Evaluation of Oxidation Performance of TRISO Fuel Particles for Postulated Air-Ingress Accident of HTGR

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In a high-temperature gas-cooled reactor, the integrity of tristructural-isotropic-(TRISO-) coated fuel particles ensures the safety of the reactor, especially in case of an air-ingress accident. The oxidation of TRISO particles with the outer layers of silicon carbide (SiC) was performed at temperatures of 900°C–1400°C in air environment. Both the microstructure and phase composition of the SiC layers were studied. The results showed that the SiC layers had a good oxidation resistance below 1100°C. However, the amorphous silica on the SiC layers formed at 1200°C and gradually crystallized at 1400°C with the presence of microcracks. The reaction rates of the SiC layers were determined by measuring the silica thickness. It was proposed that the oxidation of the SiC layers followed the linear-parabolic law with the activation energy of 146 ± 5 kJ/mol. The rate-determining step of the oxidation was the diffusion of oxygen in silica.

1. Introduction

The high-temperature gas-cooled reactor (HTGR) is considered as one of the promising reactors in the Generation IV nuclear energy system. The HTGR reference concept is a helium-cooled, graphite-moderated, thermal neutron spectrum reactor with a target coolant outlet temperature of ~900°C. The high outlet temperature offers higher efficiency electricity generation and new opportunities for a broad spectrum of process heat applications, including hydrogen production by thermochemical water splitting or high-temperature electrolysis [1]. The success of HTGR is due to its inherent safety characteristics, which rely closely upon the quality and integrity of the tristructural-isotropic-(TRISO-) coated fuel particles [2].

In the current reference TRISO-coated particle design, the kernel (microsphere) is typically formed from enriched uranium dioxide (UO2) or uranium oxycarbide (UCO) and is surrounded by successive layers of porous pyrocarbon buffer, dense inner pyrolytic carbon (IPyC), silicon carbide (SiC), and dense outer pyrolytic carbon (OPyC). The SiC layer, in particular, provides structural support to accommodate internal gas pressure and serves as the primary barrier to the release of fission products [3]. Therefore, the microstructure and properties of the SiC layer are essential to the safety of the reactors under operation conditions, even during any accidents, in the case of failure of all active cooling systems and complete loss of forced cooling.

Under normal operation conditions, the fuels work in helium loops and withstand a working temperature of ~1000°C in the HTGR. The highest normal operating fuel temperature should not be greater than 1250°C. In previous studies, postulated air-ingress accidents have got a lot of attention to the safety analyses of HTGR. In the case of off-normal transients, air ingress can result from breaches in the reactor system that link the internal and external gaseous atmospheres. The maximum fuel temperature might rise to 1300°C–1400°C. Under normal pressure and
high temperature air environment, the core components, including the fuel elements, would suffer extensive degradation and lead to a significantly enhanced release of fission products [4]. The oxidation of graphite is of primary importance with respect to the structural integrity of the graphite [5]. Much effort has been devoted to the consequences of graphite oxidation. The oxidation performance of matrix graphite under air-ingress accident conditions has not only been simulated under the conservative assumptions but also been studied thermogravimetrically for various oxygen concentrations and with temperatures from 600°C to 1600°C [6–8]. However, the matrix graphite of fuel elements is susceptible to oxidation damage. Once the graphite matrix of the compact or pebble fuel elements has been oxidized away, it may lead to the exposure of TRISO fuel particles and increase the risk of radioactivity release.

The consequences of air-ingress for TRISO fuel particles have not been adequately addressed to date. Despite the rare probability of this accident, the oxidation behavior of the TRISO particle is of great importance for protecting the reactor core and decreasing the risk of radioactivity release in case of air-ingress accidents. As the OPyC layers begin to be oxidized at temperatures higher than 700°C, the exposed SiC layers in TRISO particles would play an important role in governing fuel performance. Therefore, the investigation of the oxidation performance of the SiC layers is imperative in the safety considerations.

