
PyC	>1.95	0.75–1.03	0.30–0.40
SiC	1.85–1.95	2.10–2.70	0.50–0.80

[*]values from [34] are reported as mean±standard deviation

1.2.2 Fabrication Pathway

Based on the criteria for the diffusion couple design, a planar geometry diffusion couple was deemed to meet this requirement while still facilitating layer deposition using a FB-CVD system to produce representative PyC and SiC material. The layered carbon-SiC planar diffusion couple concept was first demonstrated by Dwaraknath and Was to study diffusion in commercially available SiC material [35,36]. The production route identified involves the deposition of three successive layers on a sapphire disk, Figure 2. The first layer is the representative PyC layer followed by the representative SiC layer with properties identified in Table 2. The final layer is a support PyC (S-PyC) layer which provides structural stability to the diffusion couple. The properties (density or microstructure) of the S-PyC were not optimized. The targeted layer thicknesses were 8–12 µm, 35–50 µm and >60 µm for the PyC, SiC and S-PyC layers respectively [30].
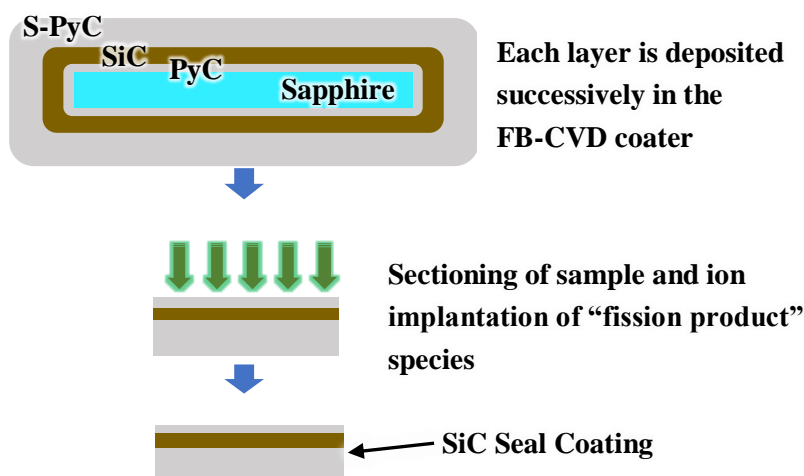
Figure 2. Schematic of diffusion couple fabrication process [33].

Fluidization was ideal on 9-mm diameter sapphire disks – the largest diameter sapphire disk tested [30]. This was also ideal as it yielded the largest sample area post-deposition. After deposition, the layered structures (PyC/SiC/S-PyC) were sectioned to nominally 3 × 4–5 mm samples, Figure 3. The difference in coefficient of thermal expansion between the deposition layers and the sapphire disk led to easy

liberation of the layered structure sample from the disk. Up to four samples per disk were able to be obtained. The 3 × 4–5 mm sample geometry was identified as the sample dimensions were constrained by the irradiation capsule design which has a limited inner volume. The "thin" sample design was also considered ideal to limit thermal gradients across the diffusion couple [29]. The simulated fission product species were introduced to the PyC layer via ion implantation to ensure the typical PyC to SiC diffusion pathway for the diffusing species of interest. A subsequent high temperature seal coating of SiC deposited in the same FB-CVD system was utilized to establish a closed system for diffusion analysis. Figure 3 shows a typical cross-section of the PyC/SiC/S-PyC structure with final SiC seal coating.
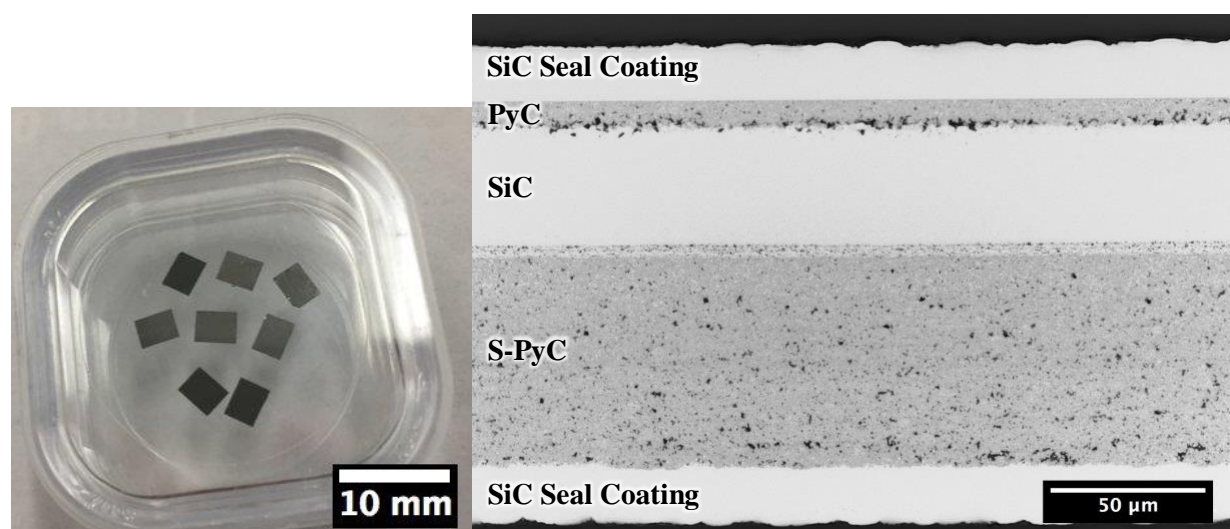
Figure 3. Photograph of sectioned PyC/SiC/S-PyC samples (left) and a cross-section optical image of a SiC seal coated sample (right).

