ORNL/TM-2018/918

FY18Q3 Quarterly Report: Radiation Enhanced Diffusion of Ag, Ag-Pd, Eu, and Sr in Neutron Irradiated PyC/SiC Diffusion Couples

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

July 2018

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

ORNL/TM-2018/918

Fusion and Materials for Nuclear Systems Division

FY18Q3 QUARTERLY REPORT: RADIATION ENHANCED DIFFUSION OF AG, AG-PD, EU, AND SR IN NEUTRON IRRADIATED PYC/SIC DIFFUSION COUPLES

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

Date Published: July 2018

Prepared by
OAK RIDGE NATIONAL LABORATORY
Oak Ridge, TN 37831-6283
managed by
UT-BATTELLE, LLC
for the
US DEPARTMENT OF ENERGY
under contract DE-AC05-00OR22725

CONTENTS

LIST OF FIGURES

LIST OF TABLES

ACRONYMS

AGR	Advanced Gas Reactor (Fuel Development and Qualification Program)
AGR-1	First AGR fuel irradiation experiment
CGF	Coating gas fraction
FBCVD	Fluidized-bed chemical vapor deposition
GD-OES	Glow-discharge optical emission spectrocopy
HFIR	High Flux Isotope Reactor
MS	Methylsilane
MTS	Methyltrichlorosilane
ORNL	Oak Ridge National Laboratory
PyC	Pyrolytic carbon or pyrocarbon
S-PyC	Support pyrocarbon
sccm	Standard cubic centimeters per minute
SiC	Silicon carbide (TRISO layer)
SIMS	Secondary ion mass spectroscopy
TRISO	Tristructural-isotropic (coated particles)

ACKNOWLEDGMENTS

This research is being performed using funding received from the DOE Office of Nuclear Energy's Nuclear Energy University Program through a joint NEET/NEUP R&D with NSUF access award (Project 16-10764). Significant support for this work was provided by Victoria Cox, J. Travis Dixon, and Tom Geer.

ABSTRACT

Obtaining accurate diffusion kinetics in materials representative of those found in tristructural-isotopic (TRISO) coated particle fuel is needed to predict the diffusive release of fission products in reactor. Planar diffusion couples with representative pyrocarbon (PyC) and silicon carbide (SiC) layers are being produced using the same fluidized-bed chemical vapor deposition (FBCVD) technology used to produce TRISO particles from the first irradiation experiment of the Advanced Gas Reactor (AGR) Fuel Qualification and Development Program. The layer properties of the planar diffusion couples are tailored to meet the specified PyC density and microstructure of the SiC layer as defined by the AGR program. The influence of these variables on diffusion is also being explored by producing PyC and SiC variants. The pathway to producing the diffusion couples is discussed and builds upon efforts described in previous reports [1–3].

1. INTRODUCTION

A need exists to explore diffusion and obtain diffusion coefficients of select fission product species in materials representative of TRISO coated particle fuel. Planar diffusion couples with representative PyC and SiC layers are being developed to explore diffusion of silver, silver and palladium, europium, and strontium (Ag, Ag+Pd, Eu, and Sr) in TRISO-SiC materials. The fission product species of interest are introduced to the PyC layer and diffuse to and subsequently into the SiC layer through the PyC. This diffusion pathway mimics the release pathway expected for fission product release from intact TRISO fuel. The planar design is optimal for ion implantation to introduce the fission product species of interest and implementation of sensitive depth profiling techniques such as glow discharge optical emission spectroscopy (GD-OES) and secondary ion mass spectroscopy (SIMS) for accurate diffusion analysis.

The development process of the planar diffusion couple design consists of three primary steps. The first step includes depositing representative layers stepwise (PyC/SiC/PyC) via FBCVD and targeting layer properties in a planar geometry to achieve the three defined diffusion couple variants (Baseline, PyC, and SiC). The second step involves implantation of fission product species into the PyC layer. The third step involves deposition of a high temperature SiC seal coating to create an isolated diffusion couple system. The scope of the diffusion analysis covers exploration of the impact of in-situ neutron irradiation on diffusion and high tempeture diffusion for the three variants and four simulated fission product systems. The planned test matrix is shown in Table 1.

