

Influence of Carbon Content on Element Diffusion in Silicon Carbide-Based TRISO Composite Fuel

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Abstract: The coating layers of Tri-structural Isotropic Particles (TRISO) serve to protect the kernel and act as barriers to fission products. Sintering aids in the silicon carbide matrix variably react with TRISO coating layers, leading to the destruction of the coating layers. Investigating how carbon content affects element diffusion in silicon carbide-based TRISO composite fuel is of great significance for predicting reactor safety. In this study, silicon carbide-based TRISO composite fuels with different carbon contents were prepared by adding varying amounts of phenolic resin to the silicon carbide matrix. X-ray Diffraction (XRD) and Scanning Electron Microscopy (SEM) were employed to characterize the phase composition, morphology, and microstructure of the composite fuels. The elemental content in each coating layer of TRISO was quantified using Energy-Dispersive X-ray Spectroscopy (EDS). The results demonstrated that the addition of phenolic resin promoted the uniform distribution of sintering aids in the silicon carbide matrix. The atomic percentage (at.%) of aluminum (Al) in the pyrolytic carbon layer of the TRISO particles reached its lowest value of 0.55% when the phenolic resin addition was 1%. This is because the addition of phenolic resin caused the Al and silicon (Si) in the matrix to preferentially react with the carbon in the phenolic resin to form a metastable liquid phase, rather than preferentially consuming the pyrolytic carbon in the outer coating layer of the TRISO particles. The findings suggest that carbon addition through phenolic resin incorporation can effectively mitigate the deleterious reactions between the TRISO coating layers and sintering aids, thereby enhancing the durability and safety of silicon carbide-based TRISO composite fuels.

Keywords: Silicon carbide; TRISO; Composite fuel; Diffusion behavior; Carbon content

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1. Introduction

With the continuous increase in global energy demand, nuclear energy has become one of the future energy choices. Nuclear fuel elements are crucial for sustaining nuclear reactor power, and their safety and economy are important foundations for advanced reactors. Tri-structural isotropic (TRISO) fuel can confine most fission products within the particles at high temperatures of 1,800°C, greatly improving the safety of nuclear reactors, and thus has been widely used in various reactor types such as high-temperature gas-cooled reactors, molten salt reactors, light water reactors, and pressurized water reactors^[1-3]. The kernel of TRISO fuel is uranium dioxide (UO₂),

uranium oxycarbide (UCO), or uranium mononitride (UN), and the outer coating layers include inner pyrolytic carbon (IPyC), silicon carbide layer (SiC), and outer pyrolytic carbon (OPyC)^[4,5]. The IPyC layer mainly serves to protect the kernel from the influence of corrosive gases, the SiC layer primarily acts as a barrier to fission products and prevents the infiltration of oxidants into the nuclear fuel, and the OPyC layer not only protects the SiC layer during compaction but also acts as the final barrier for gaseous fission products^[6]. Due to the spherical shape and relatively small particle size of TRISO particles, in existing reactors, TRISO particles are widely dispersed in inert matrices such as graphite and silicon carbide. Among them, silicon carbide-based TRISO composite fuel is a new type of accident-tolerant fuel with high thermal conductivity, high overall stability, and good compatibility with coolants.

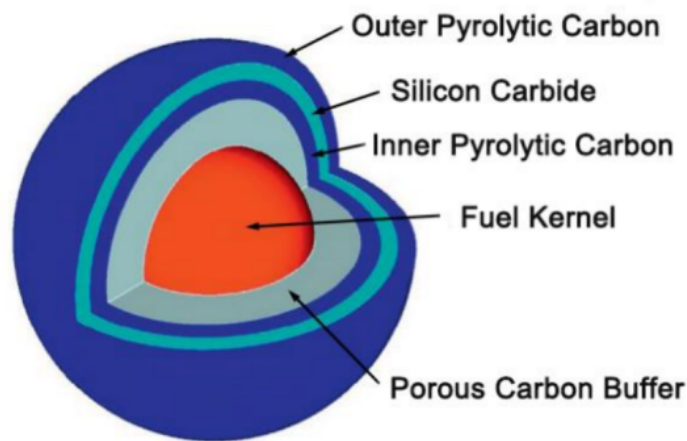


Figure 1. Schematic diagram of the cross-section of a TRISO fuel particle^[7]