2. FABRICATION OF REPRESENTATIVE PYC/SIC

The FB-CVD deposition process was based on established procedures (AGR-Surrogate-Coat-SOP-01) utilized for the fabrication of AGR-1 TRISO particles. Process development was required to establish appropriate deposition conditions due to the change in substrate geometry. The sapphire disks were fluidized along with 102 g of 400 µm ZrO_2 media to establish a fluidized bed under flowing Ar or a blend of Ar and H_2. The layers were deposited in succession while remaining at elevated temperature by cycling temperatures and precursors gases. Primary factors which impact the resultant properties include total gas flow (TGF), coating gas fraction (CGF), fluidization gas, and deposition temperature. These variables were manipulated to produce PyC and SiC layers with tailored properties to satisfy the criteria targeted in Table 2 [30].

2.1 PYC DEPOSITION

The deposition of the PyC and S-PyC was accomplished using a gas mixture of acetylene (C_2H_2), propylene (C_3H_6) and Ar. An in depth discussion of the PyC deposition effort is found in the reports by Gerczak et al. [30,31]. Initial scoping was performed to optimize the system TGF and CGF for the PyC deposition. Final depositions were carried out with TGF of 6000 standard cubic centimeters per min (sccm) with a CGF of 0.3. The CGF is defined here as the precursor gas flow divided by the TGF. The precursor gas flows for C_2H_2 and C_3H_6 were 973 sccm and 827 sccm respectively for all PyC depositions with the difference being Ar (4200 sccm).

The PyC density was manipulated by varying the deposition temperature from 1270 °C to 1390 °C. Interrupted coating runs were performed to isolate the deposited PyC layer allowing direct measurement of the PyC density. The density of the PyC was measured via sink/float density using a linear-gradient density column. This method was employed to measure the density of PyC during TRISO fuel development efforts for the AGR program [37]. Figure 4 shows sink/float density of the PyC layer as a function of deposition temperature. The range in deposition conditions resulted in measured PyC densities from 1.754 ± 0.038–2.022 ± 0.004 g/cm^3, where the $\pm$ value represents one standard deviation from the mean. The range in obtained PyC density satisfied the targeted requirements for all diffusion couple variants listed in Table 2. For the Baseline and SiC Variants the targeted PyC density was 1.90 g/cm^3 this was satisfied by deposition at 1350 °C. The PyC Variant required a density >1.95 g/cm^3, however, to ensure sufficient structural variation a density of ~2.00 g/cm^3 was sought. This was satisfied by deposition at 1300 °C. These PyC deposition conditions were utilized for the fabrication of the full diffusion couple layered structures (PyC/SiC/S-PyC) [31,33].
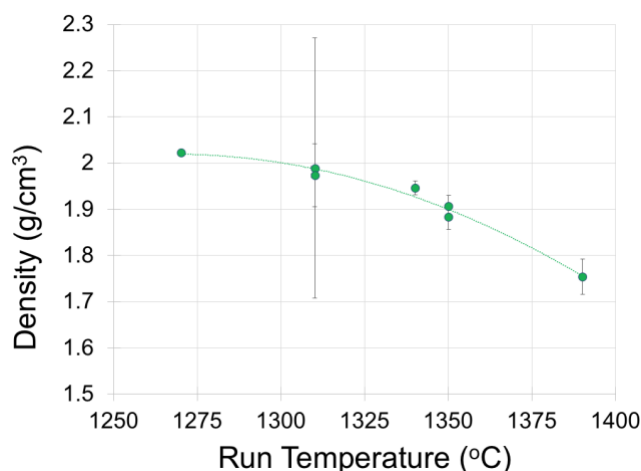
Figure 4. PyC sink/float density as a function of deposition temperature [33]**.**

The deposition conditions for the S-PyC layer varied relative to the PyC layer. The layer properties were not optimized as the S-PyC was deposited to provide structural support. The S-PyC was deposited at elevated TGF relative to the PyC layer. The higher TGF was required to sufficiently fluidization the system due to the increase in total surface area during the deposition of a thick S-PyC layer compared to the PyC layer. The CGF was 0.3 which was consistent with the PyC deposition, however, the precursor gas flows for C_2H_2 and C_3H_6 were 1460 sccm and 1240 sccm respectively for all S-PyC depositions with the remainder being Ar (6300 sccm). These conditions yielded a S-PyC thickness of 68–85 µm which was sufficient to provide structural stability to the layered diffusion couple samples [30].

2.2   SIC DEPOSITION

Development of the SiC layer was completed on full coating samples. Initial deposition conditions were derived from previous experience coating TRISO fuel particles on identical coating furnaces [30,31]. Typical TRISO SiC layers are deposited using a precursor gas of methyltrichlorosilane (MTS) in Ar + H_2 or pure H_2 fluidizing gas. Prior efforts have shown temperature and fluidization gas (Ar versus Ar + H_2) have a significant impact on the resultant SiC layer microstructure [34,38]. The addition of Ar impacts the fluidization and renucleation yielding a finer microstructure than depositions using pure H_2 fluidization gas [38]. A total of thirteen coating development runs were undertaken to obtain the SiC layers with the targeted properties (Table 2) for all three variants of interest [31].

Grain size and shape was the established metric for acceptance. Grain size is reported as major and minor axis length to capture the non-equiaxed nature of the FB-CVD deposited SiC microstructure. Grain size and shape was measured using electron backscatter diffraction (EBSD) techniques based on previously established techniques and reporting [34]. Details of the EBSD acquisition are discussed in depth in the report by Gerczak et al. [31].

The SiC layer for the Baseline and PyC Variants were deposited using MTS in Ar + H_2 at 1425 ℃ to target the fine-grained SiC microstructure obtained during deposition of AGR-1 Variant 3 and AGR-2 UCO TRISO fuel [38,39]. Initial SiC depositions focused on obtaining optimal fluidization conditions. Significant porosity was observed in the initial runs and the CGF was adjusted to obtain high quality SiC layers [31]. The CGF was increased from 0.015 to 0.023 over a series of deposition runs. The higher CGF yielded SiC with limited porosity.