Table 1. Planned diffusion couple test matrix

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, 150 & 300 h)*	Baseline: Ag, Ag+Pd, Eu, Sr PyC Variant: Ag, Ag+Pd SiC Variant: Ag, Eu Sr
High-Temperature Thermal Diffusion (1600 °C, 150 & 300 h)*	Baseline: Ag, Ag+Pd, Eu, Sr PyC Variant: Ag, Ag+Pd SiC Variant: Ag, Eu Sr
High-Temperature Thermal Diffusion (1700 °C, 150 & 300 h)*	Baseline: Ag, Ag+Pd, Eu, Sr PyC Variant: Ag, Ag+Pd SiC Variant: Ag, Eu Sr

*exposure times may be adjusted based on initial observations.

The overall development process defining the layer properties to build the PyC/SiC/Support-PyC (S-PyC) has been described in previous reports [1–3]. Prior efforts have also focused on the implantation of the diffusing species in finalized PyC/SiC/S-PyC layer structures and initial development of the SiC seal coating efforts to generate the isolated diffusion system [3]. Efforts this quarter focused on finalizing the seal coating approach and producing final seal-coated samples for neutron irradiation exposure in the High Flux Isotope Reactor (HFIR) at Oak Ridge National Laboratory (ORNL).

2. SEAL COATING DEVELOPMENT

Initial SiC seal coating development focused on methyltrichlorosilane (MTS) derived SiC coatings. These coatings were produced with similar deposition conditions to the SiC layers of interest for diffusion analysis [2,3], however, the high temperature nature of these coatings did not sufficiently retain the implanted dose associated with the fission product species of interest [3]. The retained silver profile in silver ion implanted samples was analyzed to confirm successful seal coating development due to silver's higher diffusivity in the PyC layer relative to the other fission product systems and previous challenges with silver retention in diffusion studies [4]. A lower temperature SiC layer deposition was pursued based on precedence from prior silver/SiC coated particle diffusion couples [5]. The use of low temperature methylsilane (MS) derived SiC was targeted and has shown initial success retaining silver at 700 °C, however, the integrity of the coating layer was insufficient to survive elevated exposure conditions. The seal coating trials using MS-derived SiC showed increasing layer quality and survivability as a function of increasing deposition temperatures, however, even at 900 °C the high temperature stability of the layer was insufficient to survive standalone above 1000 °C. Development of the MS-derived seal coating layers also showed sensitivity to the coating surface where deposition on the mirror-finish PyC surface present after release from the sapphire disk resulted in poor adherence for low temperature MS-derived SiC. Figure 1 shows the poor adherence of interrupted coatings of MS-derived SiC layers deposited at 700 °C and 900 °C on the PyC surface of an unimplanted sample released from the sapphire disk whereas the adherence appears intact on the S-PyC terminated surface and edges.

