



Stability of SiC-matrix microencapsulated fuel constituents at relevant LWR conditions



L.L. Snead^{*}, K.A. Terrani, Y. Katoh, C. Silva, K.J. Leonard, A.G. Perez-Bergquist

Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA

ARTICLE INFO

Article history:

Available online 9 October 2013

ABSTRACT

This paper addresses certain key feasibility issues facing the application of SiC-matrix microencapsulated fuels for light water reactor application. Issues addressed are the irradiation stability of the SiC-based nano-powder ceramic matrix under LWR-relevant irradiation conditions, the presence or extent of reaction of the SiC matrix with zirconium-based cladding, the stability of the inner and outer pyrolytic graphite layers of the TRISO coating system at this uncharacteristically low irradiation temperature, and the state of the particle–matrix interface following irradiation which could possibly affect thermal transport. In the process of determining these feasibility issues microstructural evolution and change in dimension and thermal conductivity was studied. As a general finding the SiC matrix was found to be quite stable with behavior similar to that of CVD SiC. In magnitude the irradiation-induced swelling of the matrix material was slightly higher and irradiation-degraded thermal conductivity was slightly lower as compared to CVD SiC. No significant reaction of this SiC-based nano-powder ceramic matrix material with Zircaloy was observed. Irradiation of the sample in the 320–360 °C range to a maximum dose of $7.7 \times 10^{25} \text{ n/m}^2$ ($E > 0.1 \text{ MeV}$) did not have significant negative impact on the constituent layers of the TRISO coating system. At the highest dose studied, layer structure and interface integrity remained essentially unchanged with good apparent thermal transport through the microsphere to the surrounding matrix.

Published by Elsevier B.V.

1. Introduction

Improving the accident tolerance of current or future light water reactors can be achieved in a number of ways: through a systems approach, by enhancing the accident tolerance of the fuels themselves, or through combining these approaches. Attributes of *enhanced accident tolerant fuels* as compared to the current UO_2 -Zircaloy fuel system may include: reduced enthalpy and hydrogen production due to the steam reaction, improved mechanical integrity for improved coolable core geometries and resistance to fuel dispersal at higher temperatures, or enhanced control or containment of fission products thus limiting the possibility of off-site contamination. These final points, (mitigating fission product release) are the primary motivators for a new fuel being developed and the motivation for this paper. This fuel system, referred to as the fully ceramic microencapsulated (FCM) fuel, is discussed in detail elsewhere [1–3]. However, the fundamental concept draws on the well-established gas-cooled reactor fuel technology: fissile kernels and subsequent fission by-products are contained within layered shells of pyrolytic carbon and silicon

carbide. For the LWR application, these microencapsulated fuel particles (also referred to as TRISO or tristructural isotropic fuels) are compacted into a SiC-based nano-powder ceramic matrix, yielding a non-porous SiC ceramic matrix-microencapsulated fuel pellet or the FCM fuel. This is in contrast to the gas-cooled reactor fuel system, which compacts the TRISO in a porous graphitic matrix. The presence of the SiC shell of the TRISO within the dense SiC matrix provides two additional barriers to fission product release compared to the current commercial UO_2 fuel system. In addition to the fission product retention aspects of this fuel, the relative thermal conductivity of the SiC matrix as compared to UO_2 is quite good, yielding an estimated as-irradiated fuel center-line temperature of $<700 \text{ °C}$ compared to $\sim 1100 \text{ °C}$ for mixed oxide fuel [3] leading to reduced stored energy in the core and reduced operational release of fission products from the fuel.

The potential benefits conferred from the FCM fuel assume performance of both the TRISO fuel and the nano-phase powder based sintered SiC matrix, which are currently unknown at LWR conditions. While there has been substantial data on the performance of TRISO fuels, and most recently exceedingly good performance of the new generation of fuels developed for the Advanced Gas-cooled Reactor program, [4] the application for which such fuel has been tested are typically in the 800–1300 °C range

^{*} Corresponding author.

E-mail address: SneadLL@ORNL.GOV (L.L. Snead).

(hundreds of degrees above that anticipated for the FCM). Moreover, the fast neutron fluence expected for the FCM fuel will be similar to that of UO_2 LWR fuels (depending on fuel assembly design), though it will be significantly higher than typical for gas-cooled reactors.[5] This is important as it is known that the constituent pyrocarbon layers within the TRISO undergo substantial temperature and dose-dependent dimensional changes for conditions typical of gas-cooled reactors. The integrity of the individual coating layers and the integrity of the interfaces between these layers at both the higher neutron dose and lower irradiation temperature of the expected LWR application are therefore necessary information. With respect to the SiC-based nano-powder ceramic matrix, while there are limited data [6,7] suggesting its irradiation stability, that data is also at temperatures well above the LWR fuel application temperature. Specifically, the neutron irradiation data available is provided for irradiation at 800 and 1300 °C. [6] Finally, the FCM concept with respect to its application to the current generation of commercial light water reactors requires an acceptably limited reaction between the fuel matrix and Zircaloy cladding, for which there is currently no information.

In this early stage of fuel development, the key issues of irradiation stability of TRISO coating system constituents at LWR-relevant conditions of temperature and fluence, as well as the performance of the SiC-based nano-powder fuel matrix, became a focus of study. Additionally, the presence or level of interaction between the fuel matrix and commercial Zircaloy has also been an area of research interest. Findings related to these issues are presented here.

2. Materials

Pellets for this study were fabricated through hot pressing of a specially mixed ceramic powder, and by mixing together this powder with surrogate microencapsulated fuel. The mixture was pressed in a graphite die to 1850 °C in an argon cover over a pressure range of 10–20 MPa. The powder was a mixture of SiC “nano-powder” including minute amounts of oxide additives: 1.75 wt% yttria (Y_2O_3), 3.25 wt% alumina (Al_2O_3), and 2.0 wt% silica (SiO_2). The mean diameter of all the powder particles was in the 30–40 nm range. Thorough mixing of the oxide additives with the base SiC powder is necessary to achieve optimized matrix microstructures. This was achieved by ultrasonic mixing of the powder mixtures in an alcohol medium [2]. Surrogate TRISO particles used during the fabrication of FCM pellets are the ZrO_2 -500-AK2-surrogate TRISO batch that have been previously fabricated and characterized in detail [8,9]. The optical anisotropy factor of the inner and outer pyrolytic carbon layers was measured to be 1.029 and 1.009, respectively. The AK2 particles consist of a 530 μm average diameter zirconia kernel that is coated to result in a 916 μm average diameter TRISO particle. The OPyC and SiC shell densities were previously measured to be in the range of 2.011–2.013 g/cc and 3.204–3.206 g/cc, respectively [8]. For the eventual FCM application, uranium nitride kernels in the range of 650–800 μm are being developed. [10] However, the layers surrounding the UN kernel would likely be similar in structure (if not thickness) to that studied here for the AK2 surrogate particles, thus the AK2 TRISO is assumed a viable surrogate for the purposes of this study.

The hot-pressed specimens then underwent machining to achieve geometry appropriate for reactor irradiation. Specifically, samples were machined to precise dimensions required to set the internal gap between sample and Zircaloy cladding (discussed in Section 3). As these samples were not over-coated (as one would expect in graphite-matrix gas reactor fuel [11] and in the newer generations of FCM pellets), some machining/destruction of

peripheral TRISO particles occurred. This will be seen in later optical micrographs. A number of pellets do not contain any TRISO particles and are fabricated to: (i) investigate the hot-pressing behavior of monolithic SiC and (ii) to determine the stability of monolithic nano-SiC powder based ceramic under neutron irradiation. Also, those samples without embedded TRISO particles were utilized after irradiation for determination of irradiation temperature using an isochronal annealing and thermal diffusivity process.