The depositions at 1425 ℃ resulted in a SiC grain size below of the targeted criteria; average major axis of 0.67±0.13 μm and minor axis of 0.25±0.04 μm. In subsequent runs the temperature was increased in 25 ℃ increments to impact the final grain size. The optimal deposition conditions for the Baseline and PyC Variants were identified as ~200 min deposition at 1450 ℃, 3250 sccm Ar, 3250 sccm H_2 with a coating gas fraction of 0.021 resulting in ~180 g of MTS being consumed. These conditions yielded a SiC microstructure with an average major axis of 0.85±0.33 μm and minor axis of 0.30±0.08 μm which satisfied the targeted grain size criteria (Table 2). Figure 5 shows an inverse pole figure of the local grain orientation of the SiC layer visualizing the microstructure. The deposition at 1475 ℃ resulted in an average grain size just outside the targeted criteria; average major axis of 1.03±0.38 μm and minor axis of 0.41±0.11 μm. The ± represents one standard deviation from the calculated mean [31].

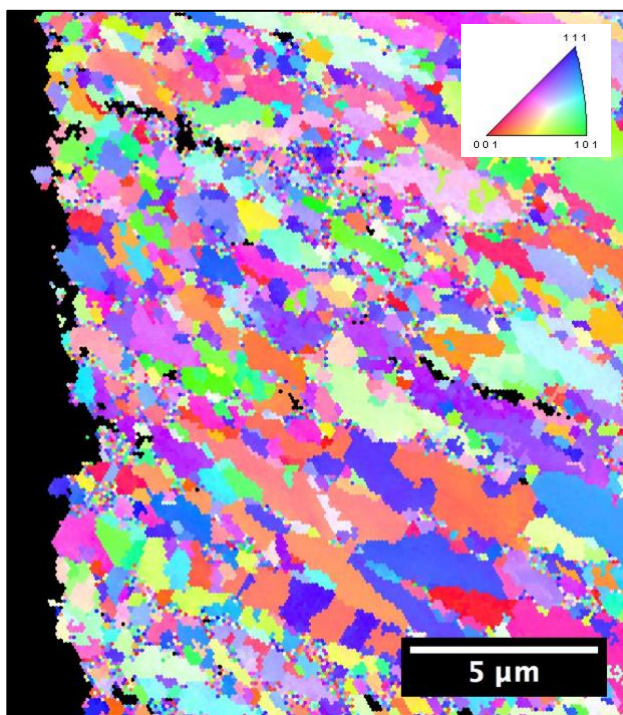**Figure 5. Inverse pole figure showing local variation in the SiC microstructure of the Baseline variant [33].**

Prior experience shows deposition in pure H_2 yields large grained SiC relative to Ar + H_2 fluidized depositions [38]. To target the large grain size sought for the SiC Variant the SiC was initially deposited in pure H_2. The change in fluidization gas required an increase in TGF from 7000 sccm to 13000 sccm to

maintain fluidization over the course of the deposition [31]. The resultant SiC displayed an increase grain size, however, the SiC layer was prone to disruptions leading to an irregular SiC microstructure. An example of the SiC microstructure with a layer disruption is shown in Figure 6. The presence of disruptions is atypical of coated particle fuel depositions and is likely resultant of the planar geometry.
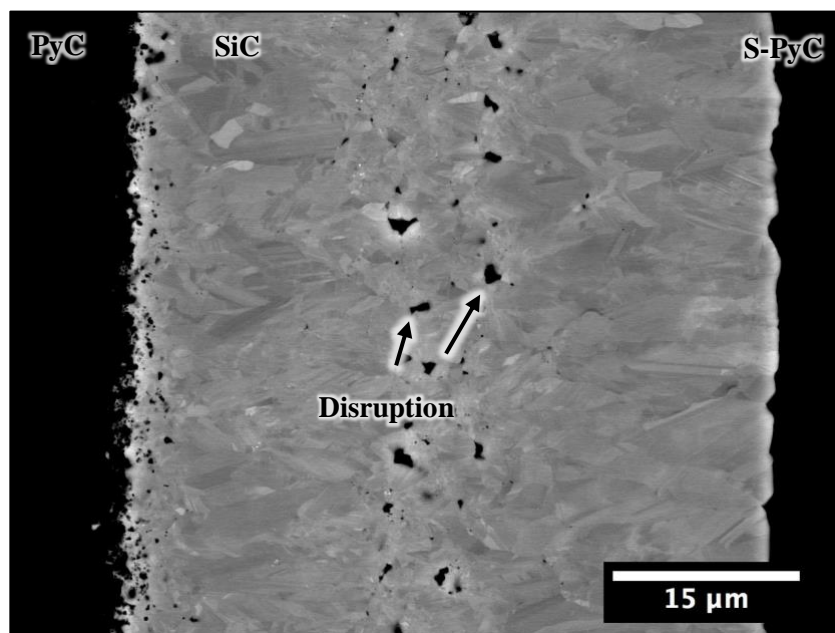
Figure 6. Scanning electron microscope, backscatter electron image of the SiC layer for a pure H$_2$ fluidized SiC showing a disruption in the SiC coating layer [31]**.**

The Ar + H$_2$ fluidized depositions did not display any layer disruptions. The series of coating runs with incrementally higher temperatures (1425–1475 ℃) confirmed the grain size could be manipulated as a function of temperature. Attempts to achieve the targeted grain size for the SiC variant at higher temperature depositions (>1475 ℃) in a Ar+ H$_2$ fluidized bed were successful in achieving larger-grained SiC with no observable disruptions [31]. The optimal deposition conditions for the SiC variant was identified as ~200 min deposition at 1550 ℃, 3250 sccm Ar, 3250 sccm H$_2$ with a coating gas fraction of 0.021 resulting in ~180 g of MTS being consumed. This deposition was 100 ℃ greater than the Baseline and PyC variant depositions. These conditions yielded a SiC microstructure with an average major axis of 2.50±1.01 μm and minor axis of 0.53±0.14 μm which satisfied the targeted grain size criteria [31]. Figure 7 shows an inverse pole figure of the local grain orientation of the SiC layer to visualize the microstructure. Comparisons of Figure 5 and Figure 7 show the qualitative difference in obtained SiC microstructures.