The silicon carbide matrix used in composite fuels is liquid-phase sintered cubic silicon carbide, which can be sintered into a highly dense matrix at low temperatures while maintaining a stable cubic silicon carbide phase and good corrosion resistance^[8]. In order to fully densify the silicon carbide matrix, it is necessary to choose metal oxides that produce a liquid phase without reacting with silicon carbide as additives, with aluminum oxide-yttrium oxide composite (Al_2O_3 - Y_2O_3) being the most commonly used^[9]. In recent years, the aluminum oxide-yttrium oxide-calcium oxide composite (Al_2O_3 - Y_2O_3 - CaO) system has been found to further reduce the sintering temperature and obtain a ceramic with cubic phase as the main phase, making it more suitable as a matrix material for ceramic encapsulated fuel. During the composite sintering of TRISO fuel and silicon carbide, the carbon in TRISO reacts with the alumina in the silicon carbide matrix according to **Equation (1)** to form aluminum carbide (Al_4C_3)^[10].



The generated Al_4C_3 reacts with water according to **Equation (2)**, causing volumetric expansion and sample failure^[9].



To address this issue, this study investigated the effect of carbon content in silicon carbide matrix materials on element diffusion. Kim studied the diffusion of sintering aids in grains and interfaces of liquid-phase sintered silicon carbide, but the effect of carbon addition on element diffusion in TRISO coating layers in liquid-phase sintered silicon carbide has not been reported^[11-13]. Therefore, this study prepared silicon carbide-based TRISO composite fuels with different carbon contents by adding varying amounts of carbon and using the liquid-phase

sintering method, and characterized the diffusion of major elements in the TRISO coating layers, providing a theoretical basis for subsequent specific applications in nuclear reactors.

2. Experimental

Beta silicon carbide (β -SiC) (Xi'an Boer, average particle size: 0.5 μm) was used as the starting material, with Al_2O_3 (Shanghai Fenghe, purity $\geq 99.99\%$), Y_2O_3 (Shanghai Diyang Chemical, purity $\geq 99.999\%$), and CaO (Aladdin, purity $\geq 98.0\%$) as sintering aids. The mass ratio of Al_2O_3 , Y_2O_3 , and CaO was 7:2:1, and the total solid content of the additives was 10%. Polyvinyl butyral (PVB) was used as the binder. Raw materials, sintering aids, and binder were combined in a polyurethane ball mill jar, along with different contents of phenolic resin as the carbon source, as shown in **Table 1**. Zirconia milling balls were added with a ball-to-powder ratio of 2:1, and anhydrous ethanol was used as the milling medium. The mixture was ball-milled for 12 h. The mixture was dried and sieved after ball milling. Two disc-shaped green bodies with a diameter of 22 mm and a thickness of 3 mm were prepared by dry pressing. A holed mold was placed on one of the green bodies to allow the TRISO fuel particles to be precisely embedded into the holes of the mold (**Figure 2(a)**). After removing the mold, the other green body was stacked on top of the TRISO-embedded green body, forming a “sandwich” layered structure (**Figure 2(b)**). The layered green bodies were placed in a graphite mold and hot-press sintered in a vacuum furnace at 1,750°C and 40 MPa for 1 h under an argon atmosphere with a heating rate of 10°C/min.

Table 1. Composition of SiC-based TRISO composite fuel (wt.%)

wt.%	Al_2O_3	Y_2O_3	CaO	Phenolic resin	β -SiC
A	7	2	1	—	Bal.
B	7	2	1	1	Bal.
C	7	2	1	2	Bal.
D	7	2	1	4	Bal.
E	7	2	1	8	Bal.