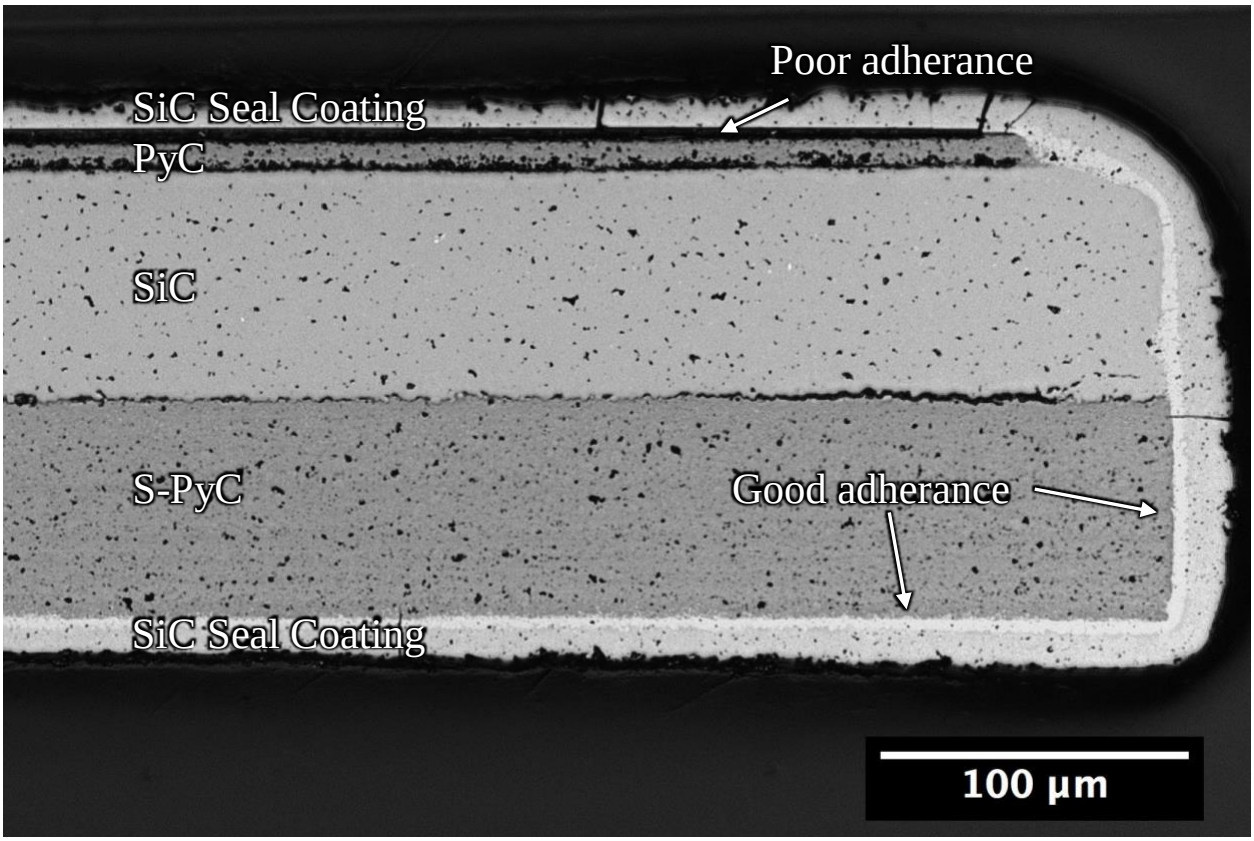

Figure 1. Optical micrograph showing poor adherence on the PyC surface of an unimplanted sample after MS-dervied SiC deposition at 700 °C and 900 °C.

The minimum ion implantation fluence used for the final PyC/SiC/S-PyC samples Ag, Ag+Pd, Eu, and Sr system was $8.4x10^{16}$ ions/cm^2 for Ag and Pd and $5.7x10^{16}$ ions/cm^2 for the Eu and Sr samples with each resulting in a change in surface finish on the PyC surface and a qualitative change in adherence of the MS-derived SiC layers relative to the initial development samples which were implanted with Ag to $4.2x10^{16}$ ions/cm^2 , however, did not show a visible change in appearance [2]. Recent MS-derived coating runs focused on exploring the retention performance on the final implantation samples to optimize the retention performance. Table 2 shows the run conditions of recent seal coating development runs.

Table 2. SiC seal coating development conditions.

Run	Precursor Gas	Run Time (min)	Temp. (°C)	Ar	H_2	MS	CGF[a]	MTS used (g)
MS-SC04	MS	120	900	6000	-	60	0.0099	-
MS-SC05-I	MS	45	700	6000	-	60	0.0099	-
	MS	120	900	6000	-	60	0.0099	-
MS-SC06	MS	120	800	6000	-	60	0.0099	-
MS-MTS-SC04-I	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).

Depth profiles were obtained using GD-OES to determine the relative difference in retained silver between different seal coating conditions. No clear silver was retained in the 900 °C MS-derived SiC seal coating (MS-SC04, Figure 2), while a clear implantation peak was observed for the 800 °C MS-derived SiC seal coating (MS-SC06, Figure 3) and 700 °C with subsequent 900 °C MS-derived SiC seal coating (MS-SC05-I, Figure 4). Because the 900 °C MS-derived SiC seal coating provides improved higher temperature stability over 800 °C MS-derived SiC, the 700 °C with subsequent 900 °C MS-derived SiC seal coating samples were selected as the low temperature seal coating approach prior to the higher temperature MTS-derived SiC seal coating.