Figure 7. Inverse pole figure showing local variation in the SiC microstructure of the SiC variant [33]**.**

3. DEVELOPMENT OF ISOLATED DIFFUISON COUPLE SYSTEM

3.1 DELIVERY OF DIFFUSING SPECIES: ION IMPLANTATION

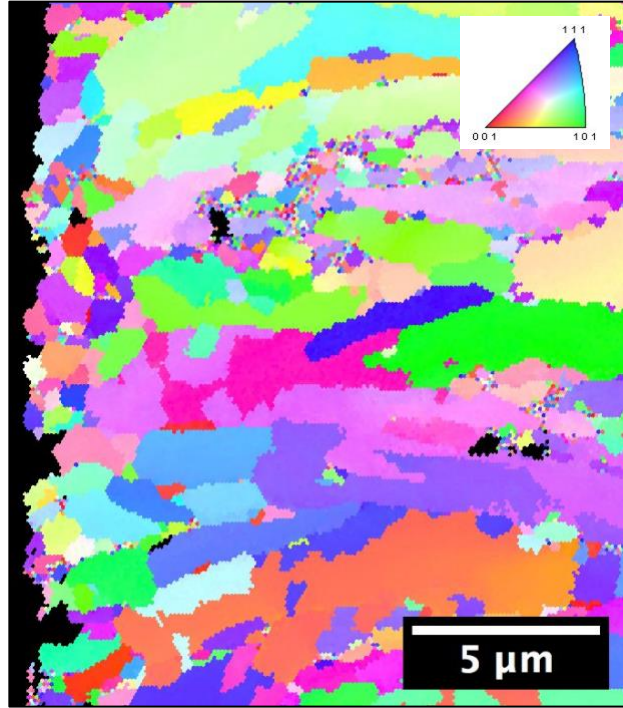Ion implantation was identified as an ideal approach to introduce the simulated fission product species into the PyC layer in the PyC/SiC/S-PyC diffusion couple samples. Direct implantation into the PyC layer ensures the diffusion pathway follows PyC → SiC for the SiC layer of interest. Ion implantation was conducted at the University of Michigan's Michigan Ion Beam Laboratory through Nuclear Science User Facility access. The implantations were conducted on a 400-kV Ion Implanter (NEC, Middleton, WI, USA). Four different systems were implanted: Ag, Ag+Pd, Eu, and Sr (Table 1) [32]. The implanted dose was based on the calculated concentration of each species in an AGR-1 TRISO fuel particle at end-of-life (EOL) [33]. The total planned dose was adjusted for the difference in total PyC/SiC surface area between a typical TRISO particle and the planar diffusion couple design. Table 3 lists the implanted fluence for each system [33]. Variation between the targeted fluence and actual fluence exists due to experimental constraints associated with attainable beam current for each specie. In particular the targeted strontium fluence was not attainable due to low achievable beam current leading to a lower than EOL dose [32]. An elevated silver dose was sought due to identified challenges in retaining silver during dose both during development of the diffusion couples design and in prior experiments reported in the literature [15,35]. For silver, an approximately 2× higher dose was implanted.

Table 3. Comparison of implantation dose to estimated dose required to meet EOL inventory [33]**.**

Fission Product System	Actual Fluence* Ions/cm^2	Est. fluence to match EOL inventory^ Ions/cm^2
Ag	8.4×10^{16}	4.0×10^{16}
Ag+Pd#	$8.4 \times 10^{16} / 8.4 \times 10^{16}$	$4.0 \times 10^{16} / 7.4 \times 10^{17}$
Eu	5.7×10^{16}	7.6×10^{16}
Sr	5.7×10^{16}	1.3×10^{18}

*All implantations were conducted at 400 kV at room temperature.
^Considers all isotopes generated through fission [40].
#Implantations were conducted in succession.

3.2   SEAL COATING

The final step in the diffusion couple fabrication process was the development of a high temperature seal coating of the PyC/SiC/S-PyC diffusion couple. The seal-coating was implemented to produce an isolated system to retain the implanted dose during high temperature neutron irradiation and thermal exposure. The seal coating development required significant development effort which primarily focused on the retention of mobile implanted species. The retention of silver was the primary point of focus of the development process as it is the most mobile of the implanted species in PyC [1].

An in depth description of the seal-coating development can be found in the prior reports by Gerczak et al. [28,30–33]. The seal coating deposition varied from standard SiC deposition. A primary variation is that the seal coating was deposited on the 3×4–5 mm, PyC/SiC/S-PyC samples and not sapphire disks. The fluidization media consisted of buffer coated ZrO_2 beads instead of ZrO_2 beads to reduce the mechanical impact on the samples and the samples were inserted into the fluidized bed at temperature. Initial efforts focused on utilizing a MTS-derived SiC layer similar to the SiC layer in the PyC/SiC/S-PyC structure. The MTS-derived SiC was considered ideal as it has demonstrated high temperature stability and radiation tolerance and limited variation in structure relative to the tailored SiC layer. However, the deposition rate was not rapid enough to retain the implanted dose at 1425 ℃ due to silver diffusion in the PyC [31]. The retained dose was measured via depth profiling using glow discharge optical emission spectroscopy (GD-OES) [32].