The microstructure of the non-irradiated pellets will be discussed more fully in Section 4.2, though all samples had the appearance of near full density. The first type of material studied here is a nano-phase powder based hot pressed SiC that is “matrix only” material, containing only constituents of the ceramic matrix of the FCM fuel. Within these samples there is a subset referred to as *lower density* (0.86–0.90 theoretical SiC density) and a subset referred to as *higher density* (0.94–0.98 theoretical). The higher density material was processed to higher temperature resulting in larger SiC grains and improved thermal conductivity. The second type of material studied is the “FCM surrogate” fuel, or samples containing surrogate AK2 TRISO particles compacted to form the SiC-based nano-powder matrix. The TRISO particles for those materials appeared randomly dispersed and were largely undamaged by the processing. However, since no particle overcoating was carried out for the samples of this study some detrimental particle–particle interaction occurred during the matrix consolidation step. The layered structure of a non-irradiated surrogate TRISO containing sample can be seen in the left-most image of Fig. 1, with a higher magnification image of the transition from the CVD SiC layer of the TRISO into the near fully dense SiC matrix into which the TRISO particles were dispersed (Fig. 1). The interface between the TRISO particle and the SiC matrix exhibited good contact with no significant voids or evidence of debonding. Close examination of the matrix microstructure showed a uniform SiC matrix with small volume fraction of isolated oxide phases. It is noted that this paper reports on an early generation of FCM fuel whose matrix is consistent with the *lower density* matrix ceramic material discussed above. Current generation materials have higher crystalline perfection and higher density and thermal conductivity, consistent with the *higher density matrix* ceramic discussed here.

3. Irradiation and experimental

A series of pellets were machined with a nominal 8.2 mm diameter (replicating a 17×17 Westinghouse PWR bundle) and irradiated in a “rabbit capsule” in position 6 of the Peripheral Target Tube (PTP) of the High Flux Isotope Reactor (HFIR). Axial position 6 is just above the reactor mid-plane resulting in a fast neutron flux of $1.01 \times 10^{15} \text{ n/cm}^2 \text{ s}$. For this position the nominal thermal neutron flux is $2.5 \times 10^{15} \text{ n/cm}^2 \text{ s}$. Peak magnitude of heat generation rate (dominated by gamma heating) in the SiC and Zircaloy cladding was estimated to be 32 and 39 W/g, respectively.

Table 1 provides a loading schematic of individual pellets within the rabbit capsule, along with the sample dimensions and accumulated fast fluences and irradiation temperatures. Each capsule was assembled containing five surrogate-containing or matrix-only samples, separated by a high-purity nuclear graphite spacer, placed inside an open-ended Zircaloy-4 cladding tube section. This assembly was placed inside an aluminum outer holder with stainless steel spacer caps on either end thus defining a gas-gap between the Zircaloy tube and the aluminum external capsule. Following a vacuum purge the capsule was back-filled with high-purity neon that served to conduct the internally generated heat across the gas gap. The fill gas, gas gap, and amount of nuclear heating determined the sample temperature. The target temperature was determined using the ANSYS code and macros associated with its

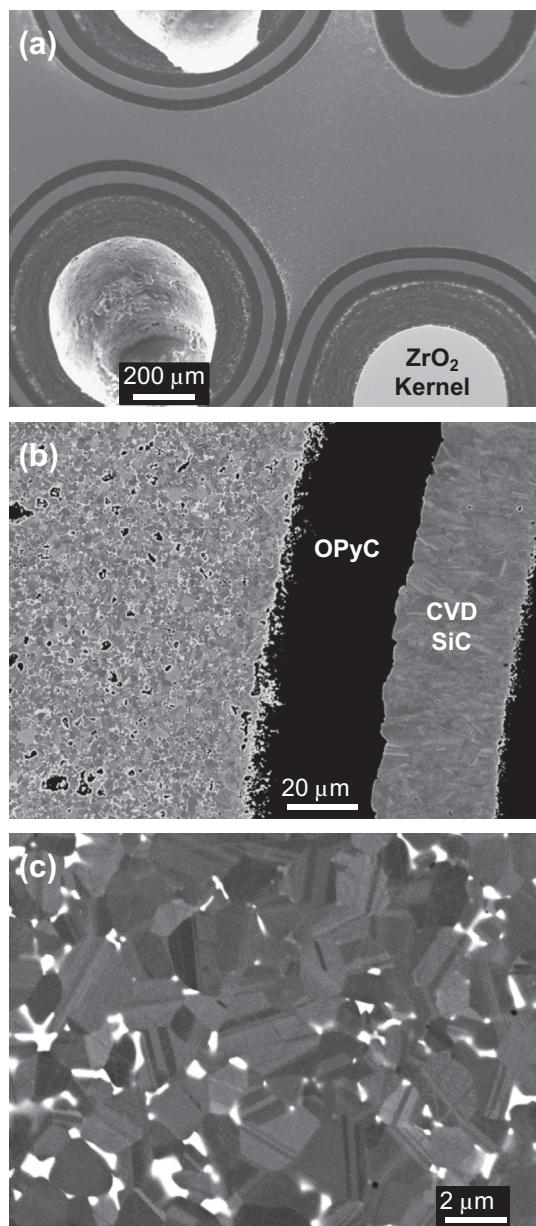


Fig. 1. (a) Low magnification SEM image of TRISO particles embedded in SiC matrix. (b) Grain microstructure in the matrix SiC and the CVD SiC shell of the TRISO particle. (c) Microstructure of matrix SiC in monolithic pellets.

use in HFIR reactor experiments. The centerline temperature of the sample pellets was calculated to be approximately 25 °C higher than the periphery based on the assumed irradiated thermal conductivity, density, and HFIR gamma heating. It is noted that for an experiment utilizing a fissile-fueled FCM where the fuel linear heat flux was set to match that of a LWR, the centerline temperature would be approximately 100–300 °C above the peripheral temperature.

Actual irradiation temperature of the samples was determined using the matrix-only samples through an isochronal annealing and room temperature thermal diffusivity approach described elsewhere [12,13]. A Netzsch Nanoflash LFA 257 was used to hold samples at pre-determined anneal temperatures for 30 min followed by a return to 100 °C for the thermal diffusivity measurement. The irradiation temperature is then determined to be the point at which the as-irradiated thermal conductivity deviated from constancy. An example of the resulting data is given in Fig. 2, providing the raw data from the FCM-EO2 sample 18A. Here

a clear recovery in conductivity can be seen at approximately 320 °C which continues in an approximately linear fashion until at least 700 °C. While thermal diffusivity is a measurement integrated over the entire diameter, the change in thermal diffusivity would first occur near the periphery of the sample (as it is at a lower irradiation temperature) and this technique is therefore considered accurate within experimental error which is a combination of factors including the isochronal temperature mesh interval, the measurement repeatability, and the error associated with the sample temperature gradient. The specific temperatures and temperature errors reported in Table 1 are associated with the outer surface of the samples and the mesh intervals and are considered conservative. It is noted that the HFIR operated at a remarkably constant flux and power level and that, typically, temporal sample temperature variations that may occur are due to gap changes internal to the irradiation vehicle. It is further noted that the post-irradiation SiC temperature monitor technique reflects the state of the temperature monitor integrated over a fluence period of roughly $1E24$ ($E > 0.1$ MeV) at the end of irradiation and therefore the data given in Table 1 are essentially snapshots near the end of each cycle. However, assuming constancy in power we may tentatively conclude that temporal fluctuations within the irradiation vehicle had not occurred by noting the near equivalence in the end-of-cycle temperature reading from each of the rabbits: the rabbits were inserted in a group and removed after 1, 2, 3, and 4 cycles respectively.