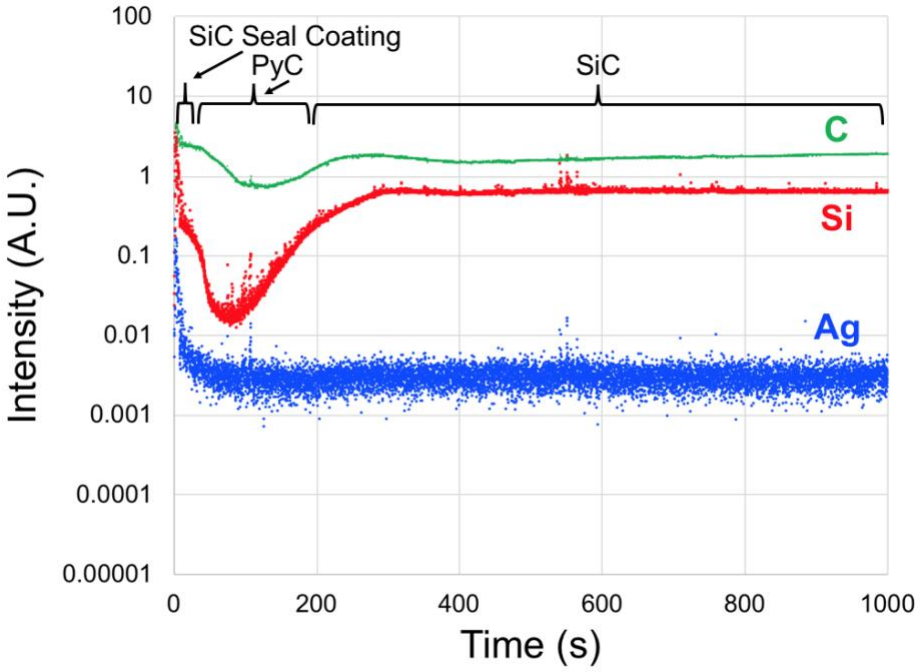

Figure 2. GD-OES depth profile of MS-SC04, 900 °C MS-derived SiC. Time correlates to depth.

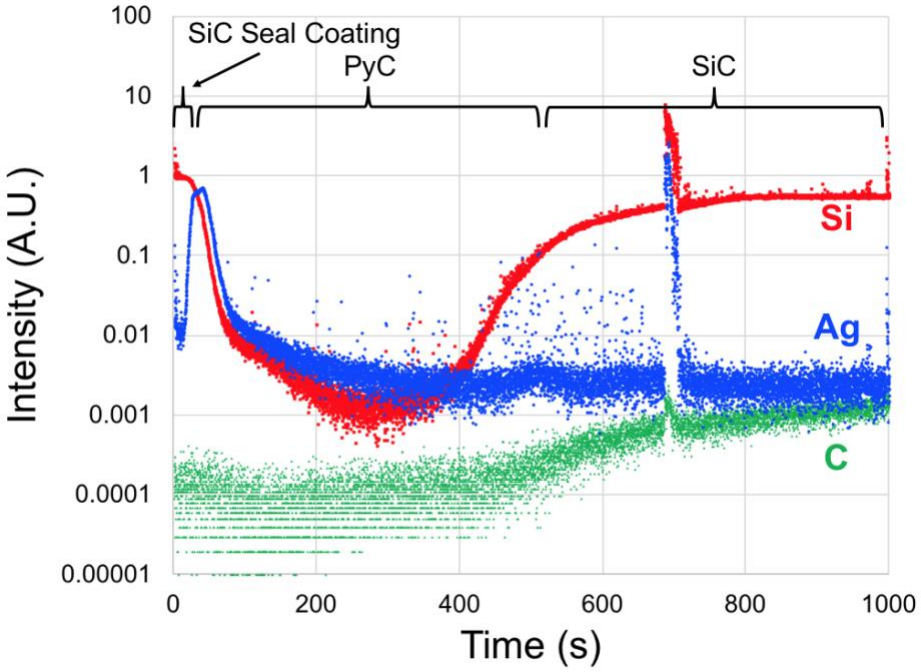

Figure 3. GD-OES depth profile of MS-SC06, 800 °C MS-derived SiC. Time correlates to depth.