Alternative "low" temperature seal coating was sought to produce an isolated diffusion system. The FB-CVD reactor has demonstrated the ability to produce SiC below 900 ℃ using a methylsilane (MS) as a precursor gas [41]. A series of depositions were pursued to develop the capability to deposit SiC at low temperatures and the subsequent stability of the MS-derived SiC [28,32]. Deposition was observed at above 700 ℃. Figure 8 shows optical images of the cross-sections of MS-derived SiC deposited at 700 ℃ and 900 ℃ on PyC. The images show a qualitative difference in structure. Post deposition heating tests show improved thermal stability of the SiC layer with elevated deposition temperature with neither layer showing complete stability above 1000 ℃. An inverse correlation with dose retention and deposition temperature was also observed with the lower temperature depositions retaining more of the initial implantation dose [28,32].
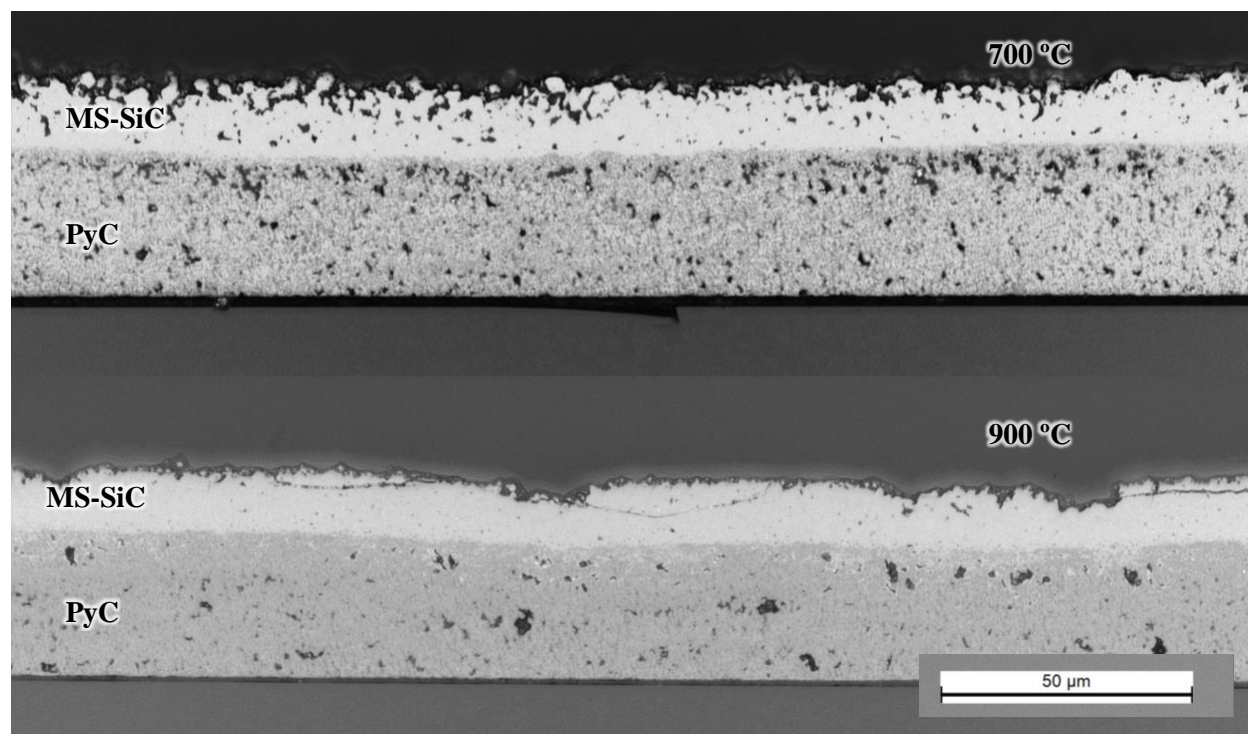
Figure 8. Optical images of MS-SiC/PyC cross-sections deposited at 700 ºC and 900 ºC [32].

Due to the limited robustness of the MS derived SiC at high temperatures and inverse relationship of dose retention with deposition temperature a multistep seal-coating process was developed. The final identified process involved three separate, interrupted depositions. The first two depositions were MS-derived SiC at 700 ºC and 900 ºC, these layers provided initial barriers to loss of the implantation dose. A final MTS-derived SiC layer deposited at 1425 ºC provided high temperature stability during irradiation testing and thermal exposures [28]. The deposition conditions for the multi-step process is shown in Table 4. The retained dose after deposition is shown in Figure 9 and establishes the fabrication of an isolated system with remaining dose available for diffusion [28]. One detrimental aspect of the low temperature MS-derived SiC was the elevated solubility relative to the MTS-derived SiC, however, this aspect was considered acceptable, but must be considered when interpreting the results of eth diffusion study.

Table 4. Multilayer SiC seal coating conditions [28].