Samples prepared for thermal diffusivity measurements and transmission electron microscopy (TEM) were obtained by sectioning the as-irradiated specimens. For the case of thermal diffusivity measurements, the as-irradiated thickness would yield too great a half-rise time after the laser pulse to be compliant with ASTM guidelines [14]. Therefore, the sample was cut in half and both halves measured with each data-point reported. The TEM samples were prepared using an FEI Quanta 3D focused ion beam (FIB) at room temperature from an area near the axial-center, periphery of the sample, and therefore as near to the reported sample temperature as possible. An FEI CM-200 TEM was used for microstructural imaging of the FCM interfaces and near-surface region of the Zircaloy-4 tube.

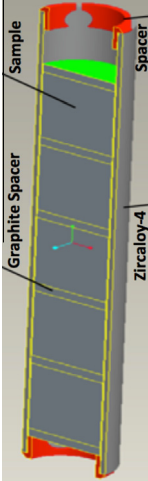
Tomographic images were obtained using a MicroXCT™ (Xradia, Inc.) system consisting of a microfocus X-ray source with a tungsten target and a Peltier-cooled CCD (Charge Coupled Device) detector system equipped with a scintillator and $\times 4$ and $\times 20$ objective lens. Two-dimensional tomographic images were acquired using a tube voltage of 40 kV and power of 8 W at $20\times$ magnification. Source to sample and detector to sample distances were -100 mm and 15 mm, respectively. 3200 angular projections were acquired by 180° object rotations with a 15 s windows for each. The acquired images were corrected with a reference image, which was obtained using 40 averaged images of 15 s per image scan. The images were reconstructed by TXMReconstructor to obtain three-dimensional tomographic images. The image resolution at $20\times$ magnification is 1.5 μm with a 1 mm field of view.

4. Results and discussion

4.1. Visual inspection, swelling and thermal conductivity

As the capsules began irradiation at the same time, capsules completed irradiation and were disassembled over a period of approximately one year. The Zircaloy-4 holders were removed from the aluminum housings without incident and the samples and spacers were pushed from the Zircaloy-4 holders without need for undue force or cutting. In all cases the samples were photographed in-cell as they were removed from the capsules and stored

Table 1
Sample and Irradiation Conditions.

Rabbit holder Schematic	Capsule	I.D.	T_{irr} (°C)	Neutron dose E25, n/m2 $E > 0.1$ MeV	Pre-Irrad diameter (mm)	Pre-Irrad thickness (mm)	Particle volume fraction (%)	Density (g/cc)
	FCM-EO1	1	325 ± 20	1.8	8.098	6.951	0	2.88
		29		1.9	8.092	6.726	0	3.2
		16		2	8.164	6.973	20	2.96
		7		2	8.088	6.965	29	2.74
		14		2.1	8.208	6.972	38	2.91
	FCM-EO2	2	320 ± 20	3.6	8.088	6.951	0	2.74
		18		3.7	8.214	6.752	0	3.2
		10		3.8	8.216	6.968	0	2.88
		5		3.8	8.072	6.993	28	2.85
		12		3.9	8.192	6.961	39	2.82
	FCM-EO3	3	360 ± 10	5.4	8.206	6.965	0	2.91
		31		5.5	8.092	6.487	0	3.2
		15		5.6	8.087	6.96	21	2.79
		8		5.7	8.198	6.965	27	2.91
		21		5.8	8.213	6.549	0	3.2
	FCM-EO4	4	320 ± 20	7.2	8.084	6.963	0	2.91
		17		7.4	8.213	6.615	0	3.2
		9		7.5	8.091	6.955	18	2.69
		6		7.6	8.198	6.989	27	2.95
		11		7.7	8.093	6.971	41	2.74

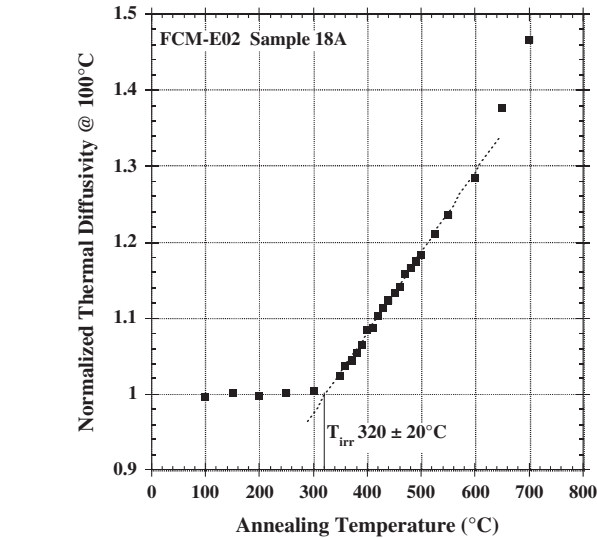


Fig. 2. An example of the isochronal annealing data providing the actual irradiation temperature.

until their activity was within acceptable limits for further testing. Without exception the FCM surrogate fuel and matrix-only samples appeared unchanged due to the irradiation. An example series of photos is given in Fig. 3, which provides top and side-view images taken in-cell of the FCM-EO2 capsule. As the samples containing surrogate TRISO for this study were not over-coated following hot pressing but were machined down to the required irradiation vehicle dimension and tolerance, the periphery of some samples clearly show exposed and disrupted TRISO.

Once the samples from the FCM-EO2 and EO4 capsules were removed from the Zircaloy-4 holder those holders were cut lengthwise exposing the inner surface of the holder for visual inspection. An image of the inner surface of the Zircaloy-4 holder from the highest dose capsule studied is provided in Fig. 4. From this figure the regions in contact with the graphite spacer and the FCM fuel can be clearly distinguished, with the graphite regions

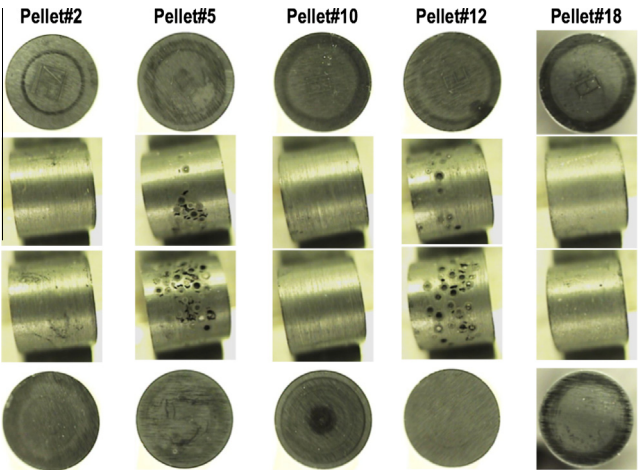


Fig. 3. In-cell optical images of FCM-EO2 samples taken after capsule disassembly.

being more optically dull as compared to the relatively optically shiny regions occupied by the FCM or SiC matrix materials. Close inspection indicates that the dull/diffuse region extends and slowly extinguishes with increasing distance from the graphite spacer.

