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Microstructure and Thermal Conductivity of Fully Ceramic Microencapsulated Fuel Fabricated by Spark Plasma Sintering

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Abstract

Fully ceramic microencapsulated pellet (FCM), consisting of tristructural isotropic (TRISO) particles embedded in silicon carbide (SiC) matrix, was fabricated using spark plasma sintering. The parameters affecting the densification of SiC matrix were first investigated, and then FCM pellets were prepared using TRISO particles with/without outer pyrolytic carbon (OPyC) layer. Effects of thermal exposure on the TRISO particles during SPS were evaluated. In addition, the thermal conductivities of FCM pellet, as well as the SiC matrix, were measured using laser flash. It was revealed that the TRISO particles with OPyC layers significantly lower the thermal conductivity of FCM pellet. Based on Maxwell-Eucken model, the predicted effective thermal conductivities of TRISO particles with/without OPyC layers were 14.4 W/mK and 25.2 W/mK, respectively. Finite elements simulation indicated that the SiC layer in TRISO particle plays a dominant role on the thermal conductivity of

FCM. The presence of OPyC layers would generate gaps/porous SiC near the interface and resist the heat flows, leading to a lower thermal conductivity of FCM.

Keywords: Fully ceramic microencapsulated pellet; Spark plasma sintering; SiC; TRISO; Thermal conductivity.

1. Introduction

Tristructural isotropic (TRISO) fuel particle consists of a spherical fuel kernel and four successive coated layers, namely porous carbon layer (buffer), dense inner pyrolytic carbon layer (IPyC), silicon carbide layer (SiC) and outer pyrolytic carbon layer (OPyC) from inner to outside. These layers serve as a pressure vessel to contain fission products and maintain structural integrity of TRISO particle ¹. TRISO particle system has been designed and optimized for high-temperature gas-cooled reactors (HTGRs). In conventional HTGRs applications, the TRISO particles are dispersed in a graphite matrix, producing compacts in form of pebbles or prismatic block ². However, the graphite matrix undergoes significant physical property changes, especially, suffers anisotropic dimensional instability, due to

irradiation, which results in a short lifetime ³. Recently, fully ceramic microencapsulated (FCM) fuel that consists of TRISO particles embedded in SiC matrix has attracted tremendous interest ⁴⁻⁹. The FCM fuel enable TRISO particles to apply in other reactor systems such as fluoride-salt cooled and water cooled reactors ⁶⁻⁸. Furthermore, the FCM fuel could offer the following potential advantages: high thermal conductivity of SiC matrix ^{4,6}, additional barriers to retain fission product ¹⁰, excellent resistance to neutron exposure ³, environmental stability and strength retention under high temperature operating conditions ⁷.

Therefore, it is expected that the FCM fuel can not only realize higher fuel burnup and power conversion efficiency of the fuel coupled with the small temperature gradient across the fuel, but also alleviate the thermal stress and enhance the accident tolerance ¹¹.

Generally, FCM fuel is compacted in form of pellets or pebbles, where the SiC matrix is densified with uniformly distributed TRISO particles of a certain volume fraction ^{5, 8, 9}. Preparation of the FCM fuel has been previously performed using hot pressing sintering with a duration of an hour or more ^{5,8}. It is assumed that the TRISO particles will not be damaged during the FCM compaction processes. The densification of FCM pellets should be achieved with limited amount of oxide additives to avoid the drawbacks of oxide phases under

irradiation (i.e., neutron absorption or swelling)^{8, 12}. Besides, lowering the fabrication temperature is of great importance to slow the grain growth in the SiC layers of the TRISO particles, which would result in unacceptable deterioration in mechanical property^{5, 8}. It is also worth mentioning that the thermal treatment from the high fabrication temperature affects the TRISO particle, especially on the disorder and mechanical degradation in the PyC layers^{13, 14}. Compared with the conventional sintering methods, the spark plasma sintering (SPS) method can achieve high densification at noticeable lower temperature and shorter time, thus minimizing the thermal treatment effects¹⁵. SiC is a complex material whose properties vary greatly dependent on the fabrication route¹⁶. Hence, a fundamental understanding of the matrix materials and SPS processing conditions is necessary to achieve the ideal properties. In FCM compact, the SiC matrix replaces the graphite matrix and becomes the most important safety feature that protects the TRISO particles from damage of mechanical effects such as abrasion. Thus the mechanical property of SiC matrix should be studied. Meanwhile, the SiC matrix not only stabilizes the TRISO particles in the FCM pellets but also functions as a good heat transfer medium¹⁷. Therefore, the thermal conductivities of both the SiC matrix and the TRISO particle are worth to be investigated.