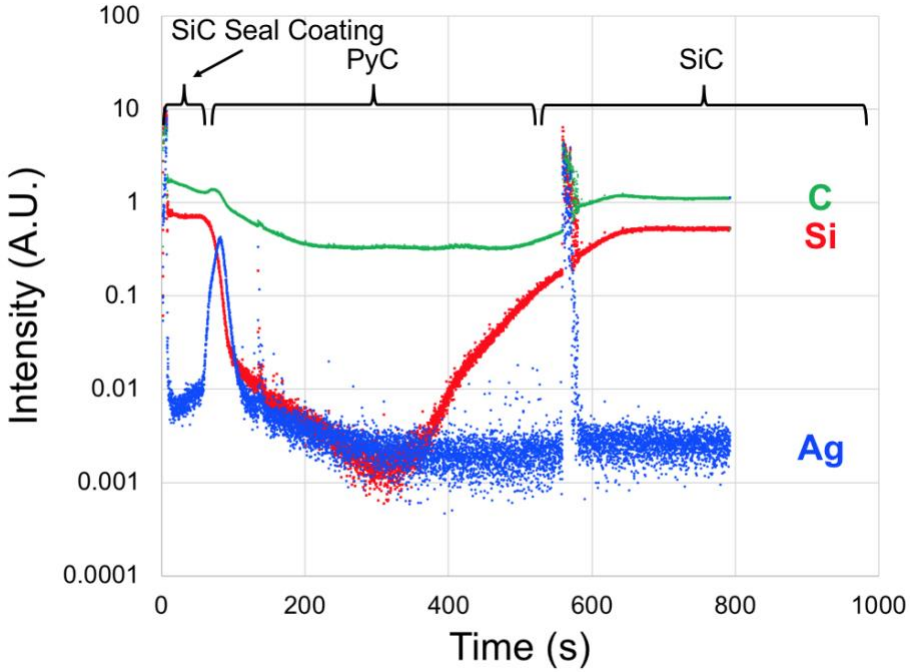

Figure 4. GD-OES depth profile of MS-SC05-I, 700 °C/900 °C MS-derived SiC. Time correlates to depth.

The seal coating run of MS-MTS-SC04-I was comprised of three separate layer depositions; a 700 °C MS-derived SiC seal coating with a subsequent 900 °C MS-derived SiC seal coating followed by a high temperature MTS-derived SiC seal coating layer at 1425 °C. After deposition the coated sample was subjected to GD-OES depth profiling and showed retained silver (Figure 5). The integrated silver intensity was approximately equivalent for the 800 °C MS-derived SiC seal coating and the sequential

700 °C/900 °C MS-derived SiC followed by 1425 °C MTS-derived SiC (MS-MTS-SC04-I) seal coating runs, where the MS-MTS-SC04-I seal coating run indicated ~96% of the total intensity measured from the 800 °C MS-derived SiC seal coated sample was present. This suggests limited loss of silver occurred during the high temperature run relative to the 800 °C MS-derived SiC seal coating. A direct comparison of the GD-OES depth profiles for 700 °C MS-derived SiC sample (MS-SC04) and 700 °C with subsequent 900 °C MS-derived SiC seal coating sample (MS-SC05-I) with MS-MTS-SC04-I was not available due to variation in instrument performance after the analysis of MS-SC05-I resultant from installation of new detectors which influenced relative intensity.

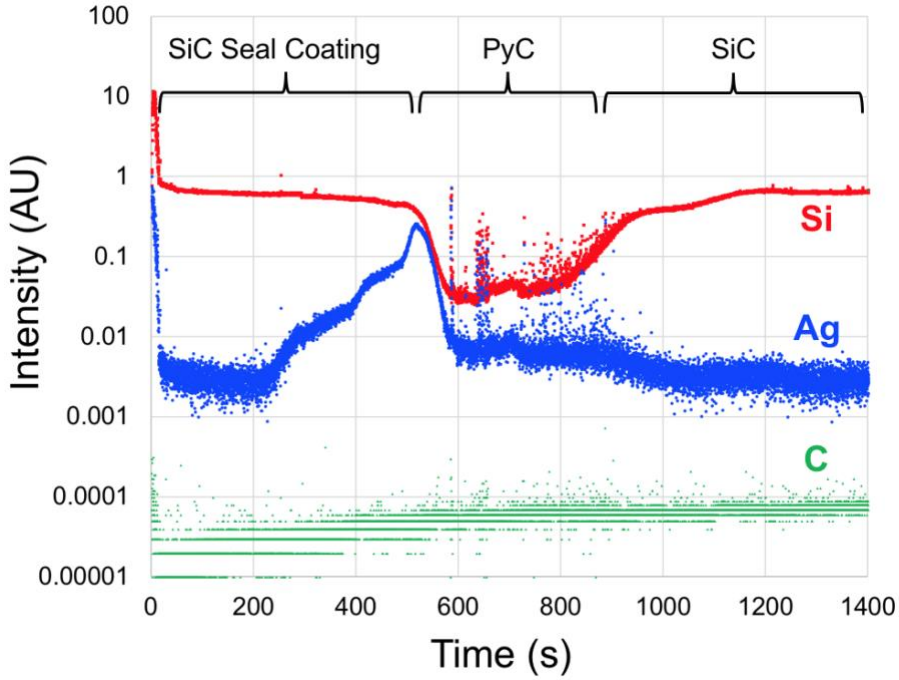

Figure 5. GD-OES depth profile of MS-MTS-SC04-I, 700 °C/900 °C MS-derived SiC followed by 1425 °C MTS-derived SiC. Time correlates to depth