The sample swelling from this study is presented in Fig. 5 along with historic data for CVD SiC. [15] From the figure, the typical temperature-dependent approach to saturation for CVD SiC is clear, with saturation occurring by $\sim 2 \times 10^{25}$ n/m² ($E > 0.1$ MeV) at an irradiation temperature of a few hundred degrees Celsius and occurring at $\sim 6 \times 10^{25}$ n/m² ($E > 0.1$ MeV) for higher irradiation temperatures. The data on swelling for the surrogate FCM samples is shown as open circles in this figure. The SiC ceramic matrix-only material is shown as open squares. No correlation between the presence of the surrogate TRISO or the relative loading of TRISO with swelling is observed. The surrogate FCM and the matrix-only materials, within experimental error, swell consistently. However, taking the data-set as a whole, it is clear that the material has achieved swelling saturation at, or very near, the lowest

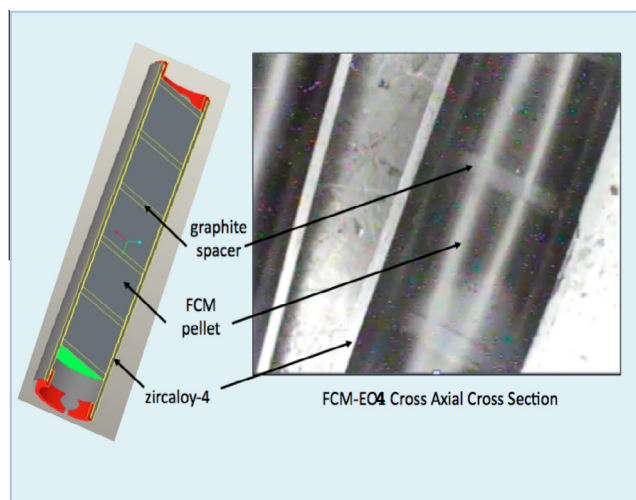


Fig. 4. In-cell optical image of inner surface of high dose FCM-EO4 axially-sectioned Zircaloy-4 holder.

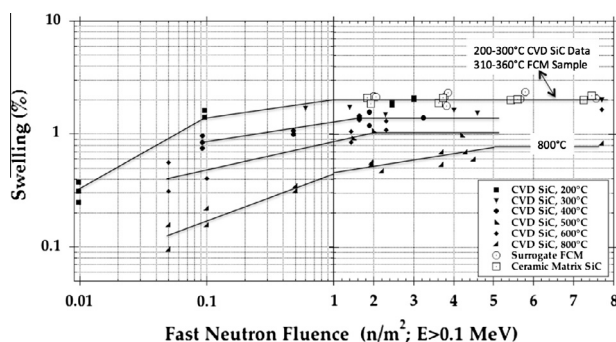


Fig. 5. Swelling of FCM matrix SiC, compacted surrogate FCM, and historic CVD SiC irradiated in HFIR as a function of fluence and temperature.

dose studied ($\sim 2 \times 10^{25} \text{ n/m}^2$ ($E > 0.1 \text{ MeV}$)). It is also clear that the SiC-based nano-powder ceramic in this irradiation temperature

range ($\sim 310\text{--}360^\circ\text{C}$) exhibits swelling behavior closer to CVD SiC irradiated at a somewhat lower temperature.

The possibility of higher swelling for SiC-based nano-powder ceramics has been suggested previously for ion and higher temperature neutron irradiation, though conclusions could only be tentatively made.[6,7] Koyanagi[7] utilized 5.1 MeV Si ions in the temperature range of $280\text{--}1000^\circ\text{C}$ at a dose rate of approximately a few dpa/hour, or about a factor of 500 times the dose rate of the current study. For the lowest temperature of his study (280°C , compared to $\sim 310\text{--}360^\circ\text{C}$ here) Koyanagi reported a twofold increase in swelling compared to CVD SiC for the same nominal dose as the current study and for a SiC-based nano-powder ceramic containing 9% sintering aid compared to $\sim 6\text{--}7\%$ for the present study. Based on detailed microstructural analysis Koyanagi concludes the significant difference in swelling for his lower temperature sample set is due to the irradiation-induced amorphization of the Y/Al containing oxides. However, this explanation does not address the possibly statistically significant difference in swelling for the Koyanagi data at $\sim 1000^\circ\text{C}$ or the Ozawa [6] neutron irradiation data at 800 and 1300°C , temperatures for which amorphization of residual oxides would not occur.

The thermal conductivity for the SiC-based nano-powder matrix material and the surrogate TRISO containing FCM are presented in Fig. 6 on the left and right, respectively. For the matrix materials the data are presented as lower density matrix material containing a higher level of sintering aids with approximately 86–90% of theoretical SiC density. As fabricated, these materials possessed ambient thermal conductivity of approximately 30 W/m K . This lower density matrix material best matches the matrix of the surrogate FCM irradiated in this study that was produced using essentially the same powder and consolidation conditions. It is noted that this is considered early-stage material with later FCM matrix being more representative of the higher density matrix. The higher density SiC matrix material irradiated in this work was in the 94–98% dense range, possessing an ambient non-irradiated thermal conductivity approaching 90 W/m K .

From the left-most plot of Fig. 6 it is seen that the thermal conductivity of the lower density and higher density SiC matrix materials has apparently saturated by the lowest fluence of this study at ambient values of $\sim 4 \text{ W/m K}$ and $\sim 7 \text{ W/m K}$. The surrogate FCM materials appear to have likewise saturated near the value of the lower density matrix material ($\sim 4 \text{ W/m K}$). It is noted that in this

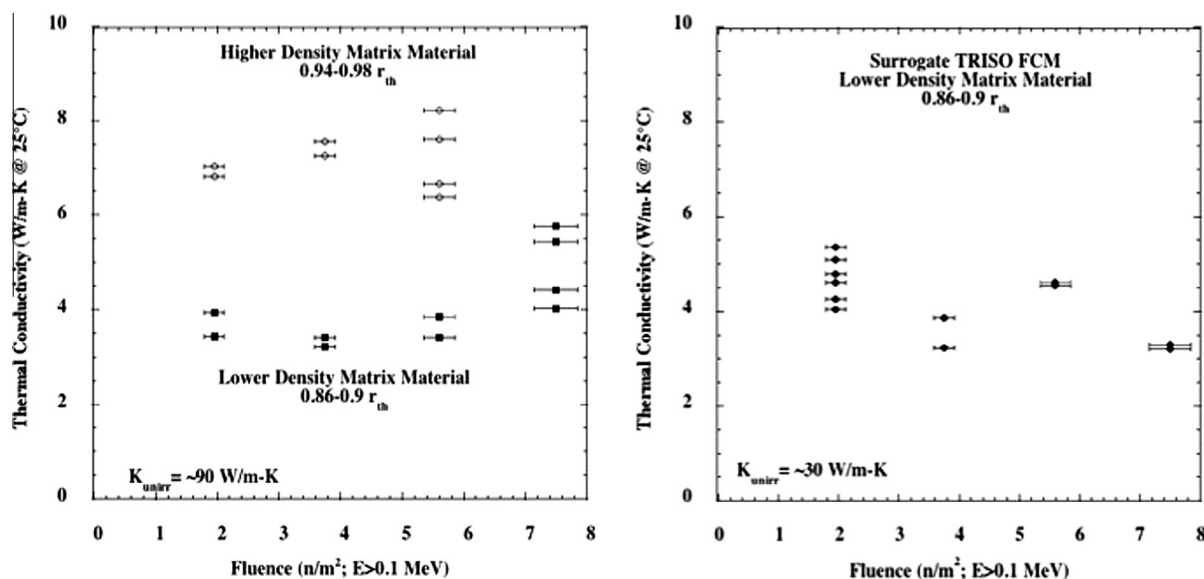


Fig. 6. Thermal conductivity of SiC-based nano-powder matrix material (left) and surrogate FCM (right).

analysis thermal conductivity as determined from the thermal diffusivity following the standard relation $k = \alpha \rho C_p$, where α and ρ are the measured diffusivity and density, respectively. A constant specific heat (C_p) associated with SiC is assumed using the algorithm provided in the Handbook of SiC Properties for Fuel Performance Modeling. [16]. Assuming a specific heat of stoichiometric SiC is not entirely correct due to the presence of the sintering aids in both the matrix material and the non-SiC constituents of the TRISO. However, this error is considered minor.