In this study, the SiC matrix and FCM pellet were fabricated using SPS technique. The influences of various sintering conditions on the microstructure of SiC matrix were investigated. The thermal effects during the SPS process on the microstructure of the PyC layers in TRISO particles were discussed. The hardness and Young's modulus of SiC matrix was determined using micro-indentation. The thermal conductivities of SiC matrix and FCM pellet with TRISO particles with/without OPyC layers were evaluated using laser flash technique. The effective thermal conductivity of TRISO particle was also predicted using the Maxwell-Eucken model ¹⁸. In addition, the presence of the OPyC layers on the thermal conductivity of FCM pellet was discussed.

2. Experimental procedure

2.1. Material Preparation

The starting powder was fine β -SiC with an average particle size of ~40 nm (99.9%, Aladdin Chemical Co., Ltd., China). A mixture oxides powder of Al_2O_3 and Y_2O_3 with an average particle size of ~30 nm (99.99%, Aladdin Chemical Co., Ltd., China) were added in the ratio corresponding to the yttrium aluminum garnet (YAG) stoichiometry ($\text{Al}_2\text{O}_3 : \text{Y}_2\text{O}_3 = 5:3$ in

molar ratio) as sintering additives. The amount of oxide additives was at a range of 2 wt%–10 wt%. The powder mixture was mixed by ball milling using SiC media in a polypropylene jar for 24 h in isopropyl alcohol. The mixture was dried, crushed, and then screened through a 60-mesh sieve. The simulated TRISO particle samples were made by fluidized bed chemical vapor deposition using zirconia particles with a diameter of $\sim 510\text{ }\mu\text{m}$ as kernels instead of fuel. The average thickness of the buffer, IPyC, SiC, and OPyC layers were about 95, 40, 35 and $40\text{ }\mu\text{m}$, respectively. Some TRISO particles were exposed in air at $800\text{ }^{\circ}\text{C}$ for 8 hours to oxidize the OPyC layers.

2.2. SPS fabrication

Prior to high-temperature consolidation, the powder feedstock was cold pressed inside a steel die. Monolithic green bodies prepared via biaxial cold pressing at $\sim 5\text{ MPa}$ exhibited green density about 30% of theoretical SiC density. Subsequently, the green bodies were individually spark plasma sintered (KCE-FCT-HP D 25/4-SD, FCT Systeme GmbH, Germany) using graphite dies at $1850\text{ }^{\circ}\text{C}$ under a uniaxial pressure of 10–20 MPa for 10–20 min. The load was released and the electrical power was shut down by the end of the

dwelling time to allow rapid cooling to room temperature. The various SPS conditions for the fabrication of SiC matrix (S1–S6) were listed in Table 1.

2.3. Characterization

The morphology and chemical composition of the starting SiC powder was observed using transmission electron microscope (TEM) (TALOS F200X, FEI, USA) and X-ray photoelectron spectroscopy (XPS) (AXIS Ultra DLD, Kratos, Japan), respectively. Focused ion beam (FIB) (GAIA3, Tescan, Czech Republic) combined with SEM was used for sample preparation for the HREM observations. The bulk density (ρ) of the specimen after consolidation was determined using the Archimedes' method, with water as the immersing medium. The relative density of sintered materials was calculated using the theoretical density of the SiC matrix. The oxide additives of Al_2O_3 and Y_2O_3 ($\text{Al}_2\text{O}_3 : \text{Y}_2\text{O}_3 = 5:3$ in molar ratio) would react to form the YAG compound during the sintering of SiC. So, the theoretical density of the SiC matrix could be estimated according to the ratio of mixture, using theoretical density for YAG and SiC of 4.54 g/cm^3 and 3.21 g/cm^3 , respectively¹⁹. The microstructure of FCM pellet sample was examined using a scanning electron microscope (SEM) (Inspect F50, FEI, USA). The phase analysis of the SiC matrix and TRISO particle

was determined by means of X-ray diffractometer (XRD) (Ultima IV, Rigaku, Japan) and Raman spectroscopy (LabRAM HR Evolution, HORIBA Jobin Yvon, France). The measurement of hardness and Young's modulus were performed on the finely polished SiC by micro-indentation technique (MHT, Anton Paar, Austria), using a Vickers indenter at a maximum load of 2 N. Arrays of indentations were performed on each specimen with an interval of 100 μm , which is much more than 20 times the indentation depth of $\sim 2.5 \mu\text{m}$. Thermal conductivity (k) was measured at room temperature using laser-flash technique. A plate sample ($10 \text{ mm} \times 10 \text{ mm} \times 3 \text{ mm}$) was prepared for the thermal diffusivity (α) measurement using the Laser Flash Analyzer (LFA447, Netzsch, Germany). The specific heat capacity (c_p) was measured using the differential scanning calorimeter (DSC 8000, Perkin Elmer, America) with a disk sample ($\sim 5 \text{ mm}$ diameter $\times$ 1.5 mm thickness). Then the thermal conductivity (k) can be determined using the relation: $k = \alpha \cdot \rho \cdot c_p$.