The air oxidation of SiC materials (e.g., sintered α-SiC, high-purity β-SiC, and SiC-based composites) has attracted tremendous research interest for decades, due to its wide application in high-temperature components [9–11]. Two forms of SiC oxidation, such as the passive oxidation regime (weight gain) and the active oxidation (weight loss), were reported. SiC forms a silica layer comparable to silicon, and the oxidation of both materials follows a linear-parabolic or parabolic law. However, since the microstructure and properties of the SiC layers in TRISO particles are different from those of the SiC plate despite the same coating procedure, the oxidation mechanisms of the SiC layers are also needed to be clarified [12]. The impact of annealing in air atmosphere on TRISO particles has been investigated with temperatures up to 1600°C [13–15]. The results showed that intense regression of the SiC barrier beneath the rough silica layer occurred at 1600°C, which was affected by the interaction between TRISO particles and the alumina crucible [13]. The mechanisms and kinetics of the oxidation process of the TRISO particles with the outer layers of SiC in air environment under different temperatures still need to be investigated to evaluate the microstructure evolution of the silica layer.

In the present work, the oxidation of TRISO particles with the outer layers of SiC was investigated in air environment at the temperature range of 900°C–1400°C. The composition and microstructure of the SiC layers after oxidation was characterized and analyzed. The oxidation kinetics of the SiC layer were studied, including oxidation rate, activation energy, and the rate-controlling step, which aims to predict the SiC degradation rate in case of an air-ingress accident in operation.

2. Experimental Procedure

2.1. High-Temperature Oxidation. The TRISO particle samples were made by fluidized bed chemical vapor deposition using zirconia particles with a diameter of ~500 μm as simulated kernels. The average thickness of the buffer, IPyC, SiC, and OPyC layers was 200 μm, 40 μm, 24 μm, and 40 μm, respectively. Before the oxidation test, the TRISO particle samples were exposed in air at 800°C for 8 hours to oxidize the OPyC layers and obtain the TRISO particles with the outer layers of SiC, as shown in Figure 1.

High-temperature oxidation behavior for the TRISO particles with the outer layers of SiC was investigated in atmospheric environment at 1 atm pressure under the isothermal conditions. The furnace was horizontally held with an alumina tube and has a 20 cm long hot zone. The TRISO particle samples were placed on the platinum crucible in the alumina reaction tube with both ends open. The samples were heated from room temperature at the programmed heat rate of 5°C/min up to the testing temperatures (900°C–1400°C). After keeping at the testing temperature for the desired time (0–48 h), the samples were cooled to room temperature in furnace naturally. To minimize contamination, the alumina reaction tube was aged in atmospheric environment for 50 h at 1400°C before beginning the experiments. Besides, the effects of interaction between the TRISO particle samples and the platinum crucible were neglected in the present work.

2.2. Characterization. The surface morphology and cross-section microstructure of the SiC layers in TRISO particles was characterized using a scanning electron microscope (SEM) (Inspect F50, FEI, US). The thickness of the silica on the SiC layer after oxidation was measured at approximately twenty points at the cross sections of TRISO particles. The phases of reactive products on the surfaces of TRISO particles were examined by X-ray diffraction (XRD) (Ultima IV, Rigaku, Japan) and by Raman spectroscopy (LabRAM HR Evolution, Horiba, France) with an incident laser beam of 532 nm (Nd: YAG). The XRD samples were made by around a number of 20 particles, which were pasted onto a horizontal glass slide and kept closely packed using the silicone paste that has no XRD spectra. For Raman spectroscopy measurement, the TRISO particle was placed on the sample stage under the Raman microscope objective. And the 50x microscope objective was used to focus the laser and collected the backscattered light.

3. Results and Discussion

3.1. The Microstructure of the SiC Layers. Figure 2 shows the surface morphology of the SiC layers before and after oxidation at different temperatures for 24 h. The as-deposited SiC layer exhibited faceted morphology on the outer surface (Figure 2(a)). No significant variation in the morphology was observed after oxidation below 1100°C (Figure 2(b)). However, the edge of the SiC grains became smooth after oxidation at 1200°C, which indicates the oxidation of SiC
occurred (Figure 2(c)). Because the oxidation temperature was not high enough to cause an obvious change of the surface morphology, just the sharp edge became smooth could be observed. Besides, the thickness of the oxide layer was too thin to cover the faceted morphology of the SiC grains. Thus, there were still some pits that could not be covered by the oxide layer, where the oxidation would occur.