Terrani [3] has previously estimated the thermal conductivity of FCM fuel, comparing it with commercial UO_2 as a function of irradiation. In that analysis it was assumed that the thermal defect resistance approach [17] could be used with the compiled data on CVD SiC [16] to arrive at an as-irradiated conductivity as a function of temperature. For similar irradiation conditions to the current study Terrani predicts a thermal conductivity near ambient of $\sim 10 \text{ W/m K}$ in the irradiated, saturated condition. This is considerably higher than the $\sim 7 \text{ W/m K}$ measured in this study. However, it is noted that the Terrani analysis assumes the irradiation swelling and phonon-scattering behavior of CVD SiC. As discussed earlier, the swelling of the FCM matrix material is somewhat greater than the swelling of CVD SiC, on the order of 0.25% or more. It has been previously shown that a correlation exists between thermal defect resistivity and the magnitude of swelling in SiC, [16,15] and that this correlation is essentially independent of irradiation temperature in the saturation swelling regime of SiC (~ 200 – 800°C). This then allows a thermal conductivity degradation to be calculated for the apparent swelling difference between CVD SiC and the FCM matrix material. Following this approach an additional reduction in thermal conductivity of $\sim 3 \text{ W/m K}$ for high density FCM matrices, and $\sim 2 \text{ W/m K}$ for the lower density FCM matrices is calculated, essentially rectifying the difference in as-irradiated thermal conductivity between CVD SiC and the SiC-based nano-powder matrix material. However, this position is somewhat unsatisfying as the thermal defect approach assumes that the added defect resistance, which is related to the concentration of simple vacancies and vacancy clusters, is also directly related to the interstitial-driven swelling. As will be speculated in the next section, the enhanced swelling of this material may not be due to an increased concentration of vacancies, but may be caused by the presence and swelling of the residual sintering aids. If indeed the added swelling in the SiC-based nano-powder matrix is due to the presence of sintering aids then added phonon-scattering at grain boundaries and triple-junctions is also a potential explanation for the lower thermal conductivity of this material.

4.2. Microstructure and interface stability

The microstructure of the non-irradiated SiC-based nano-powder of the FCM fuel has been investigated in detail and presented previously by the authors [2]. Fig. 7 captures representative microstructures for a 6 wt.% yttria–alumina additive material at various magnifications with SiC–SiC grain boundaries and entrained oxide pockets examined in phase contrast mode. As seen in Fig. 7b, an amorphous grain boundary oxide layer on the order of a few nanometers is present. Fig. 7b also provides a high-resolution image of a crystalline entrained oxide pocket at the triple junction. It is noted that entrained oxides of crystalline alumina, crystalline YAG ($\text{Y}_3\text{Al}_5\text{O}_{12}$), mixtures of the two, as well as amorphous mixtures including silica have been observed in the entrained oxide pockets of SiC-based nano-powder materials. This is to be expected upon investigation of the ternary alumina–yttria–silica phase diagram and the additive mixture composition. For the material thus far studied for FCM application, only crystalline alumina and YAG have been observed within these pockets. These observations remain consistent with previously reported results [18].

In the non-irradiated condition, the surrogate FCM samples underwent X-ray micro-tomography to determine, in part, the effect of processing on the OPyC and SiC layers. However, the effect of processing conditions on the particle integrity was carried out in detail previously as part of the fuel process optimization studies essentially ensuring the processing conditions selected for this study resulted in near defect-free compacts. The larger purpose of micro-tomography for this study was to understand the effect of fast neutron irradiation on the constituent layers of the microencapsulated fuel and the interfaces between these layers. More specifically involving the IPyC, the SiC layer, and the OPyC layers. As the buffer layer receives the majority of in-service damage through slowing down of the fission fragments, the fast neutron irradiation testing of this experiment is not considered representative of the application.

As discussed previously, the FCM application temperature is expected to vary radially through the compact and as a function of the fluence from ~ 400 to 700°C . Assuming reasonable layer interfacial integrity the local heating due to the uranium nitride kernel will only perturb the TRISO temperature by 50 – 100°C above the surrounding matrix [3]. This temperature is considerably lower than the operating temperature of high temperature gas reactor

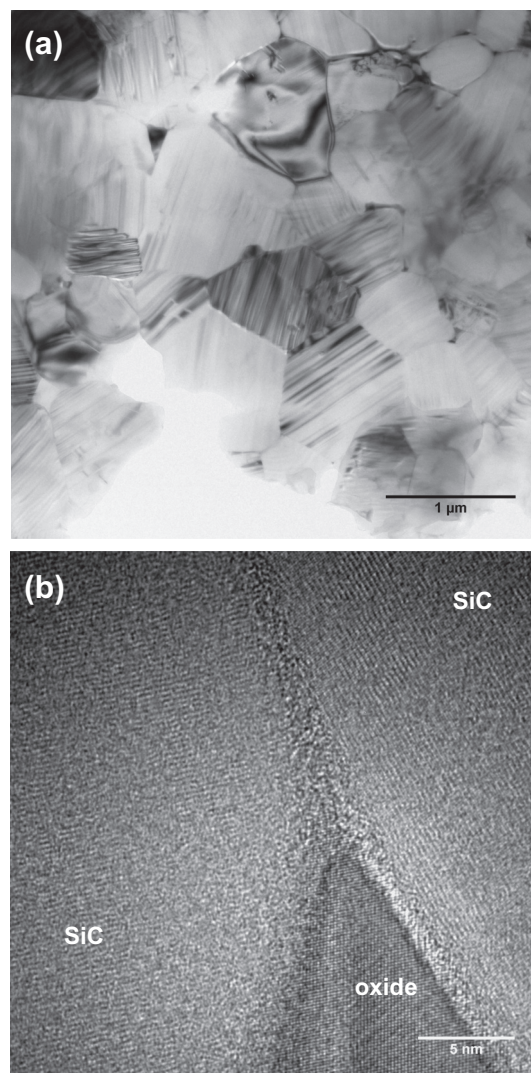


Fig. 7. (a) Bright field image of nano-phase powder based sintered SiC microstructure with 6 wt.% yttria–alumina, (b) phase contrast image of the grain boundary between two silicon carbide grains filled with amorphous oxide along with a triple-joint filled with a crystalline oxide.

TRISO fuels and the temperatures at which those fuels were typically studied: >800 °C. Due to the difficulty in fabricating pyrolytic graphite coupons that would be representative of IPyC and OPyC layers and would also be useful for thermophysical property measurements, description of the irradiation response of TRISO PyC is largely based on bulk graphite behavior and should be considered guidance rather than truly informing of the accurate behavior. The CEGB report [19], whose data forms the basis for TRISO fuel performance codes such as PARFUME [20], discusses the behavior of PyC as a function of fast neutron dose and irradiation temperature. As typical of all graphitic materials, an initial irradiation-induced volumetric shrinkage for PyC is presented as a function of density, anisotropy, and irradiation temperature (and other factors related to crystalline perfection). This shrinkage occurs both parallel and perpendicular to the PyC deposition plane, though eventually the rate of shrinkage diminishes with a reversal to growth behavior (“turnaround”) occurring in the perpendicular direction at moderate fluence. According to the CEGB analysis the contrast in irradiation temperature between the HTGR (>1000 °C) and LWR (<700 °C) irradiation temperatures would result in a reduced magnitude of dimensional change and slightly retarded fluence for onset of turnaround at the LWR temperature. Extrapolating the CEGB analysis to the PyC graphite of this study one could assume a maximum shrinkage of a few percent occurring (both perpendicular and parallel to the deposition direction) at a dose near the intermediate dose of the current study. For the maximum dose of this study a continued near linear shrinkage would be expected while the PyC would likely move through nil-volume change into swelling behavior. However, it is re-emphasized that current understanding of the behavior of TRISO PyC behavior under irradiation is unsatisfying and should only be qualitatively applied. Moreover, the irradiation temperature of the current study (~ 310 – 360 °C) is significantly less than the lower end of the discussed range in the CEGB report (600 °C). It is noted that irradiation creep for PyC, for which there is essentially no reliable data at HTGR or LWR relevant temperatures, would act to mitigate the evolving stress, is ignored in the discussion above. Moreover, it is likely that irradiation creep would have (at best) a weak dependence on irradiation temperature and therefore would be active in the temperature regime of interest here.