3. Results and discussion

Figure 1 is a representative TEM image of the starting SiC powder. The variation in powder size appeared to be broad with a range of 40 nm to 150 nm. It was found that the surface of SiC nanopowder was covered by a layer of amorphous silicon oxide with a thickness of ~ 1

nm. Detailed chemical characterization for impurity phase was performed using XPS by chemical bond analysis. Figure 2 shows the spectra for O_{1s} ($E_b = \sim 538$ eV), C_{1s} ($E_b = \sim 291$ eV), Si_{2p} ($E_b = \sim 106$ eV) and Si_{2s} ($E_b = \sim 153$ eV) signals²⁰ of both SiC powder and the SiC matrix sample fabricated using SPS. The presence of O_{1s} peak implies that the oxygen element, which existed on the surface of SiC nanopowder (Figure 1), was in the form of SiO_2 or SiO_xC_y ^{8, 21}. The ratio of the intensity of O_{1s} to Si_{2p} of the starting SiC powder (2.1) was close to that of the pure SiC matrix sample (2.0) fabricated using SPS without oxide additives, which indicates the oxidation of SiC matrix during SPS procedure can be neglected.

3.1 The phase, microstructure and mechanical property of the SiC matrix

Figure 3 presents the XRD patterns of the starting SiC powder, the mixed SiC powder with 5wt% oxide additives and SPS SiC matrix, respectively. The XRD spectra of the starting SiC powder correspond to stoichiometry β -SiC, showing the extra peak at $2\theta \sim 33.5^\circ$ and a broadening peak at $2\theta \sim 35.3^\circ$, which could be attributed to the existence of a high density of stacking faults in the regular cubic sequences²². In the mixed SiC powder, it revealed that β -SiC presented as a major phase with a minor amount of Y_2O_3 except for Al_2O_3 , suggesting

the concentration of Al_2O_3 (2 wt.%) was below the detectability limit of XRD²³. In this study, the low amount of oxide additives was designed to acquire high radiation resistant of SiC matrix. For the SPS SiC matrix sample, the XRD pattern only presents SiC polycrystalline structure. It indicates the annihilation of the stacking faults in starting SiC powder¹⁴, and the oxide additives precipitated as glass phases in SiC matrix after SPS processing²⁴.

Figure 4 shows the microstructure of SiC matrix (S1–S6) using SPS at 1850 °C, where SiC appeared as a gray phase, while the black spots and bright areas corresponded to pores and oxide phases at the SiC grain boundaries, respectively. The SiC grains exhibited equiaxed shape with sizes from 0.5 μm to 1.5 μm , meaning that the grains have grown nearly ten-times larger compared with the starting powder (Figure 1). Figures 4A–4C represent the SiC matrix (S1–S3) sintered under 10 MPa, 15 MPa and 20 MPa, respectively, with oxide additives of 5 wt.% and dwelling time of 10 min. The sample sintered under 10 MPa of pressure (S1) contained a large amount of pores, while higher sintering pressure (15 MPa for S2 and 20 MPa for S3) produced an enhanced densification. The lower sintering pressure (15 MPa) was preferred to prevent TRISO particles from being damaged during the FCM

compaction process. The addition of oxide additives with different content (2 wt.% for S4 and 10 wt.% for S5) had significant effects on the microstructure of the SiC matrix, as shown in Figures 4B, 4D and 4E. The SiC matrix with 2 wt.% oxide additives (S4) showed a poor sinterability with a lot of pores. With addition of 10 wt.% oxide additives (S5), a fully dense SiC matrix could be achieved. It was also observed that the sample S5 had much smaller and homogenous grain size distribution, indicating the oxide additives aggregated at grain boundaries inhibited the grain growth. Compared with sample S2, no apparent changes were observed in sample S6 with a longer dwelling time of 20 min (Figure 4F), which indicates the densification procedure could not be facilitated using a prolonged time period at 1850 °C.