Precursor Gas	Run Time (min)	Temp. (°C)	Ar	H_2	MS	CGF[a]	MTS used (g)
MS	45	700	6000	-	60	0.0099	
MS	120	900	6000	-	60	0.0099	
MTS	56	1425	3500	3500	-	0.0224	60

[a]CGF is coating gas fraction, all gas flow rates are in standard cubic centimeters per minute (sccm).
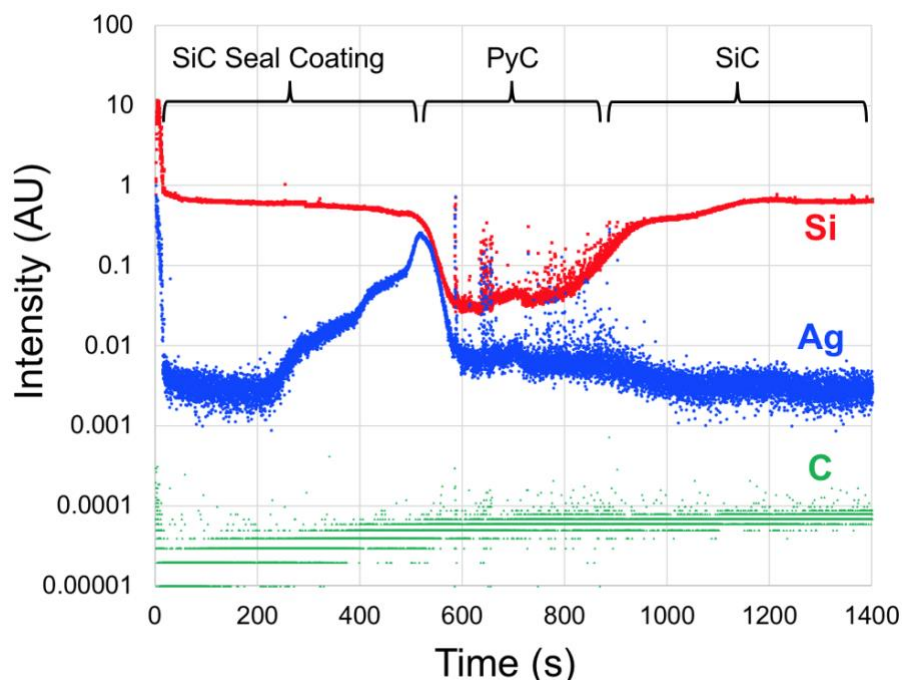
Figure 9. GD-OES depth profile of multilayer SiC seal coating on silver implanted Baseline PyC/SiC/S-PyC diffusion couple. Time correlates to depth [28].

3.3 FINAL SAMPLE PRODUCTION AND TESTING STATUS

Layered diffusion couple samples consisting of PyC/SiC/S-PyC with tailored properties were produced following the deposition conditions identified for each specific variant (Baseline, PyC, and SiC) described in Section 2. Ion implantation was conducted by the University of Michigan's Michigan Ion Beam Laboratory to introduce the diffusion species and an isolated system was obtained through the development of a high temperature seal coating (Table 4). Samples have been produced to complete the test matrix identified in Table 1 including both neutron irradiation and thermal exposure samples. A total of 120 unique diffusion couples samples were produced to satisfy the test matrix.

The neutron irradiation testing has been completed. The rabbit capsule assembly was completed in June, 2018 and is outline in the report "Assembly of rabbit Capsules for Irradiation of Pyrolytic Carbon / Silicon Carbide Diffusion Couples in the High Flux Isotope Reactor – ORNL/SPR-2018/876" [42]. Two capsules were constructed for the planned 0.5 and 1.0 dpa irradiations. The capsules were subsequently inserted into HFIR cycle 481 in location B3, position 6. Capsule DC01 experienced 120 hours of total irradiation time, while Capsule DC02 experienced 263.02 hours. The capsules are currently awaiting disassembly followed by subsequent sample analysis and confirmation of irradiation conditions.

Thermal testing is ongoing in a Thermal Technology Inc. graphite element ASTRO furnace. The system is capable of exposures up to 1800 °C. The neutron equivalent samples (Table 1) will be thermally exposed upon completion of the SiC thermometry analysis [43]. The thermometry analysis is required to validate the capsule irradiation temperature. High temperature thermal diffusion exposures have been initiated. The first thermal exposures were tested up to 1700 °C for 150 hours. The samples maintained their integrity with no visible deterioration, Figure 10.
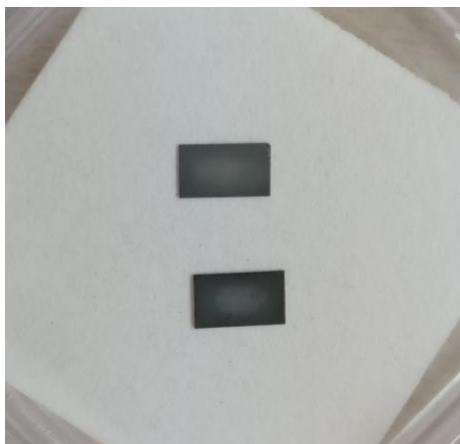
Figure 10. Seal-coated PyC/SiC/S-PyC samples as-fabricated (top) and after thermal exposure at 1700 ºC, 150 hours (bottom).

4. SUMMARY

An extensive research and development effort was successfully completed to produce diffusion couples to explore diffusion of several fission product systems (Ag, Ag+Pd, Eu, and Sr) in representative TRISO layer materials. The final design was constrained by several experimental criteria based on observations from TRISO fuel behavior. The final design consisted of ion implanted PyC/SiC/S-PyC layer structures subsequently seal coated to produce an isolated system for exposure and diffusion analysis. The Baseline variant's PyC and SiC layer properties were tailored to represent the layer properties of AGR TRISO fuel. The PyC and SiC Variants explored differences in their PyC (density) and SiC (grain size) layer properties to understand the impact of these properties on fission product diffusion. Samples have been fabricated to explore both neutron irradiation effects and high temperature thermal diffusion. Sample exposure and diffusion analysis is ongoing.

5.   REFERENCES

[1]   K. Verfondern, Fuel performance and fission product behaviour in gas cooled reactors, Vienna, 1997.

[2]   D.A. Petti, J. Maki, J. Hunn, P. Pappano, C. Barnes, J. Saurwein, S. Nagley, J. Kendall, R. Hobbins, An Overview of the DOE Advanced Gas Reactor Fuel Development and Qualification Program, J. Mater. 62 (2006) 62–66.