The silver profile of MS-MTS-SC04-I (Figure 5) shows diffusion of the implanted species into the SiC seal coating layers with elevated intensity in depths associated with the 700 °C/900 °C MS-derived SiC coating layers, however, a primary peak at the seal coating SiC and PyC interface remains present along with an apparent concentration profile across the thickness of the PyC layer. This profile is representative of the starting profile for diffusion analysis and is deemed appropriate to initiate diffusion analysis. Insights on diffusion will be determined from changes in the measured concentration profiles as a function of exposure time. The sensitivity of GD-OES may be limited relative to the concentrations of interest. As such other techniques such as SIMS may be required. The use of SIMS has been successfully demonstrated in prior studies of diffusion of fission product species in SiC [6–8].

3. FINAL SAMPLES FOR HFIR IRRADIATION

The 700 °C with subsequent 900 °C MS-derived SiC seal coating followed by a high temperature MTS-derived SiC layer at 1425 °C coating approach, demonstrated by MS-MTS-SC04-I, was implemented on the ion implanted PyC/SiC/S-PyC samples to populate the test samples for insertion into the HFIR. Table 3 shows the coating runs required to populate the test matrix and samples included in each run.

A total of six separate runs were required to populate the samples for inclusion in the HFIR irradiation. A variation in coating process was included for the single crystal 4H-SiC and monolithic CVD-SiC samples directly implanted with silver. These seal coating runs are represented by CVDSiC-MTS-SC02, 4HSiC-MTS-SC01, and 4HSiC-MTS-SC02. These samples were overcoated with 3–4 microns of MTS-derived SiC. The motivation for this MTS-derived SiC seal coating was to protect the implantation surface during exposure as decomposition of the immediate surface has been observed in prior experiments [9]. The high temperatures during the coating also serves to anneal implantation damage. The polycrystalline nature of the seal coating layer also acts as a sink for the diffusing impurity species of interest, which is critical to indirectly observe diffusion in the single crystal 4H-SiC system.

Table 3. SiC seal coating production run conditions.

Run	Precursor Gas	Run Time (min)	Temp. (°C)	Ar	H_2	MS	CGF[a]	MTS used (g)
MS-MTS-SC05-I	MS	45	700	6000	-	60	0.0099	
	MS	120	900	6000	-	60	0.0099	
	MTS	59	1425	3500	3500	-	0.0213	60
MS-MTS-SC06-I	MS	45	700	6000	-	60	0.0099	
	MS	120	900	6000	-	60	0.0099	
	MTS	57	1425	3500	3500	-	0.0220	60
MS-MTS-SC07-I	MS	45	700	6000	-	60	0.0099	
	MS	120	900	6000	-	60	0.0099	
	MTS	58	1425	3500	3500	-	0.0217	60
MS-MTS-SC08-I	MS	45	700	6000	-	60	0.0099	
	MS	120	900	6000	-	60	0.0099	
	MTS	59	1425	3500	3500	-	0.0213	60
MS-MTS-SC09-I	MS	45	700	6000	-	60	0.0099	
	MS	120	900	6000	-	60	0.0099	
	MTS	59	1425	3500	3500	-	0.0213	60
MS-MTS-SC10-I	MS	45	700	6000	-	60	0.0099	
	MS	120	900	6000	-	60	0.0099	
	MTS	82	1425	3500	3500	-	0.0154	60
CVDSiC-MTS-SC02	MTS	19	1425	3500	3500	-	0.0220	20
4HSiC-MTS-SC01	MTS	19	1425	3500	3500	-	0.0220	20
4HSiC-MTS-SC02	MTS	19	1425	3500	3500	-	0.0220	20

[a]CGF is coating gas fraction, all gas flow rates are in standard cubic centimeters per minute (sccm).