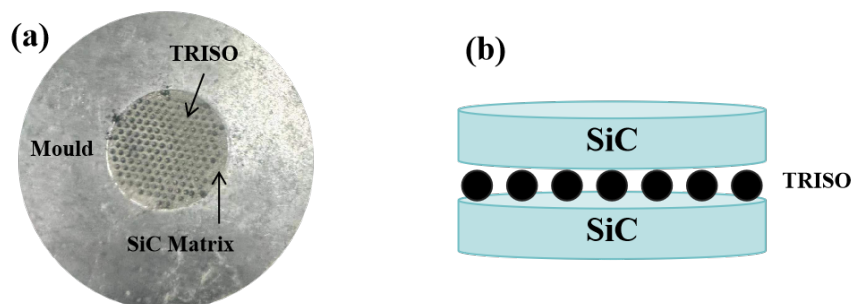


Figure 2. (a) Precise embedding of TRISO particles into SiC green body, (b) Schematic diagram of the SiC-TRISO-SiC “sandwich” structure

3. Results and discussion

3.1. Macrostructure and phase analysis

Figure 3(a) shows a photograph of the polished surface of the SiC-based TRISO composite fuel after sintering. The dashed circles indicate the TRISO fuel particles embedded in the SiC matrix. It can be observed that the TRISO particles are orderly distributed in the SiC matrix. The arrangement of the TRISO particles determines important properties such as the temperature distribution and fission gas release in the fuel element. Therefore,

the ordered arrangement of TRISO particles is expected to improve the safety of advanced reactors. **Figure 3(b)** presents the XRD patterns of the five sintered samples A to E. The main phase in all five samples is 3C-SiC, and the diffraction peaks are sharp and distinct. Although samples B to E were prepared with different contents of phenolic resin as the carbon source, no obvious carbon diffraction peaks were observed, indicating that the added carbon reacted with other elements to form carbides, similar to **Equation (1)**.

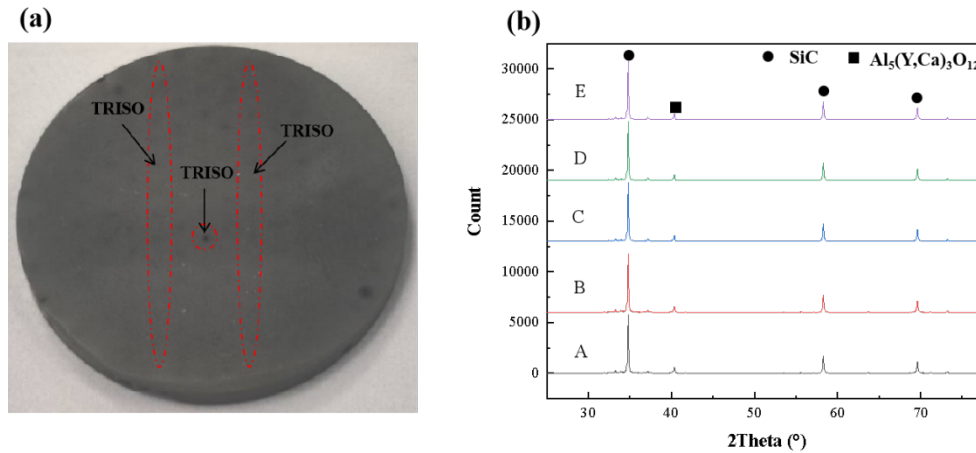


Figure 3. (a) Photograph of the polished surface of SiC-based TRISO composite fuel, (b) XRD patterns of samples A to E

3.2. Microstructure of SiC-based TRISO composite fuel fracture surface

Figure 4 shows the morphology of the fracture surface of SiC-based TRISO composite fuel. It can be observed that the surface of the TRISO particles in sample A, without the addition of phenolic resin, is relatively rough. This indicates that the sintering aids in the SiC matrix reacted with the outermost carbon layer of the TRISO fuel according to **Equation (1)**, forming dense Al_4C_3 with volume expansion, resulting in a loose surface of the TRISO particles^[14]. In sample B, with the addition of 1% phenolic resin, the surface of the TRISO particles is relatively smooth, and no obvious crack propagation is observed in the matrix surrounding the TRISO particles. In samples C to E, with the addition of 2% to 8% phenolic resin, although the surface of the TRISO particles is relatively smooth, obvious cracks are observed in the matrix surrounding the TRISO particles.