Recently, micro-tomography has become a useful tool for the non-destructive inspection of irradiated gas-cooled reactor fuels. [21,22] This technique is now being used as a routine tool for the DOE AGR program developmental TRISO particles of similar fabrication pedigree to the FCM TRISO particles of the current study, though those fuels were irradiated at HTGR relevant conditions and contain fissile fuel kernels. As discussed in the previous paragraph, the effect of fast neutron irradiation is to cause initial

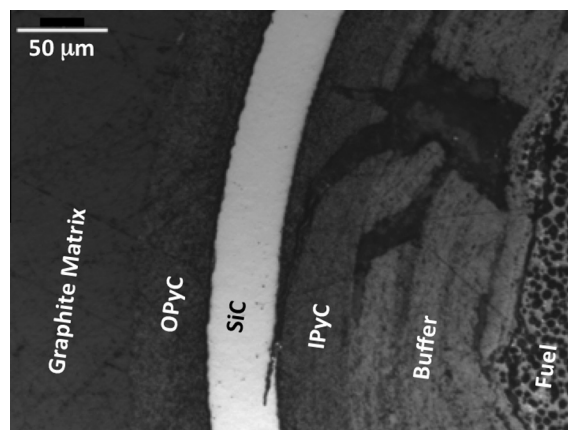


Fig. 8. Optical image of polished cross section of AGR TRISO fabricated at Oak Ridge National Laboratory fabricated under similar conditions to those in the present study and irradiated in the Advanced Test Reactor at Idaho National Laboratory at high temperature.

dimensional shrinkage in the buffer, IPyC and OPyC layers, with a turnaround to expansion occurring more rapidly for higher irradiation temperature of the HTGR relevant irradiation. As the pyrocarbon-derived layers undergo shrinkage, tensile stresses within and shear stresses between layers build, leading to bulk material fracture, interfacial failure, and failure of adjoining layers such as the SiC shell through stress transfer. Shrinkage, debonding, and stress-induced cracking of the SiC-shell have been observed in the recent AGR program HTGR fuels with a representative image provided in Fig. 8. In particular, gross dimensional change has occurred in the buffer layer (driven by fission product recoil and fast neutron damage) and the IPyC layer. As mentioned previously, due to the combined damage of the fission product recoils and the fast neutrons the buffer layer suffers greater shrinkage than the IPyC and OPyC layers and in the vast majority of cases initiates pyrocarbon layer cracking. It is also noted that failures of the type shown in Fig. 8 are infrequent with only a tiny fraction resulting in failure or compromise of the SiC shell.

Microtomography has been applied to the multiple intermediate and high dose samples of this study (FCM-E02, and FCM-E04 surrogate TRISO containing samples) to determine the overall state of the layers and layer interfaces with images provided in Fig. 9. The FCM-E02 sample was selected for imaging (not shown in Fig. 9) and because the historic data for 600 °C unrestrained PyC suggests this would be near the maximum shrinkage for the IPyC in both directions parallel and perpendicular to deposition. How-

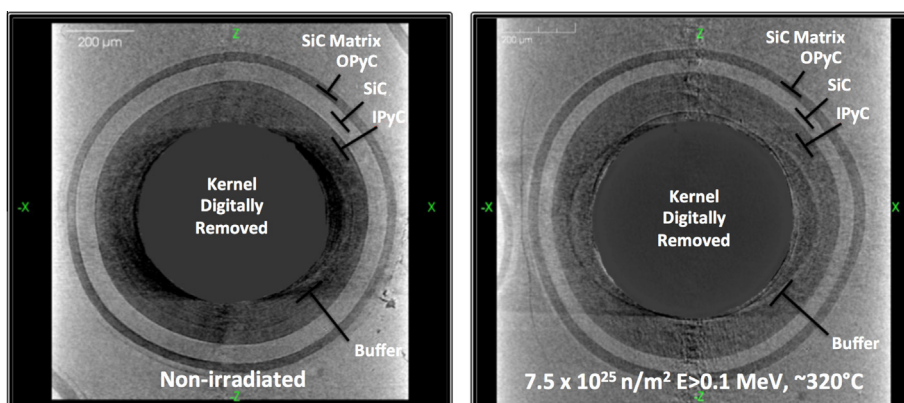


Fig. 9. Representative X-ray micro-tomography image of non-irradiated (a) and irradiated (b) surrogate FCM fuel with emphasis on microencapsulated fuel layers.

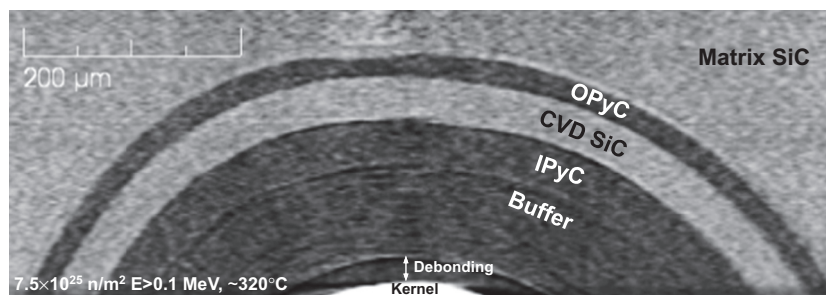


Fig. 10. High resolution X-ray micro-tomography image of the FCM-EO4 sample.

ever, the image is unremarkable and essentially identical to the non-irradiated image. Inspection of the non-irradiated image of Fig. 9 (left figure) and others similarly inspected revealed all fuel layers including the SiC shell to be intact and showing no signs of cracking due to processing. Supporting the SEM imaging provided in Fig. 1, the interface between the matrix and the OPyC exhibits good adhesion with no visible porosity. The right-most image of Fig. 9 provides a micro-tomographic slice through the center of the highest dose sample of this study and of a TRISO removed from the periphery of the fuel compact and therefore at the lowest irradiation temperature. It is assumed that the highest dose and lowest temperature provides the most conservative (harsh) performance test given that this condition leads to maximum swelling in the SiC matrix and shell and has the largest associated PyC dimensional change. The irradiated image of Fig. 9 is also unremarkable, with all layers intact and showing good adhesion, though close inspection of the interface between the SiC and IPyC and the IPyC and buffer suggest the onset of layer decohesion. However, this is only suggestive as the interfacial darkening was not significantly different than observed in some non-irradiated particles and can be caused by the tomographic imaging conditions used. Higher resolution imaging of the FCM-EO4 sample is provided in Fig. 10, allowing a better view of the interfaces. From the image the darkening line between the IPyC and buffer is more defined.

Higher resolution imaging of the microstructure was obtained by TEM imaging sections of non-irradiated and the high-dose irradiated sample (FCM-EO4) of Figs. 11 and 12. Focused ion beam sections were taken near each of the interfaces (excluding the buffer

interface) and the general microstructures and state of the interfaces investigated. Following irradiation, the interface between the matrix and the OPyC was seen to be continuous, showing no apparent increased porosity or adverse impact of irradiation, as seen in Fig. 11. The interface between the CVD SiC shell and the inner and outer pyrolytic carbon is provided in Fig. 12 on the left and right of the figure, respectively. On the left image of Fig. 12 the interface between the IPyC and SiC is apparently porous due to artifacts from the FIB milling, though the bond between the layers clearly remains intact. For the right image of Fig. 12, the interface between the IPyC and the SiC shell also seen to be intact, though a small debond crack has appeared which may or may not be an artifact of FIB milling. One might expect different behavior in swelling between the IPyC and OPyC layer due to slight microstructural differences in the two layers, and one may also expect irradiation-induced dimensional changes to effect their interfaces differently due to differing surface roughness. Regardless, for this near-life-time dose and lower temperature bound for the FCM fuel both tomography and TEM results indicate essentially no structural changes to the interfaces.