At the given temperature (1850 °C), the influences of the SPS sintering conditions on the density and mechanical property of SiC matrix were analyzed, as shown in Table 2. The SiC matrix sintered at 1850 °C with 5 wt.% oxide additives for 10 min (S2) yielded a density of 2.97 g/cm³ (91% relative density). Relative density increased with an increase of the amount of sintering additives from 2 wt.% to 10 wt.% (S4, S2 and S5). A 98% relative density was obtained with 10 wt% oxide additives (S5). The density of the SiC matrix hardly changed with the dwelling time varied from 10 min to 20 min (S2 and S6), which indicates

SPS could achieve compaction process at a short dwelling time. Meanwhile, the hardness and the Young's modulus of the sample S2 was 21.3 GPa and 313 GPa respectively, which fell into the range of hardness (21.1–29.7 GPa) and Young's modulus (300–400 GPa) for sintered β -SiC¹, implying the SPS is an effective method for the fabrication of SiC matrix. Both the hardness and the Young's modulus of the SiC matrix increased as a function of the relative density. Inversely, the SiC matrix of near full density (98% relative density) sintered with 10 wt.% oxide additives (S5) showed a slight decrease of the hardness and Young's modulus. It could attribute to a large amount of oxide additives in sample S5 that located at the grain boundaries (Figure 4E) as glass phases after sintering could lower the hardness and Young's modulus of the SiC matrix²¹.

Therefore, the presence of the oxide additives could realize high densification as well as deteriorate the hardness and Young's modulus of the SiC matrix. To achieve a high-density SiC matrix with low amount of oxide additives and intact TRISO particles embedded (i.e., FCM pellet), the SPS was performed at 1850 °C with 5 wt.% oxide for 10 min of dwelling time and 15 MPa of pressure in this study, which had the same sintering condition as sample S2.

3.2 The microstructure of the FCM

Figure 5A and 5B show the FCM pellet with TRISO particles (~24 vol.%) and the FCM pellet with the same number of TRISO particles (~20 vol.%) with the OPyC layers removed by oxidation in air, respectively. The TRISO particles appeared randomly dispersed, and remained undamaged with no collision occurred during the matrix consolidation process. In FCM fuel, this is an essential performance metric in order to act as the fuel particle pressure vessel and prevent fission products from escaping¹⁰.

Figure 6A was taken in the vicinity of a TRISO particle with OPyC layer and shows the presence of gap at the interface between the TRISO particle and the SiC matrix. Besides, a porous SiC layer with a thickness of ~15 μm (Figure 6A2) was observed near the interface. The original thickness of the OPyC layer was about 40 μm , while a thickness of ~25 μm (measured from the cross section at hemispherical TRISO particles) for the OPyC layer was observed after SPS. That is, the OPyC layers presented a thickness reduction of ~15 μm apparently after SPS. Figure 6B presents the image of the TRISO without the OPyC layers in FCM. The SiC layers in the TRISO particles remained intact after SPS process. As shown in the higher magnification image, the interface between the TRISO particle and the SiC matrix

exhibited good contact without apparent voids or debonding. Furthermore, sintering at the interface of the SiC layer and the SiC matrix occurred without apparent interface (Figure 6B2), which would facilitate the heat transfer.

The visible gap observed at the interface of the OPyC layer and the SiC matrix might be caused by the mismatch of thermal expansion coefficient. Because pyrolytic carbon has a larger thermal expansion coefficient of $6-8 \times 10^{-6}/\text{K}$ ²⁵, which is almost twice larger than that of β -SiC ($3.2 \times 10^{-6}/\text{K}$ ²⁶), the OPyC layers would shrink more than the SiC matrix during the cooling. Both the presence and absence of pores in the SiC matrix near the OPyC layer was reported in different studies without scientific explanations, in which the FCM pellets were produced using hot pressing^{5,9}. Therefore, the reactions between the OPyC and SiC can be ruled out. In this study, the reduced thickness of the OPyC layers was observed after SPS (Figure 6A1). This indicated that the oxidation of OPyC could occur during SPS (at a vacuum degree of about 0.1 Pa), leading to gas product of CO/CO₂. Besides, as reported in previous study, the reactions between SiC and CO/CO₂ could generate SiO (g) and C when the partial pressure of CO/CO₂ was low (see Figures 1 and 2, Ref.[27], active oxidation of SiC would occur when the CO/CO₂ pressure was lower than 0.1 Pa)²⁷. Therefore, the

formation of porous SiC might be caused by the trapped gas products from reactions at the interface of the OPyC layer and the SiC matrix during SPS. The pores or gaps at the interface between the TRISO particle and the SiC matrix would be detrimental to the heat transfer from TRISO particle to SiC matrix. So a high vacuum degree of sintering system would be required to control/eliminate the formation of the pores.