The sample matrix for samples to include in the HFIR irradiation is shown in Table 4. A total of 30 samples are included in each capsule with targeted irradiations conditions of 0.5 and 1.0 displacements per atom (dpa) at a targeted average specimen temperature of 1100 °C. The rabbit capsule construction is detailed 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" [10]. A drawing of the capsule design is shown in Figure 6, while samples loaded into the graphite holder are shown in Figure 7. The maximum sample dimensions are 3.35 mm x 5.55 mm x 0.30 mm. Of the samples provided for tolerance checks only single crystal 4H-SiC were out of tolerance. This required a second seal coating run (4HSiC-MTS-SC02) to produce an appropriate number of direct ion implanted single crystal 4H-SiC available for HFIR irradiation. Blank Baseline variant PyC/SiC/S-PyC samples were also produced to fill the sample holder volume and provide relevant samples to the NSUF inventory library for potential future analysis. The capsules were successfully assembled, meeting an NSUF defined milestone [10], and the fabrication package is currently under review and should be submitted to HFIR shortly.

Table 4. Planned samples for HFIR irradiations

0.5 dpa*	**Simulated Fission Product System**				
Variant	**Ag**	**Ag+Pd**	**Eu**	**Sr**	**Blank**
Baseline	3	2	2^	2	4
SiC	3	0	2	2	0
PyC	0	0	0	0	0
CVD-SiC	5	0	0	0	0
4H-SiC	5	0	0	0	0

1.0 dpa*	**Simulated Fission Product System**				
Variant	**Ag**	**Ag+Pd**	**Eu**	**Sr**	**Blank**
Baseline	3	2	2	2	4
SiC	3	0	2	2	0
PyC	0	0	0	0	0
CVD-SiC	5	0	0	0	0
4H-SiC	5	0	0	0	0

*dpa = displacements per atom

^one Eu Baseline sample was compromised and therefore not included in the final build

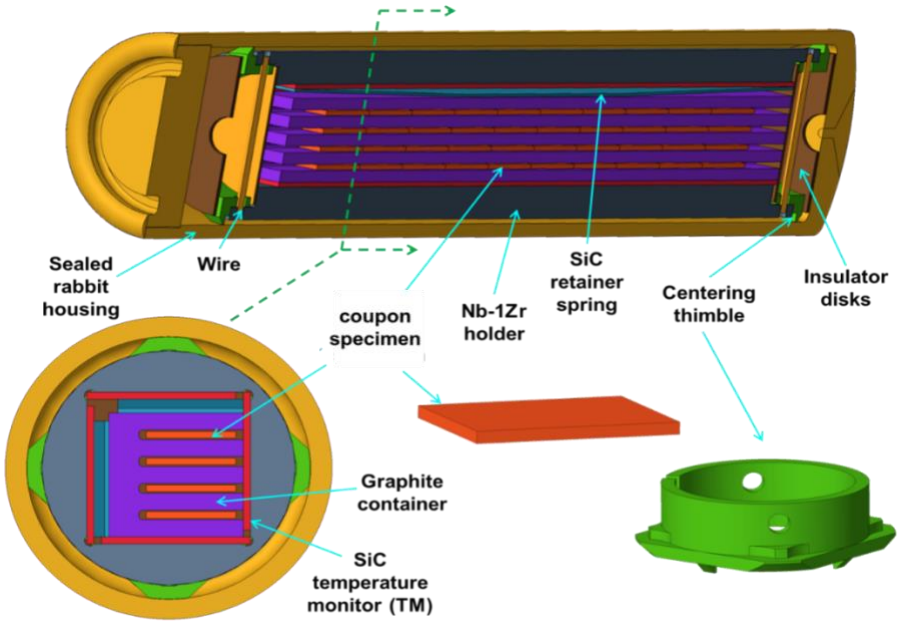

Figure 6. Schematic of capsule design concept, reproduced from [11].

Figure 7. Diffuison couple samples loaded in graphite container and view down the length of graphite container in capsule housing, reproduced from [10].

4. THERMAL EXPOSURES

Diffusion analysis and characterization will be developed first on the high temperature exposure diffusion couples while the HFIR irradiation is ongoing. This is also preferred as the additional challenge of working with neutron irradiated materials is time intensive and limits responsiveness. Table 1 lists the planned diffusion couple exposures with high tempeture exposure targets of 1500 °C, 1600 °C, and 1700 °C to explore accident condition temperatures. Additional seal coating is required to populate the necessary number of samples to explore diffusion at all planned steps as the total number of samples required for irradiation in HFIR have been completed. A subset of completed diffusion couple samples are immediately available to initiate the high temperature exposure study.