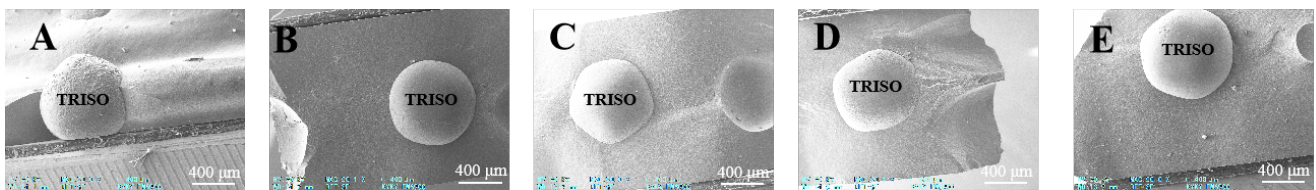


Figure 4. Morphology of the fracture surface of SiC-based TRISO composite fuel

Figure 5 shows the microstructure of the fracture surface of SiC-based TRISO composite fuel. In sample A, without the addition of phenolic resin, the SiC grains are arranged in a layered structure. No clear boundary was observed between the TRISO particles and the SiC matrix. Instead, a dense SiC layer formed at the interface between the two phases, as indicated by the dashed line in sample A. In sample B, with the addition of 1% phenolic resin, a clear boundary is formed between the TRISO particles and the SiC matrix, as indicated by the dashed line. The grain size of the composite fuel matrix with different carbon contents was measured using nano Measurer software. The average grain size of sample A is 1.07 μm . With increasing carbon content, the average grain size decreases. The average grain sizes of samples B, C, D, and E are 0.74 μm , 0.96 μm , 0.85 μm , and 0.94 μm ,

respectively. This is because the liquid-phase sintering of SiC follows a dissolution-precipitation mechanism [15-17]. At high temperatures, the sintering aids transform into a liquid phase, and the carbon readily reacts with the liquid-phase sintering aids to form carbides that dissolve into the matrix. During cooling, the solubility of these carbides decreases, and they easily precipitate as heterogeneous second phases, inhibiting the growth of SiC grains.