After oxidation at 1300°C, the surface morphology changed from multifaceted to smooth with the formation of a thin oxide layer (Figure 2(d)). The SiC grains were almost covered by the formation of the oxide layer, which could prevent inward diffusion of oxygen and the oxidation of SiC. When the oxidation temperature was further increased to 1400°C, apparent oxidation occurred with the increasing amount of
oxide on the SiC surface (Figure 2(e)). The surface of the oxide scale appeared a combination of elongated and spherical structure, which is the characteristic of the cristobalite formation. As reported, during the crystallization of amorphous silica, the nucleation of silica grains forms an elongated structure and then turns to a spherical structure with the growth of silica grains [16]. That is the reason why the elongated and spherical structure could be observed after high-temperature oxidation of SiC. Meanwhile, microcracks formed in the oxide layer (Figures 2(d) and 2(e)), which could be due to the volume change from the crystallization of amorphous silica and the phase transformation of crystallized silica during the cooling process. The formation of microcracks would reduce the protection of the oxide layer for SiC from oxidation. What is worse, a significant volume change might also loosen the structure of the oxide layer and lead to poor adhesion at the interface of the oxide layer and SiC.

Figure 3 shows the cross-section microstructure of the SiC layers before and after oxidation at the temperatures of 1100°C–1400°C for 24h. There were no significant microstructure differences observed from the cross-section between the as-deposited SiC layer and the SiC layer after oxidation at 1100°C. However, a thin oxide layer on the SiC coating was appeared after oxidation at 1200°C, and the thickness was about 0.41 μm. Due to the roughness of the as-deposited SiC layer, the oxide layer was rather rough. After oxidation at 1300°C, the thickness of the oxide layer increased to ~0.7 μm. Besides, the surface of the oxide layer became more flat, which indicates the oxide had filled in the roughness of the as-deposited SiC layer. When the oxidation temperature was further increased to 1400°C, the thickness of the oxide layer increased significantly to ~1.24 μm. No through-thickness cracks were observed.

3.2. The Phase Composition of the SiC Layers. Figure 4 shows the effects of oxidation temperature on the XRD patterns of TRISO particles after oxidized for 24 h. Three typical phases could be identified in the XRD pattern of the as-deposited sample, namely, ZrO₂, PyC, and SiC. To amplify the small intensity, k’ the results showed that the silica formed was corresponding to the silica phase appeared with weak in-

3.3. The Oxidation Behavior of the SiC Layers. To study the oxidation behavior of the SiC layers in TRISO particles, oxidation tests were further performed at different temperatures for different times. The oxide layer thickness as a function of the oxidation time is shown in Figure 6. When the temperature was below 1000°C, the changes in the surface morphology of the SiC layer were barely noticeable.

It indicates that the SiC had good oxidation resistance at a temperature below 1000°C. Besides, it seems no measurable oxidation occurred at 1100°C within 36 h exposure until the oxidation time was prolonged to 48 h. The dense oxide layer produced on the surface of the SiC layer could prevent the inward diffusion of oxygen. With the increase of oxidation temperature, the diffusion rate of oxygen in the silica increased, so did the oxidation rate. As a result, the thickness of the silica layer increased obviously with the increase of oxidation time at the higher temperature (≥1200°C). As shown in Figure 6, the silica layer thickness was 1.9 μm after exposure at 1400°C for 48 h, which is almost twice that at 1300°C for the same dwelling time.

When SiC material is exposed in air environment under high temperature, a dense silica layer would be formed on the SiC surface. The inward diffusion of oxygen through the oxide layer is impeded, which inhibits further oxidation of the underlying SiC. As a result, the oxidation of SiC would be slow, which leads to the regression of SiC within the passive oxidation regime. In air environment at high temperature, the passive oxidation between SiC and oxygen is expressed by the following equation [9, 19]:

\[
\text{SiC}(s) + \frac{3}{2}\text{O}_2(g) = \text{SiO}_2(s) + \text{CO}(g)
\] (1)

Figure 7 shows the oxidation kinetics of SiC in air environment using a dual logarithm coordinate. In the dual logarithm coordinate, a linear oxidation law presents a linear with a slope of 1, while a parabolic oxidation law presents a linear with a slope of 0.5 [20]. However, the slopes derived from Figure 7 were in a range of 0.75 to 0.67, which decreased with the increase of oxidation temperature. It indicates that the oxidation kinetics at the temperature range of 1200°C–1400°C could not be expressed using a simple linear or parabolic law. That is, the oxidation evolves both linear and parabolic, which is reported as
the linear-parabolic law. For the linear-parabolic law, the Deal–Grove model is often used to describe the relationship between the thickness of silica and the oxidation time, as follows [20]:

\[ x^2 + Ax = Bt, \]  