[3]   C.W. Forsberg, Developments in Molten Salt and Liquid-Salt-Cooled Reactors, Proc. ICAPP '06. (2006).

[4]   K.A. Terrani, L.L. Snead, J.C. Gehin, Microencapsulated fuel technology for commercial light water and advanced reactor application, J. Nucl. Mater. 427 (2012) 209–224. doi:10.1016/j.jnucmat.2012.05.021.

[5]   B.P. Collin, AGR-2 Irradiation Test Final As-Run Report, Idaho Falls, 2014.

[6]   R.N. Morris, C.A. Baldwin, P.A. Demkowicz, J.D. Hunn, E.L. Reber, Performance of AGR-1 high-temperature reactor fuel during post-irradiation heating tests, Nucl. Eng. Des. 306 (2016) 24–35. doi:10.1016/j.nucengdes.2016.04.031.

[7]   J.D. Hunn, C.A. Baldwin, F.C. Montgomery, T.J. Gerczak, R.N. Morris, G.W. Helmreich, P.A. Demkowicz, J.M. Harp, J.D. Stempien, Initial examination of fuel compacts and TRISO particles from the US AGR-2 irradiation test, Nucl. Eng. Des. 329 (2018) 89–101. doi:10.1016/j.nucengdes.2017.09.017.

[8]   J.B. Malherbe, Diffusion of fission products and radiation damage in SiC, J. Phys. D. Appl. Phys. 46 (2013). doi:10.1088/0022-3727/46/47/473001.

[9]   B.G. Kim, S. Yeo, Y.W. Lee, M.S. Cho, Comparison of diffusion coefficients and activation energies for ag diffusion in silicon carbide, Nucl. Eng. Technol. 47 (2015) 608–616. doi:10.1016/j.net.2015.05.004.

[10]   I.J. Van Rooyen, M.L. Dunzik-Gougar, P.M. Van Rooyen, Silver (Ag) transport mechanisms in TRISO coated particles: A critical review, Nucl. Eng. Des. 271 (2014) 180–188. doi:10.1016/j.nucengdes.2013.11.029.

[11]   E.J. Olivier, J.H. Neethling, The role of Pd in the transport of Ag in SiC, J. Nucl. Mater. 432 (2013) 252–260. doi:10.1016/j.jnucmat.2012.07.033.

[12]   J.H. Neethling, J.H. O'Connell, E.J. Olivier, Palladium assisted silver transport in polycrystalline SiC, Nucl. Eng. Des. 251 (2012) 230–234. doi:10.1016/j.nucengdes.2011.09.064.

[13]   R.E. Bullock, Fission-product release during postirradiation annealing of several types of coated fuel particles, J. Nucl. Mater. 125 (1984) 304–319. doi:10.1016/0022-3115(84)90558-0.

[14]   J.J. van der Merwe, Evaluation of silver transport through SiC during the German HTR fuel program, J. Nucl. Mater. 395 (2009) 99–111. doi:10.1016/j.jnucmat.2009.09.024.

[15]   T.J. Gerczak, B. Leng, K. Sridharan, J.L. Hunter, A.J. Giordani, T.R. Allen, Observations of Ag diffusion in ion implanted SiC, J. Nucl. Mater. 461 (2015). doi:10.1016/j.jnucmat.2015.03.027.

[16]   B. Leng, H. Ko, T.J. Gerczak, J. Deng, A.J. Giordani, J.L. Hunter, D. Morgan, I. Szlufarska, K. Sridharan, Effect of carbon ion irradiation on Ag diffusion in SiC, J. Nucl. Mater. 471 (2016). doi:10.1016/j.jnucmat.2015.11.017.

[17]   D. Shrader, S.M. Khalil, T. Gerczak, T.R. Allen, A.J. Heim, I. Szlufarska, D. Morgan, Ag diffusion in cubic silicon carbide, J. Nucl. Mater. 408 (2011). doi:10.1016/j.jnucmat.2010.10.088.

[18]   S. Khalil, N. Swaminathan, D. Shrader, A.J. Heim, D.D. Morgan, I. Szlufarska, Diffusion of Ag along Σ3 grain boundaries in 3C-SiC, Phys. Rev. B - Condens. Matter Mater. Phys. 84 (2011) 1–13. doi:10.1103/PhysRevB.84.214104.

[19]   H. Nabielek, P.E. Brown, P. Offermann, Silver Release from Coated Particle Fuel, Nucl. Technol. 35 (1977) 483–493. doi:10.13182/NT35-483.

[20]   E. Friedland, J.B. Malherbe, N.G. van der Berg, T. Hlatshwayo, A.J. Botha, E. Wendler, W. Wesch, Study of silver diffusion in silicon carbide, J. Nucl. Mater. 389 (2009) 326–331.

doi:10.1016/j.jnucmat.2009.02.022.

[21]   E. Friedland, N.G. Van Der Berg, J.B. Malherbe, J.J. Hancke, J. Barry, E. Wendler, W. Wesch, Investigation of silver and iodine transport through silicon carbide layers prepared for nuclear fuel element cladding, J. Nucl. Mater. 410 (2011) 24–31. doi:10.1016/j.jnucmat.2010.12.243.

[22]   E. Lopez-Honorato, D.X. Yang, J. Tan, P.J. Meadows, P. Xiaow, Silver diffusion in coated fuel particles, J. Am. Ceram. Soc. 93 (2010) 3076–3079. doi:10.1111/j.1551-2916.2010.04055.x.

[23]   T.T. Hlatshwayo, J.B. Malherbe, N.G. Van Der Berg, L.C. Prinsloo, A.J. Botha, E. Wendler, W. Wesch, Annealing of silver implanted 6H-SiC and the diffusion of the silver, Nucl. Instruments Methods Phys. Res. Sect. B Beam Interact. with Mater. Atoms. 274 (2012) 120–125. doi:10.1016/j.nimb.2011.12.006.