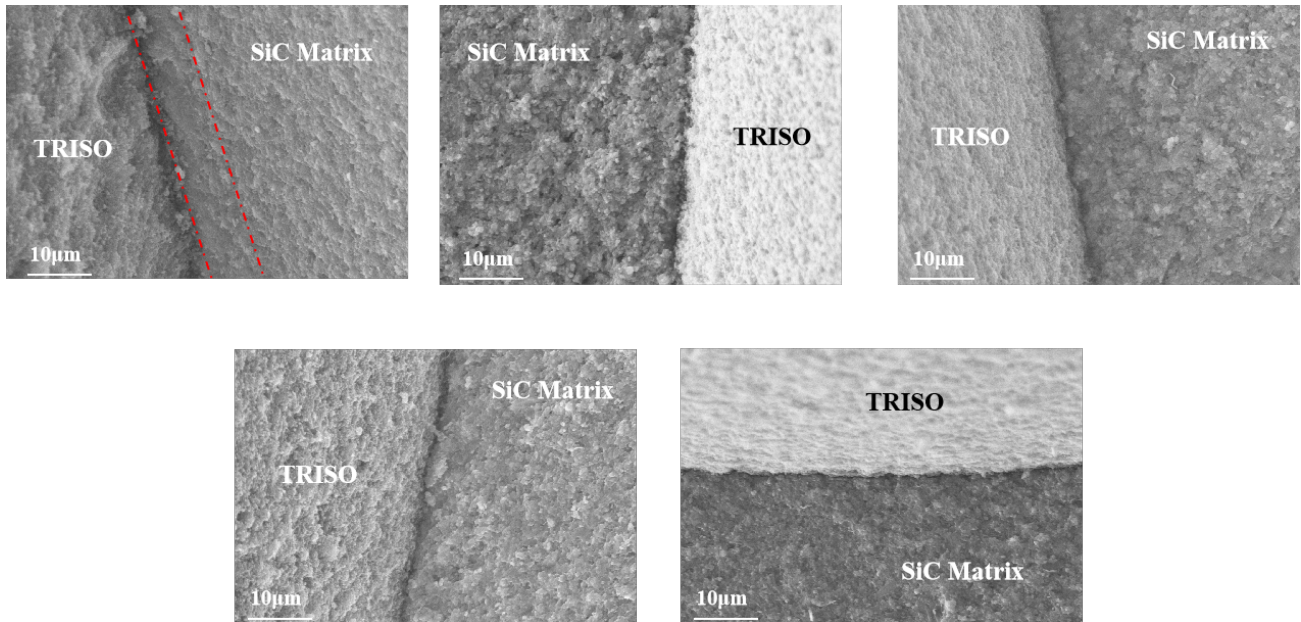


Figure 5. Microstructure of the fracture surface of SiC-based TRISO composite fuel

3.3. Element diffusion at the interface between SiC matrix and TRISO particles

We performed Energy Dispersive X-ray Spectroscopy (EDS) analysis on samples A to E, and the surface scanning distribution maps of the cross-sections are shown in **Figure 6**. It can be observed that in sample A, the Al element is mainly segregated at the grain boundaries and defects of the SiC matrix. When carbon is added to the samples, the Al element is uniformly distributed in the SiC matrix. This is because during hot-pressing sintering, the molten Al_2O_3 reacts with the directly contacted SiC at the interface to form the ionic and brittle phase Al_4C_3 [10]. The formation of this phase reduces the load transfer at the interface, thereby decreasing the mechanical properties of the material. Moreover, the formed Al_4C_3 readily reacts with water according to **Equation (2)**, forming aluminum hydroxide ($\text{Al}(\text{OH})_3$), which deteriorates the corrosion resistance of the material [14]. When a certain amount of carbon is added to the SiC matrix, the carbon diffuses into the molten Al_2O_3 through self-diffusion and is dispersed in the molten sintering aids. The solubility of carbon in the sintering aids is low, and it reacts with the metallic elements in the sintering aids to form carbides. The diffusion rate of carbides in metal oxides is lower than that in SiC. Therefore, the reaction-formed carbides uniformly diffuse into the SiC matrix and form a dense oxide layer during the cooling stage of sintering, increasing the density of the material.