Thermal exposures will be carried out using an Thermal Technology Inc. graphite element ASTRO furnace located at ORNL. The system is capable of temperatures up to 1800 °C and exposures up to and potentially beyond 300 hours allowing utilization for the planned diffusion study. The system operates under argon or helium. The furnace has a 3” diameter working zone and can hold all samples for each required condition simultaneously. Two identical furnace units are available for use which limits any accessibility challenges. Figure 8 shows an ASTRO furnace unit.

Figure 8. ASTRO furnace to be used for thermal exposure of diffusion couple samples.

The diffusion couple samples will be exposed in graphite containers identical to those used for the HFIR irradiations to maintain a similar exposure system to that present in the HFIR irradiated samples. The graphite container also limits temperature gradients across the thin diffusion couple samples. The first samples to be explored will be the 150 hours, 1700 °C exposure samples. These samples will be subsequently analyzed by depth profiling techniques to provide a standard for analysis and diffusion behavior. The 1700 °C exposure represents a bounding condition and the following exposure conditions can be modified based on the observed diffusion behavior.

5. SUMMARY AND NEXT STEPS

A low temperature SiC seal coating process which retains significant implantation dose has been developed and refined. The low temperature SiC seal coating process has been implemented to produce the required samples for capsule assembly and ultimate insertion into HFIR. This allows for the study of in-situ neutron radiation effects on fission product diffusion in representative TRISO materials and the impact of select layer properties on diffusion. The capsules are planned for insertion this upcoming quarter. The exposure furnace for the high temperature diffusion has been identified and the first exposures will be carried out and subsequent depth profiling and characterization will commence in the next quarter.

6. REFERENCES

1. Gerczak, T.J., et al., *Progress on Fabrication of Planar Diffusion Couples with Representative TRISO PyC/SiC Microstructure*. ORNL/TM-2017/704, 2017. Oak Ridge: Oak Ridge National Laboratory.
2. Gerczak, T.J., et al., *FY18Q1 Quarterly Report: Radiation Enhanced Diffusion of Ag, Ag-Pd, Eu, and Sr in Neutron Irradiated PyC/SiC Diffusion Couples*. ORNL/TM-2018/766, 2018. Oak Ridge: Oak Ridge National Laboratory.
3. Gerczak, T.J., et al., *FY18Q2 Quarterly Report: Radiation Enhanced Diffusion of Ag, Ag-Pd, Eu, and Sr in Neutron Irradiated PyC/SiC Diffusion Couples*. ORNL/TM-2018/835, 2018. Oak Ridge: Oak Ridge National Laboratory.
4. Verfondern, K. (Ed.), *Fuel Performance and Fission Product Behaviour in Gas Cooled Reactors*. IAEA-ECDOC-978, 1997. Vienna: International Atomic Energy Agency.
5. López-Honorato, E., et al., *Silver Diffusion in Coated Fuel Particles*. Journal of the American Ceramic Society, 2010. 93(10): p. 3076-3079.
6. Gerczak, T.J., et al., *Observations of Ag Diffusion in Ion Implanted SiC*. Journal of Nuclear Materials, 2015. 461: p. 314-324.
7. Leng, B., et al., *Effect of Carbon Ion Irradiation on Ag Diffusion in SiC*. Journal of Nuclear Materials, 2016. 471: p. 220-232.
8. Dwaraknath, S.S., and Was, G.S., *Radiation enhanced diffusion of cesium, strontium, and europium in silicon carbide*. Journal of Nuclear Materials, 2016. 474: p. 76-87.
9. Gerczak, T.J., et al., *Effect of exposure environment on surface decomposition of SiC–silver ion implantation diffusion couples*. Journal of Nuclear Materials, 2015. 456: p. 281-286.
10. Le Coq, A.G., et al., *Assembly of Rabbit Capsules for Irradiation of Pyrolytic Carbon / Silicon Carbide Diffusion Couples in teh High Flux Isotope Reactor*, ORNL/SPR-2018/876, Oak Ridge National Laboratory, Oak Ridge, TN, 2018.
11. C.M. Petrie et al., *Design and Thermal Analysis for Irradiation of Pyrolytic Carbon / Silicon Carbide Diffusion Couples in the High Flux Isotope Reactor*, ORNL/TM-2017/390, Oak Ridge National Laboratory, Oak Ridge, TN, 2017.