As discussed in detail elsewhere [16,23], the microstructure of CVD SiC (and otherwise stoichiometric cubic SiC) for the irradiation dose and temperature of this study is comprised of nanometer-scale loops or “black spot defects.” As irradiation temperature nears the upper temperature for the FCM application, Frank loops would be expected. Through TEM examination of samples in this work, such microstructure exists in both the CVD TRISO shell of the surrogate FCM shell and within the grains of the FCM matrix. TEM observation of the grain boundary interfaces and captured

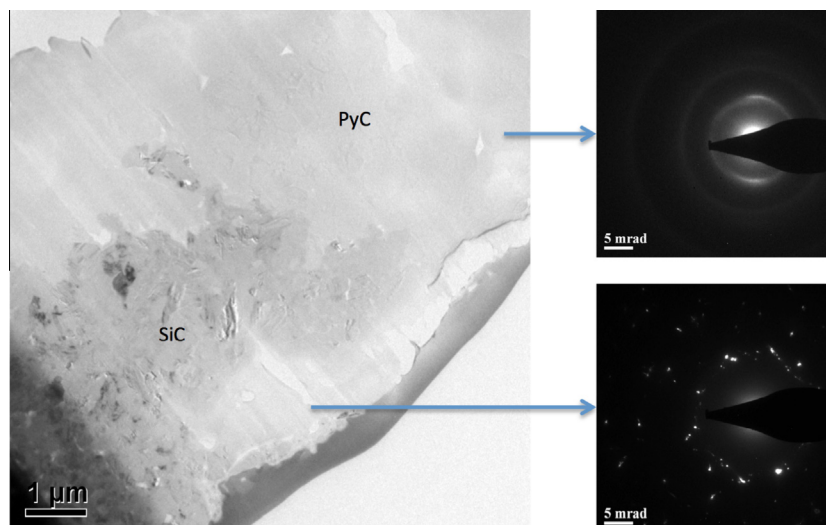


Fig. 11. Matrix-OPyC: TEM image of the interface between the OPyC and the SiC-based nano-powder matrix following 320 °C, 7.5 dpa irradiation.

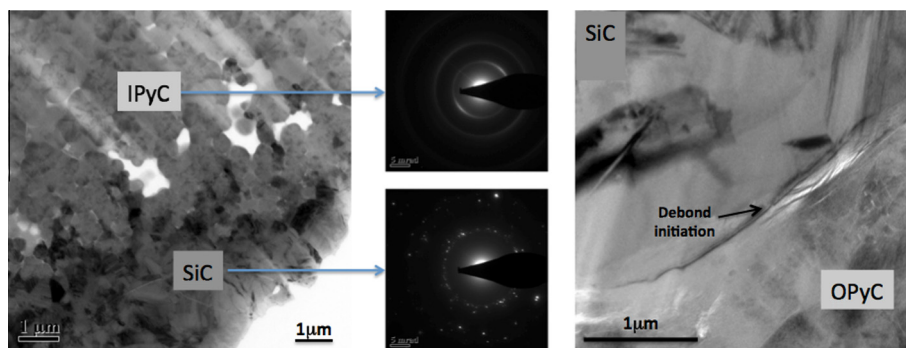


Fig. 12. SiC–OPyC: TEM bright field image of CVD SiC shell/outer pyrolytic carbon interface following 320 °C, 7.5 dpa irradiation. Note scale changes from left to right figures.

oxide pockets within the SiC-based nano-powder ceramic matrix was carried out. The oxides within the pockets remained crystalline following irradiation and no gross change was observed at the SiC grain boundaries. Moiré fringes were observed radiating from the pockets, indicative of oxide swelling and local strain. More detailed microstructural investigation of the SiC-based nano-powder ceramic and the linkage between the sintering aids and swelling will be the subject of further study.

4.3. Matrix SiC–Zircaloy clad interaction

Information on the reaction and diffusion of SiC and Zr is available in the literature in support of semiconductor [24] and composite [25,26] and fuel [27] development activities. In the work of Bhanumurthy [25] a powder-and-cup approach was applied in the temperature range of 900–1100 °C. The reaction of Zr with SiC led to the formation of $\text{ZrC}/\text{Zr}_5\text{Si}_3\text{C}/\text{Zr}_2\text{Si}/\text{ZrC}_x$ compounds in the diffusion zone, consistent with local equilibria in the ternary Zr–Si–C phase diagram. Fukai et al. [28] examined the reaction between SiC and Zr at 1200 and 1300 °C. The complete diffusion path at 1300 °C was established as $\text{SiC}/\text{ZrC}/\text{Zr}_5\text{Si}_3\text{C}_x/\text{SiZr}_2/\text{ZrC}_x/\text{Zr}$ for a reaction period over 1800 s. That work aided in the description of the SiC and Zr in the C–Si–Zr phase diagram provided by Schuster [29] and Chen [26].

The previous fundamental studies on SiC–Zr reactions have been focused on for temperatures in excess of 900 °C, with experimental design based on the existing data, or aimed at improving upon the database above that temperature. From the existing experimental and theoretical kinetics information available [24–27] very little reaction is expected for the temperature of the present study (<400 °C) between pure zirconium and pure SiC. However, due to the presence of the sintering aids and the potential synergistic effect of irradiation the potential for FCM-clad interaction was considered a possibility. Fig. 13 provides a cross sectional image taken from the inner surface of the highest dose capsules (FCM-EO4, see Table 1) in an area where the FCM fuel would contact the inner clad. In this region there were discontinuous “patches” of reaction covering the surface. Fig. 13 was taken from one of these patches. It was previously noted (see Fig. 4) that the inner surface of the tube, for all capsules, was visually shiny with a slightly dulled surface corresponding to the graphite spacer locations. A cross-sectional view of the fuel-clad interface is presented in Fig. 13, provided by a FIB section of the inner diameter of the FCM-EO4 Zircaloy cladding at an axial point where the FCM fuel was in contact. As seen in the figure, a thin film of carbon is present on top of the Zircaloy (on the order of a micron). As part of the FIB process, platinum is deposited onto the sample and is observed in the figure. The carbon film is adherent to the Zircaloy-4 surface, though was cracked during the final thinning steps.

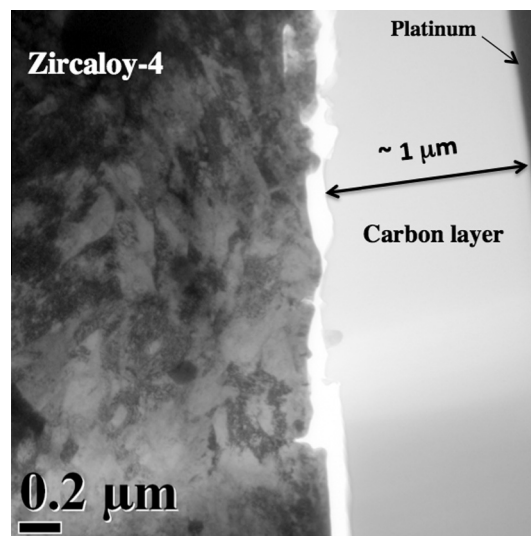


Fig. 13. Bright field, cross-sectional TEM image of the inner Zircaloy-4 surface.