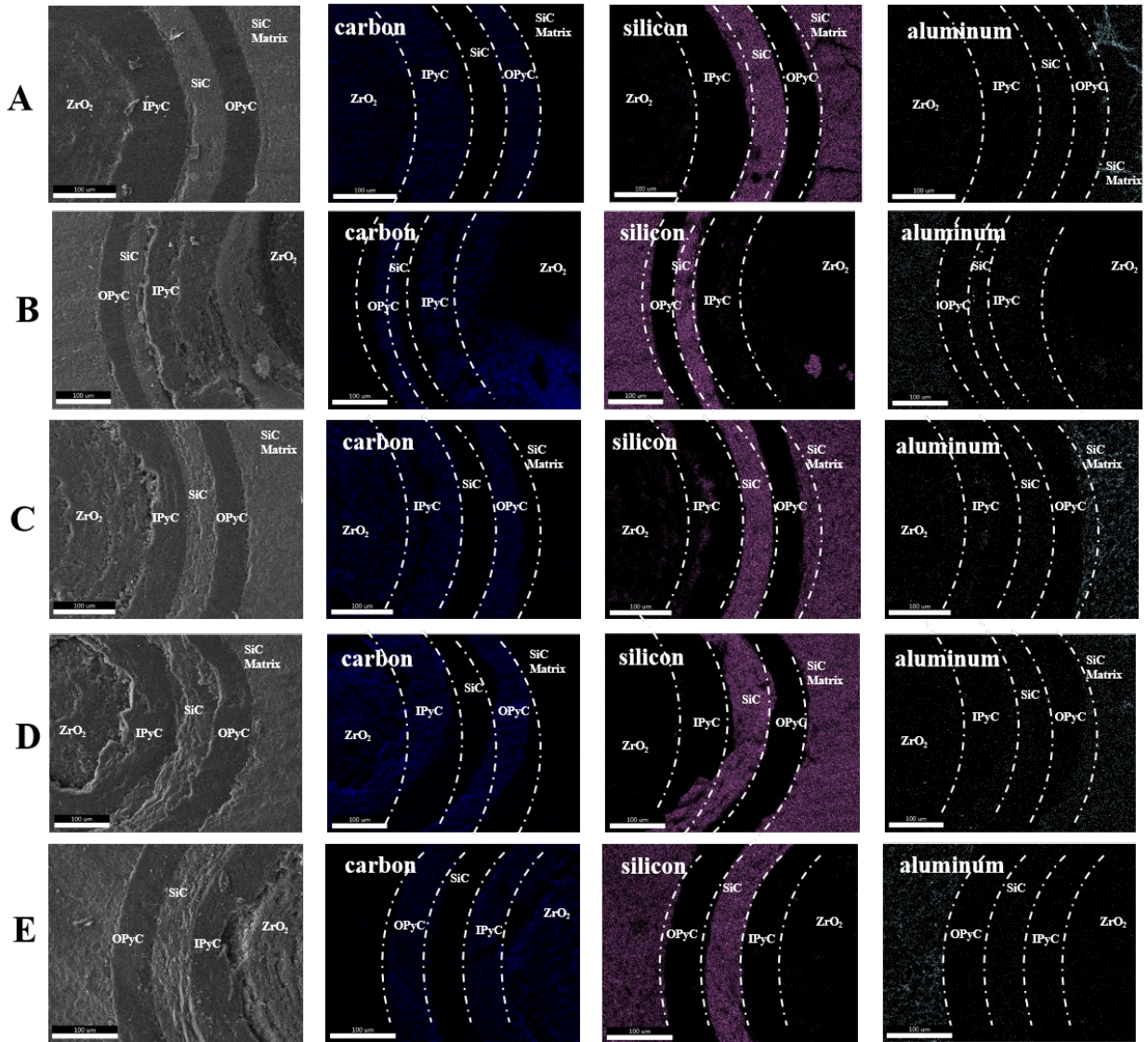


Figure 6. Surface scanning distribution maps of the cross-sections of SiC-based TRISO composite fuel

To further explore the effect of carbon content on the diffusion behavior of elements in the composite fuel, EDS point scanning was used to measure the element content in different coating layers of the TRISO particles, as shown in **Table 2**. It can be observed that with increasing carbon content, the carbon content in the outermost dense pyrolytic carbon layer of the TRISO particles first increases and then decreases, reaching the highest value of 95.56 at.% in sample C with 2% phenolic resin addition. The oxygen content shows a fluctuating trend, with sample B having the lowest oxygen content of 3.82 at.%. The aluminum content first decreases and then increases, with samples B, C, and D having relatively low contents of 0.25 at.%. The silicon content shows a continuous decrease. In the SiC layer of the TRISO particles, with increasing carbon content, the carbon content first increases and then decreases, reaching the highest value of 73.19 at.% in sample B with 1% phenolic resin addition. The oxygen content first decreases and then increases, with sample B having the lowest oxygen content of 3.08 at.%. The aluminum content shows a fluctuating trend, with sample B having the lowest content of 0.55 at.%. The silicon content also shows a fluctuating trend, with sample B having the lowest content of 22.75 at.%. In the innermost dense pyrolytic carbon layer of the TRISO particles, with increasing carbon content, the carbon content shows a fluctuating trend, the oxygen content first decreases and then increases, the aluminum content first

decreases and then increases, with samples B and C having relatively low contents of 0.25 at.%, and the silicon content shows a fluctuating trend, with sample B having a relatively low content of 0.21 at.%.