Figure 7 presents the line mapping of Raman spectra through the porous SiC from the OPyC layer to SiC matrix. The peaks at $\sim 796\text{ cm}^{-1}$ corresponds to the TO band of β -SiC with second-order peaks between 1400 cm^{-1} and 1800 cm^{-1} , while the two peaks at $\sim 1360\text{ cm}^{-1}$ and $\sim 1580\text{ cm}^{-1}$ are the D band and G band for amorphous carbon, respectively. It can be seen that the SiC matrix only presents the Raman peaks of SiC, and the OPyC layer only shows the Raman peaks of amorphous carbon. However, both the Raman spectra of SiC and amorphous carbon appeared in the region of porous SiC. The presence of carbon in the porous SiC further confirmed the reactions between SiC and CO/CO₂ with the formation of SiO (g) and carbon. Besides, the intensity of the D band and G band in the porous SiC tended to increase when close to the OPyC layer. Thus, the progression of the reactions between SiC and CO/CO₂ was related to the diffusion of CO/CO₂ from the interface of the OPyC layer and

the SiC matrix. The possibility that the Raman spectra of carbon detected in the porous SiC was originated from the OPyC layer was excluded, because no Raman spectra of carbon could be detected from the SiC layer in TRISO particle, even when it was close to the OPyC layer.

TEM was employed to further characterize the microstructure at the interface between TRISO particle with OPyC layer and SiC matrix, with the specimen cut across the interface using FIB technique. FIB section was taken near the interfaces of TRISO particle with OPyC layer and SiC matrix, as shown in Figure 8A. The interface between the OPyC layer and the SiC matrix was seen to be rough and porous. Besides, many large pores were also observed in the porous SiC zone (it should be noted that some big pores were caused by FIB milling).

Furthermore, the distribution of carbon in the porous SiC was also presented in the bright-field TEM image with the energy-dispersive X-ray spectroscopy (EDS) mapping of C and Si (Figure 8D). This is in agreement with the results of the Raman line mapping of Figure 7. And both small and large size of carbon were involved, a range of 50 nm to 300 nm. For comparison, the characterization of the microstructure at the interface between TRISO particle without OPyC layer and SiC matrix was also performed using TEM, as is shown in Figure 9. The interface between the SiC layer and the SiC matrix clearly remains

intact and keeps tight cohesion without apparent interface. The differences in the microstructure between the SiC layer and the SiC matrix can also be observed. The SiC grain size in the SiC matrix is smaller (range from 300 nm to 1 μm) than that in the SiC layer. Moreover, EDS mapping of O, Y and Al indicates the segregation of the oxide additives at the triple points and grain boundaries in the SiC matrix (Figure 9D).

3.3 The thermal effects on the microstructure of TRISO particle during SPS

As was discussed above, the SPS process resulted in both the annihilation of the stacking faults (Figure 3) and the grain growth in SiC matrix compared with the starting SiC powder (Figures 1 and 4). It is also worth noting that the thermal effects of the high fabrication temperature on the microstructure of TRISO particles, especially the PyC layers. Figure 10 shows Raman spectra for the PyC layers, which exhibit two relatively broad D band and G band. The band at 1600 cm^{-1} is an overlap of broadened G and D' (1620 cm^{-1}) bands due to the highly disordered pyrolytic carbon²⁸. The D band and D' represent the in-plane defects, while the G band represents the ordered structure in the graphene planes^{13, 29}. The split of G and D' bands could be observed after the SPS procedure at $1850\text{ }^{\circ}\text{C}$, which indicates the thermal experience decreased the degree of disorder in the PyC layers³⁰. Besides, the split of

the G and D' bands became more significant with an increase of the dwelling time, suggesting more significant change in on the degree of disorder in the PyC layers during SPS.

According to previous studies, the Raman spectra of PyC layers can be deconvoluted into four peaks at about 1220 cm^{-1} (I band), 1335 cm^{-1} (D band), 1500 cm^{-1} (D'' band) and 1600 cm^{-1} (G band) ¹³. Then, the full width at half maximum (FWHM) of the D band and intensity ratio of the D'' bands (i.e., the area ratio of the 1500 cm^{-1} peak to the sum of four peaks shown in Figure 11C) can be related to the degree of in-plane and out-of-plane disorder in PyC layers, respectively ^{13, 30, 31}. Figure 11 shows the FWHM of the D band and intensity ratio of the D'' bands for the PyC layers, respectively. The inset (Figure 11C) shows the fitting of Raman spectra of PyC layers using four bands. For the OPyC layers, the FWHM of the D band decreased significantly from ~110 cm^{-1} (as-deposited) to ~50 cm^{-1} (1850 °C–10 min), and then to about 40 cm^{-1} (1850 °C–20 min). Similarly, the intensity ratio of the D'' decreased from ~0.35 (as-deposited) to ~0.09 (1850 °C–10 min), and then to ~0.05 (1850 °C–20 min). Such changes indicate a decrease of both the in-plane disorder and the out-of-plane defects in the OPyC layers due to the thermal effects after SPS ¹³. and the concentration of defects decreased obviously with an increase of dwelling time. The IPyC

layers showed similar trends as the OPyC layers. However, the buffer layers exhibited less changes, especially in term of the the intensity ratio of the D", which can attribute to the dominant defects in PyC layers of different densities according to the previous study ¹³. It was reported that a combination of a high degree of in-plane and out-of plane defects prevail in high density PyC (e.g, IPyC and OPyC layers) ¹³. However, in low density PyC (e.g, Buffer layer), the microstructure could remain almost unchanged after thermal treatment due to the dominant defects of five-membered rings ¹³.