where \( x \) is the silica thickness (μm), \( t \) is the oxidation time (h), \( B/A \) is the linear oxidation rate (μm/h), and \( B \) is the parabolic rate constant. The parabolic oxidation rate \( B \) is related to the linear oxidation rate \( B/A \) and the parabolic oxidation rate constant \( C \) by the relation:

\[ B = \frac{B/A^2}{C}. \]
oxidation rate ($\mu m^2/h$). It is noted that $B/A$ and $B$ are the rate coefficients for the interfacial reaction and the diffusion of oxidants, respectively. By fitting the relationship between the silica thickness and the oxidation time using equation (2), both the linear and parabolic rates were obtained and are summarized in Table 1. The linear and parabolic oxidation rates of SiC significantly increased with the increase of temperature. The growth rates of the silica oxidized at 1400°C are a little lower than the reported values (Table 1) [14]. According to the oxidation kinetics of the SiC layers, the microstructure evolution of the silica under different temperatures in air environment could be evaluated.

Meanwhile, the temperature dependence of the oxidation rate can be described using the Arrhenius equation:

$$k = K_0 \cdot \exp\left(\frac{-E_a}{RT}\right),$$  

where $k$ is the oxidation rate ($\mu m^2/h$), which is corresponding to the parabolic oxidation rate in this study, $K_0$ is the frequency factor ($\mu m^2/h$), $E_a$ is the activation energy (kJ/mol), $R$ is the ideal gas constant ($R = 8.314 \times 10^{-3} \text{kJ/(mol·K)}$), and $T$ is the temperature (K). Using equation (3) to fit the experimental data, the activation energy ($E_a$) can be estimated. Figure 8 shows the Arrhenius plot of the obtained parabolic rate constant versus temperature. The activation energy of the parabolic rates was yielded to be $146 \pm 5 \text{kJ/mol}$ at the temperature range of 1200°C–1400°C. As reported in the previous literature, the activation energy values have ranged from 120 kJ/mol to 400 kJ/mol [14, 21, 22]. There is a general trend that the higher the temperature, the greater the activation energy. It is commonly accepted that the relatively low activation energy of 80 kJ/mol–120 kJ/mol may correspond to the permeation of oxygen molecule in amorphous silica and the high activation energy of 230 kJ/mol–400 kJ/mol may suggest the diffusion of oxide ion in amorphous silica or cristobalite [22]. The activation energy value obtained in the present work ($146 \pm 5 \text{kJ/mol}$) is close to value for the diffusion of the oxygen molecules in amorphous silica. Therefore, the rate-controlling step was likely the diffusion of the oxygen molecules in the silica [23].

The continuing oxidation of SiC relies on the diffusion of oxygen through the covering silica layer, and thus, the diffusion kinetics control the oxidation rate of SiC. Initially, the formed layer was amorphous, but at temperatures above
1400°C, devitrification of silica occurred, leading to the formation of \( \alpha \)-cristobalite. Originally, it was considered that oxygen permeability in amorphous silica is high; however, some studies suggest that it might be similar for \( \alpha \)-cristobalite. At higher temperatures, the viscous nature of silica may promote diffusion of oxygen. Some critical issues might arise, cristobalite undergoes a phase transformation associated with volume change during the cooling process that can lead to fracture and spallation. The formation of microcracks would provide the diffusion paths for oxygen and thus accelerated SiC oxidation significantly. Both the linear and parabolic oxidation rates of the SiC layers at 1400°C were almost triple those at 1300°C.

### 4. Conclusions

The oxidation of TRISO particles with the outer layers of SiC in air environment was investigated at the temperature range of 900°C–1400°C. The SiC layer had a good oxidation resistance at a temperature below 1100°C. The silica formed was amorphous at 1200°C–1300°C and gradually crystallized at 1400°C with the major phase of \( \alpha \)-cristobalite. The presence of carbon was detected after oxidation above 1200°C. Besides, the crystallization and phase transformation of silica resulted in the formation of cracks in the silica layer due to the volume change.

The thickness of the silica layer increased obviously with the increase of temperature. The oxidation kinetics of SiC followed the linear-parabolic law. Both the linear and parabolic oxidation rates were calculated according to the relationship between the thickness of the silica layer and the oxidation time. The calculated activation energy was 146 ± 5 kJ/mol, suggesting that the rate-controlling step of the oxidation was the diffusion of the oxygen molecule in silica.

### Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

### Conflicts of Interest

The authors declare that they have no conflicts of interest.

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