The Zircaloy-4 microstructure is consistent with the irradiation and ion-milling conditions. The presence of dislocations typically created during room-temperature FIB milling of Zircaloy are observed. The microstructure and microchemistry of the film and Zircaloy-4 were probed using standard diffraction and EDS spectroscopy. Of note is that the carbon layer was amorphous with no other elemental presence. Similarly, the Zircaloy-4 displayed EDS lines consistent with Zircaloy and an absence of silicon. Without a more extensive study of the system a definitive conclusion cannot be made as to the source of the carbon. However, the supporting evidence that no visible signs of reaction occurred on the outer surface of the FCM pellet coupled with the lack of silicon in the Zircaloy-4 and a lack of zirconium silicide formation (a very stable compound) on the surface suggests that silicon has not been stripped from the FCM matrix. There is also no sign of FCM sintering aid concentration at the interface, which would occur if the fuel had reacted and stripped silicon. From this it is tentatively concluded that the source of carbon is external to the FCM fuel, most likely the graphite spacer which is noted to produce the more “visibly dull” finish on the Zircaloy inner surface. It is further noted that the overall reaction was minimal.

5. Concluding remarks

The irradiation behavior of surrogate microencapsulated fuel and the nano-phase powder based sintered SiC matrix have been

carried out to determine material stability and viability at light water reactor relevant conditions. Primary findings of this study are as follows:

- Surrogate fuel compacts and ceramics derived from the nano-meter scale SiC powder hot pressed with yttria and alumina sintering aids result in an as-irradiated swelling somewhat greater than that of stoichiometric forms of SiC such as CVD SiC. The increment is minor and the thermal conductivity degradation is consistent with known values of CVD SiC considering the added irradiation-induced swelling.
- Irradiation near 300 °C has no apparent deleterious effect to the constituent layers of the microencapsulated fuel (the IPyC, SiC, or OPyC layers). Following irradiation no gross cracking or debonding between layers occurs.
- No reaction between the SiC-based nano-powder matrix and Zircaloy-4 was observed to the highest dose studied.

Acknowledgements

The authors would like to thank Joel McDuffee and Bob Sitterson for their effort in the design and construction of irradiation capsules. The authors would like to thank Dr. John Hunn for the use of the AGR program TRISO tomography image. Transmission electron microscopy was supported by ORNL's Shared Research Equipment (ShaRE) User Facility, which is sponsored by the Scientific User Facilities Division, Office of Basic Energy Sciences, US Department of Energy. Irradiations were carried out in the High Flux Isotope Reactor, and office of Science funded user facility. Surrogate TRISO particles were produced as part of previous work supported by the U.S. Department of Energy, Office of Nuclear Energy, under the Very High Temperature Reactor Technology Development Office Advanced Gas Reactor Fuel Development and Qualification Program. The work presented in this manuscript was supported by the Advanced Fuels Campaign of the Fuel Cycle R&D program in the Office of Nuclear Energy, US Department of Energy.

References

- [1] L.L. Snead, K.A. Terrani, F. Venneri, Y. Kim, J.E. Tulenko, C.W. Forsberg, P.F. Peterson, E.J. Lahoda, *Trans. Am. Nucl. Soc.* 104 (2011) 668.
- [2] K.A. Terrani, J.O. Kiggans, Y. Katoh, K. Shimoda, F.C. Montgomery, B.L. Armstrong, C.M. Parish, T. Honoki, J.D. Hunn, L.L. Snead, *J. Nucl. Mater.* 426 (2012) 268.
- [3] K.A. Terrani, L.L. Snead, J.C. Gehin, *J. Nucl. Mater.* 427 (2012) 209.
- [4] D. Petti, J. Maki, J. Hunn, P. Pappanpo, C. Barnes, J. Saurwein, S. Nagely, J. Kendell, R. Hobbs, *JOM* 62 62.
- [5] J.J. Powers, W.J. Lee, F. Venneri, L.L. Snead, C.K. Jo, D.J. Hwang, J.H. Hwang, J.H. Chun, Y.M. Kim, K.A. Terrani, Fully Ceramic Microencapsulated (FCM) Replacement Fuel for LWR's ORNL (2013).
- [6] K. Ozawa, Y. Katoh, L.L. Snead, T. Nozawa, T. Hinoki, A. Hasegawa, In: *Fusion reactor materials semiannual report DOE-ER-0313/46* 46 (2009) 4.
- [7] T. Koyanagi, S. Kondo, T. Hinoki, *J. Nucl. Mater.* 417 (2011) 435.
- [8] A.K. Kercher, J.D. Hunn, Results from ORNL Characterization of ZrO₂-500-AK2 Surrogate TRISO Material (2005).
- [9] J.D. Hunn, ORNL Data Compilation for the IAEA CRP-5 Coated Particle Fuel Quality Control Benchmark Exercise (2008).
- [10] R. Hunt, *JNM*, 2013 (accepted for publication).
- [11] P.J. Pappano, T.D. Burchell, J. Hunn, M. Trammell, *J. Nucl. Mater.* 381 (2008) 25.
- [12] L.L. Snead, A.M. Williams, A.L. Qualls, Revisiting the use of SiC as a Post irradiation temperature monitor, in: M.L. Grossbeck (Ed.), *The Effects of Radiation on Materials: 21st International Symposium, 2003*, ASTM International, West Conshohocken, PA, 2003.
- [13] J.L. Rempe, K.G. Condie, D.L. Knudson, L.L. Snead, *IEEE Trans. Nucl. Sci.* 57 (2010) 1589.
- [14] ASTM, Standard Test Method for Thermal Diffusivity by the Flash Method, 2001.
- [15] L.L. Snead, Y. Katoh, S. Connery, *J. Nucl. Mater.* 367–370 (2007) 677.
- [16] L.L. Snead, T. Nozawa, Y. Katoh, B.T. S. K. S, P.D. A, *J. Nucl. Mater.* 371 (2007) 329.
- [17] L.L. Snead, *J. Nucl. Mater.* 326 (2004) 114.
- [18] L.S. Sigl, H. Kleebe, *J. Am. Ceram. Soc.* 76 (1993) 773.
- [19] CECA, NP-MHTGR Material Models of Pyrocarbon and Pyrolytic Silicon Carbide, July 1993.
- [20] G.K. Miller, D.A. Petti, J.T. Maki, Development Of An Integrated Performance Model For Triso-Coated Gas Reactor Particle Fuel, HTR-T 2002 meeting, Petten, Netherlands, April 2002.
- [21] M. Naghedolfeizi, J.S. Chung, R. Morris, G.E. Ice, W.B. Yun, Z. Cai, B. Lai, *J. Nucl. Mater.* 312 (2003) 146.
- [22] C.A. Baldwin, J.D. Hunn, R.N. Morris, F.C. Montgomery, C.M. Silva, P.A. Demkowicz, First Elevated-Temperature Performance Testing of Coated Particle Compacts from the AGR-1 Irradiation Experiment, HTR October 28–November 1 2012, Paper HTR-2012-3-027, Tokyo, Japan, 2012.
- [23] Y. Katoh, N. Hashimoto, S. Kondo, L.L. Snead, A. Kohyama, *J. Nucl. Mater.* 351 (2006) 228.
- [24] K. Idczak, P. Mazur, L. Markowski, M.S.-cim, M. Musiał, *Appl. Surf. Sci.* (2012) 8349.
- [25] K. Bhanumurthy, R. Schmid-Fetzer, *Scripta Mater.* 45 (2001) 547.
- [26] H.M. Chen, Y. Xiang, S. Wang, F. Zheng, L.B. Liu, Z.P. Jin, *J. Alloys Comp.* 474 (2009) 76.
- [27] K.A. Terrani, C. Silva, J. Kiggans, Z. Cai, D. Shin, L.L. Snead, *J. Nucl. Mater.* 437 (2013) 171.
- [28] T. Fukai, M. Naka, J.C. Schuster, *Trans. JWRI* 25 (1996) 59.
- [29] J.C. Schuster, *Ceram. Trans.* 35 (1993) 43.