The thermal effects of the SPS procedure on the microstructure of the PyC layers could not only decrease the mechanical properties, but also degrade radiation resistance performance due to the reduction of disorders (e.g., anisotropic swelling) ^{3,13}. Therefore, the detrimental effect on TRISO particles due to the sintering process of FCM should be avoided by lowing the sintering temperature or shortening the dwelling time. Compared with the hot pressing sintering ^{8,9}, SPS technique can achieve high densification at a much shorter time (e.g., 10 min in this study), thus minimizing the microstructural degradation in TRISO particle induced by the thermal experience.

3.4 The thermal conductivity of SiC matrix and FCM

Since one of the purposes of the FCM fuel was designed to transfer the fission heat originated from the embedded TRISO fuel particles, the thermal conductivity is an important parameter to predict the thermal efficiency of the fuel. Table 3 summarized the thermal diffusivity and thermal conductivity of the SiC ceramics (S1–S6) of various sintering conditions and the FCM pellets (F1–F3) with different TRISO particles. The thermal conductivity of the SiC ceramics increases slightly from 46.4 W/m K to 72.4 W/m K with an increase of relative density from 81% to 98% fabricated in different sintering conditions. It indicates that the porosity has a significant influence on the thermal conductivity of SiC matrix. The SiC matrix (S5) of near full density (98% relative density) exhibited the highest thermal conductivity (72.4 W/m K) in spite of the large content of the low thermal conductivity oxide additives (10 wt.%). The thermal conductivity of the SiC with 5 wt.% oxide additives sintered at 1850 °C for 10 min (S2) was 57.3 W/m K. Because the sintering conditions of FCM pellets were similar to that of the sample S2, the thermal conductivity of the SiC matrix in FCM pellet was also assumed to be 57.3 W/m K.

With the presence of TRISO particles embedded in the SiC matrix, both the thermal diffusivity and the thermal conductivity of the FCM pellets reduced considerably as shown in Table 3. The decrease in the thermal conductivity was caused by the reduction in the thermal diffusivity with the addition of TRISO particles, which consist of low thermally conductive zirconia kernels and coated layers ³². Sample F1 is the FCM pellet with 24 vol.% TRISO particles with OPyC layers, whose thermal conductivity was measured to be 44.6 W/m K. F2 is the FCM pellet that contained the same number of TRISO particles as F1 but without OPyC layers. The thermal conductivity of F1 was lower than that of F2 (50.3 W/m K), owing to the presence of the OPyC layers and the gaps/pores near the interface of the OPyC layers and SiC matrix in F1. F3 is the FCM pellet consists of 24 vol.% TRISO particles without OPyC layers, meaning the number of the TRISO particles was more than that of F1. However, the thermal conductivity of F3 (47.7 W/m K) was higher than that of F1. Therefore, for the same volume fraction of particles in FCM compact, the number of the TRISO particles without OPyC layers was much more than the TRISO particles with OPyC layers, which not only enabled higher the fuel kernel volume fraction, but also improved the thermal efficiency of the FCM with higher thermal conductivity.

3.5 The effective thermal conductivity of TRISO particle

The effective thermal conductivity of whole TRISO particle is a critical parameter to determine the temperature distribution within a fuel compact. In this work, the Maxwell-Eucken equation was employed to analyze the effective thermal conductivity of the TRISO particle, which is can be used to describe the thermal conductivity of isolated spherical inclusions dispersed in a continuous homogeneous matrix and presented by ¹⁸:

$$k_{eff} = k_m \left[\frac{k_i + 2k_m + 2v_i(k_i - k_m)}{k_i + 2k_m - v_i(k_i - k_m)} \right] \quad (1)$$

where v represents the volume fraction, k is the thermal conductivity, k_{eff} is the effective thermal conductivity of the composite and the subscripts m and i refer to the matrix and inclusions, respectively. Assuming the FCM is a composite, the effective thermal conductivity of TRISO particles was calculated to be 14.4 W/m K according to Equation (1), using the thermal conductivity of the SiC matrix, FCM pellet and the volume fraction of TRISO particles (Table 3). The value obtained in this study is slightly higher than that presented in a previous study (12.01 W/mK) ⁹, which might come from differences in the microstructure of both SiC matrix and TRISO particles after the fabrication of FCM pellets.