Table 2. Content of main elements in different coating layers of TRISO particles (at. %)

		A	B	C	D	E
Carbon	OPyC	92.03	92.46	95.56	94.32	94.98
	SiC	44.52	73.19	43.48	50.10	36.27
	IPyC	92.20	94.51	95.05	94.13	93.34
Oxygen	OPyC	6.82	6.87	3.82	5.08	4.31
	SiC	5.96	3.28	3.08	4.13	2.33
	IPyC	6.25	4.92	4.12	5.06	5.68
Aluminum	OPyC	0.30	0.24	0.25	0.25	0.30
	SiC	1.06	0.55	1.23	0.94	1.34
	IPyC	0.35	0.24	0.25	0.29	0.33
Silicon	OPyC	0.63	0.22	0.18	0.18	0.19
	SiC	47.70	22.75	52.44	44.24	59.01
	IPyC	0.79	0.21	0.40	0.38	0.25

Based on the above analysis, it can be concluded that with the addition of a certain amount of carbon to the matrix, the contents of Si, Al, and oxygen (O) in the outermost pyrolytic carbon layer of the TRISO particles decrease to some extent, indicating that the addition of carbon reduces the diffusion rate of elements from the SiC matrix to the coating layers of the TRISO particles and inhibits the reaction between the alloying elements and the dense pyrolytic carbon outer layer of the TRISO particles. This is because in the Al-C-Si ternary system in the matrix, the following **Equation (3)** occurs^[18-20]. During this reaction, two liquid phases are formed: a stable SiC + aluminum silicon carbide (Al₄SiC₄) phase and a metastable Al₄SiC₄ + Al₄C₃ phase. This reaction consumes a large amount of carbon. With the addition of phenolic resin, the Al and Si in the matrix preferentially react with the carbon from the phenolic resin to form the aforementioned metastable liquid phase, rather than preferentially consuming the pyrolytic carbon in the outer coating layer of the TRISO particles. As the reaction proceeds, the metastable Al₄C₃ extends to a larger SiC region. Due to the extremely low solubility of carbon in the molten metal oxides, it precipitates again in a supersaturated state during the cooling stage of sintering. Therefore, the addition of a certain amount of carbon to the SiC matrix promotes the uniform distribution of sintering aids in the matrix, increases the density of the material, and protects the outermost pyrolytic carbon layer of the TRISO particles from damage, thereby enhancing the safety of the nuclear reactor.

4. Conclusion

- (1) SiC-based composite fuel with orderly arranged TRISO particles was successfully fabricated by hot-pressing sintering.
- (2) In the composite fuel samples without the addition of phenolic resin, no clear boundary was observed between the TRISO particles and the SiC matrix. In the composite fuel samples with the addition of

phenolic resin, a distinct boundary formed between the TRISO particles and the SiC matrix. When the phenolic resin content was 1%, no obvious crack propagation was observed in the matrix surrounding the TRISO particles.

- (3) With the addition of phenolic resin to the samples, the carbon from the phenolic resin promotes the uniform distribution of sintering aids in the SiC matrix through self-diffusion. Meanwhile, the carbon from the phenolic resin preferentially reacts with the metallic elements in the sintering aids to form carbides, thereby inhibiting the reaction between the metallic elements and the dense pyrolytic carbon outer layer of the TRISO particles. When the phenolic resin content is 1%, the Al content in the outermost pyrolytic carbon layer of the TRISO particles is minimized, preserving the integrity of the TRISO particles in the composite fuel and enhancing the safety of the nuclear reactor.

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Disclosure statement

The authors declare no conflict of interest.

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