[24]   H.J. MacLean, R.G. Ballinger, L.E. Kolaya, S.A. Simonson, N. Lewis, M.E. Hanson, The effect of annealing at 1500 °C on migration and release of ion implanted silver in CVD silicon carbide, J. Nucl. Mater. 357 (2006) 31–47. doi:10.1016/j.jnucmat.2006.05.043.

[25]   H.Y. Xiao, Y. Zhang, L.L. Snead, V. Shutthanandan, H.Z. Xue, W.J. Weber, Near-surface and bulk behavior of Ag in SiC, J. Nucl. Mater. 420 (2012) 123–130. doi:10.1016/j.jnucmat.2011.09.028.

[26]   W. Amian, D. Stöver, Diffusion of Silver and Cesium in Silicon-Carbide Coatings of Fuel Particles for High-Temperature Gas-Cooled Reactors, Nucl. Technol. 61 (1983) 475–486. doi:10.13182/NT61-475.

[27]   D.A. Petti, J. Buongiorno, J.T. Maki, R.R. Hobbins, G.K. Miller, Key differences in the fabrication, irradiation and high temperature accident testing of US and German TRISO-coated particle fuel, and their implications on fuel performance, Nucl. Eng. Des. 222 (2003) 281–297. doi:10.1016/S0029-5493(03)00033-5.

[28]   T.J. Gerczak, A.A. Campbell, J.D. Hunn, B.C. Jolly, A.T. Schumacher, R.L. Seibert, FY18Q3 Quarterly Report : Radiation Enhanced Diffusion of Ag , Ag-Pd , Eu , and Sr in Neutron Irradiated PyC / SiC Diffusion Couples, (2018).

[29]   C.M. Petrie, Design and Thermal Analysis for Irradiation of Pyrolytic Carbon / Silicon Carbide Diffusion Couples in the High Flux Isotope Reactor, (2017).

[30]   T.J. Gerczak, A.A. Campbell, J.D. Hunn, B.C. Jolly, A.T. Schumacher, Progress on Fabrication of Planar , Representative PyC / SiC Diffusion Couples, 2017.

[31]   T.J. Gerczak, A.A. Campbell, J.D. Hunn, B.C. Jolly, A.T. Schumacher, FY18Q1 Quarterly Report : Radiation Enhanced Diffusion of Ag , Ag-Pd , Eu , and Sr in Neutron Irradiated PyC / SiC Diffusion Couples, 2018.

[32]   T.J. Gerczak, A.A. Campbell, J.D. Hunn, B.C. Jolly, A.T. Schumacher, FY18Q2 Quarterly Report : Radiation Enhanced Diffusion of Ag , Ag-Pd , Eu , and Sr in Neutron Irradiated PyC / SiC Diffusion Couples, (2018).

[33]   T.J. Gerczak, J.D. Hunn, B.C. Jolly, A.T. Schumacher, X. Hu, A.A. Campbell, J.A. Dyer, Development of Planar PyC / SiC Diffusion Couples to Investigate Irradiation Effects and Microstructural Variation on Fission Product Diffusion, (2018).

[34]   T.J. Gerczak, J.D. Hunn, R.A. Lowden, T.R. Allen, SiC layer microstructure in AGR-1 and AGR-2 TRISO fuel particles and the influence of its variation on the effective diffusion of key fission products, J. Nucl. Mater. 480 (2016). doi:10.1016/j.jnucmat.2016.08.011.

[35]   S. Dwaraknath, G.S. Was, Development of a multi-layer diffusion couple to study fission product transport in β-SiC, J. Nucl. Mater. 444 (2014) 170–174. doi:10.1016/j.jnucmat.2013.09.040.

[36]   S.S. Dwaraknath, G.S. Was, The diffusion of cesium, strontium, and europium in silicon carbide, J. Nucl. Mater. 476 (2016) 155–167. doi:10.1016/j.jnucmat.2016.04.034.

[37]   J.D. Hunn, G.E. Jellison, R.A. Lowden, Increase in pyrolytic carbon optical anisotropy and density during processing of coated particle fuel due to heat treatment, J. Nucl. Mater. 374 (2008) 445–452. doi:10.1016/j.jnucmat.2007.10.003.

[38]   R.A. Lowden, Fabrication of Baseline and Variant Particle Fuel for AGR-1, Oak Ridge, 2006.

[39]   C.M. Barnes, D.W. Marshall, B.L. Tomlin, J.T. Keeley, C.M. Barnes, Results of Tests to

Demonstrate a Six-Inch - Diameter Coater for Production of TRISO- Coated Particles for Advanced Gas Reactor Experiments, (2008).

[40] J.W. Sterbentz, JMOCUP As-Run Daily Depletion Calculation for the AGR-1 Experiment in ATR B-10 Position, Idaho Falls, 2009.

[41] J.H. Miller, Methylsilane derived SiC particle coatings produced by fluid-bed chemcial vapor depostion, The University of Tennessee, 2006.

[42] A.G. Le Coq, K.D. Linton, R.C. Gallagher, T.J. Gerczak, K.A. Terrani, C.M. Petrie, Assembly of Rabbit Capsules for Irradiation of Pyrolytic Carbon / Silicon Carbide Diffusion Couples in the High Flux Isotope Reactor, (2018).

[43] A.A. Campbell, W.D. Porter, Y. Katoh, L.L. Snead, Method for analyzing passive silicon carbide thermometry with a continuous dilatometer to determine irradiation temperature, Nucl. Instruments Methods Phys. Res. Sect. B Beam Interact. with Mater. Atoms. 370 (2016) 49–58. doi:10.1016/j.nimb.2016.01.005.