Furthermore, the effective thermal conductivity of TRISO particle without OPyC layer was calculated to be ~ 25.2 W/m K, which was much higher than that of the TRISO particle with OPyC layer. The difference can attribute to the presence of the OPyC layer with the low thermal conductivity. Besides, the thermal resistance at the gaps between the OPyC layer and the SiC matrix, together with the porous SiC formed near the OPyC layer would also underestimate the effective thermal conductivity of TRISO particle.

Table 4 summarizes the basic physical parameters of the SiC matrix and TRISO particle, including the theoretical heat capacity³³ and reported thermal conductivities of the individual layers in TRISO particle³². Based on the parameters in Table 4, the way heat flows through the matrix in the vicinity of a single TRISO particle within an external temperature gradient could be evaluated, as shown in Figure 12. Two cases have been considered. One was for the TRISO particle with the OPyC layer and the other was for TRISO particle without OPyC. Both the red arrow and grey streamline refer to the heat flux. Although the heat can flow through TRISO particle, most of the heat flows around the outside of TRISO particle (red arrows in Figure 12), due to the low thermally conductive TRISO particle. When assessing heat flow through a TRISO particle, regions of high heat flux lie on the SiC layer in TRISO

particle as the heat flow lines become squeezed on the passage through the SiC layer (grey streamlines in Figure 12). That is, the thermal conductivity of the SiC layer plays a dominant role on the effective thermal conductivity of TRISO particle. However, the presence of the OPyC layer with lower thermal conductivity hindered the way heat flows through the SiC layer. Besides, for the FCM pellets contained TRISO particles with OPyC layers, the gaps at the interface and the porous SiC formed near the OPyC layer would further resist the way heat flows through the SiC layer. Therefore, it's reasonable that the effective thermal conductivity of TRISO particle without OPyC layer was higher than that of the TRISO particle with OPyC layer.

Generally, for a composite material with multilayered structure, the calculation of effective thermal conductivity was based on the heat flux direction predicted in the model, such as series and parallel models that are in extreme cases¹⁷. However, the Maxwell-Eucken model used in this study assumed an external temperature gradient, which is different from the service condition, i.e., the heat conduction from fuel-kernels to SiC matrix. Therefore, the calculated effective thermal conductivity for TRISO particle or FCM might not reflect the real effective thermal conductivity of TRISO particle or FCM in nuclear reactor.

Nonetheless, the FCM pellet using TRISO particles without OPyC layers would exhibit a higher thermal conductivity.

4. Conclusions

To achieve a high-density SiC matrix with low amount of oxide additives and intact TRISO particles embedded, the fabrication of FCM pellets were performed at 1850 °C with 5 wt.% oxide additives for 10 min of dwelling time under 15 MPa of pressure using SPS technique.

The high temperature fabrication of SPS procedure resulted in significant decrease of both the in-plane disorder and the out-of-plane defects in the PyC layers with an increase of dwelling time.

Thermal conductivity of the FCM pellet was determined using laser flash technique. The thermal conductivity of the FCM pellet with 24 vol.% TRISO particles embedded was measured to be 44.6 W/m K. In contrast, the thermal conductivity of the FCM pellets that consist of the same number and the same volume fraction of TRISO particles without OPyC layers was 50.3 W/m K and 47.7 W/m K, respectively. Therefore, the FCM pellets with TRISO particles without OPyC layers could improve the thermal conductivity of the FCM,

owing to the interface between the SiC matrix and the SiC layer exhibited good contact without significant voids or evidence of debonding.

The effective thermal conductivity of TRISO particle was analyzed using Maxwell-Eucken model. The effective thermal conductivity of TRISO particle with OPyC layer was calculated as 14.4 W/m K, while 25.2 W/m K for TRISO particle without OPyC layer. The way heat flows through the matrix in the vicinity of a single particle within an external temperature gradient was also simulated, suggesting the SiC layer plays a dominant role on the effective particle conductivity. Both the presence of the OPyC layers and the pores or gaps near the OPyC layer/SiC matrix interface formed during sintering process hindered the heat flows through the SiC layer and resulted in a lower thermal conductivity.

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Figure captions

Figure 1 Transmission electron microscope (TEM) images of the starting SiC nanopowder.

Figure 2 XPS spectra of the starting SiC powder and the pure SPS SiC sample.

Figure 3 XRD patterns of the starting SiC powder, the mixed powder with 5wt.% sintering additives and SiC matrix after SPS.

Figure 4 SEM images (A–F) correspond to the microstructure of SiC ceramics (S1–S6) using SPS processing at 1850 °C with various sintering conditions.

Figure 5 FCM samples with (A) TRISO particles with OPyC layers and (B) TRISO particles without OPyC layers embedded in SiC matrix.

Figure 6 The interface between (A) the TRISO particle with OPyC layer and (B) TRISO particle without OPyC layer and the SiC matrix, with the higher magnification image of A2 and B2 showing the porous SiC and the interface, respectively.

Figure 7 The line mapping of Raman spectra through the porous SiC from the OPyC layer to SiC matrix.

Figure 8 TEM images of the microstructure near the interface between TRISO particle with OPyC layer and SiC matrix, with EDS mapping for C in porous SiC.

Figure 9 TEM images of the microstructure near the interface between TRISO particle without OPyC layer and SiC matrix, with EDS mapping for O, Al and Y in the SiC matrix.

Figure 10 Raman spectra for (A) the OPyC layer, (B) the IPyC layer and (C) the buffer layer for different dwelling time for SPS.

Figure 11 (A) the full width at half maximum (FWHM) of the D band and (B) the intensity ratio of the D'' bands, i.e., the area ratio of the 1500 cm^{-1} peak to the sum of four peaks at about 1220 cm^{-1} (I band), 1335 cm^{-1} (D band), 1500 cm^{-1} (D'' band) and 1600 cm^{-1} (G band) shown in the inset (C).

Figure 12 The model of the way heat flows through the matrix in the vicinity of a single (A) TRISO particle with OPyC layer and (B) TRISO particle without OPyC layer within an external temperature gradient.

Table captions

Table 1 The SPS conditions for the fabrication of SiC matrix (S1–S6) at 1850 °C.

Table 2 Density (relative density * in parenthesis) and mechanical property of the SiC matrix (S1–S6) fabricated with various sintering conditions.

Table 3 Specific heat capacity (c_p), thermal diffusivity (α) and thermal conductivity (k) of the SiC matrix (S1–S6) and the FCM pellet (F1–F3) with different volume fraction (v_i) of TRISO particles.

* The relative density of sintered materials was calculated using the theoretical density of the SiC matrix according to the ratio of mixture, using theoretical density for YAG and SiC of 4.54 g/cm³ and 3.21 g/cm³, respectively.

Table 4 A summary of diameter, density, heat capacity (c_p) and thermal conductivity (k) for the heat flux model through the matrix in the vicinity of a single TRISO particle.

Table 1 The SPS conditions for the fabrication of SiC matrix (S1–S6) at 1850 °C

Sample	Sintering pressure (MPa)	Oxide additives (wt.%)	Dwelling time (min)
S1	10		
S2	15	5	
S3	20		10
S4		2	
S5	15	10	
S6		5	20

Table 2 Density (relative density [†] in parenthesis) and mechanical property of the SiC matrix (S1–S6) fabricated with various sintering conditions

Sample	Density (g/cm ³)	Hardness (GPa)	Young's modulus (GPa)
S1	2.70 (83%)	15.7	271
S2	2.97 (91%)	21.3	313
S3	3.14 (96%)	25.6	380
S4	2.63 (81%)	14	264
S5	3.24 (98%)	23.3	356
S6	3.01 (92%)	19.2	318

[†] The relative density of sintered materials was calculated using the theoretical density of the SiC matrix according to the ratio of mixture, using theoretical density for YAG and SiC of 4.54 g/cm³ and 3.21 g/cm³, respectively.

Table 3 Specific heat capacity (c_p), thermal diffusivity (α) and thermal conductivity (k) of the SiC matrix (S1–S6) and the FCM pellet (F1–F3) with different volume fraction (v_i) of TRISO particles

Sample	v_i (vol.%)	c_p (J/g°C)	α (mm ² /s)	k (W/mK)
S1	0	0.675	26.66	49.0
S2		0.681	28.32	57.3
S3		0.685	30.75	65.3
S4		0.667	25.89	46.4
S5		0.673	32.81	72.4
S6		0.681	29.04	59.5
F1	24	0.685	22.44	44.6
F2	20	0.671	25.48	50.3
F3	24	0.675	23.93	47.7

Table 4 A summary of diameter, density, heat capacity (c_p) and thermal conductivity (k) for the heat flux model through the matrix in the vicinity of a single TRISO particle

Materials	Diameter (μm)	Density (g/cm^3)	c_p ($\text{J}/\text{g}^\circ\text{C}$)	k (W/mK)
ZrO ₂ kernel	510	5.6	0.460 ³²	3
Buffer	700	0.88	0.771 ³²	5.7 ²⁹
IPyC	780	1.93	0.771 ³²	13.5 ²⁹
SiC	850	3.19	0.661 ³²	168 ²⁹
OPyC	930	1.96	0.771 ³²	13.5 ²⁹
SiC matrix	-	2.97	0.681	57.3