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Effects of water vapor on the oxidation and the fracture strength of SiC layer in TRISO fuel particles

Fangcheng Cao ¹, Wei Hao ¹, Xin Wang ², Fangwei Guo ^{1,*}, Xiaofeng Zhao ^{1,*}, Nadia Rohbeck ³
and Ping Xiao ³

¹Shanghai Key Laboratory of Advanced High-temperature Materials and Precision Forming,
Shanghai Jiao Tong University, Shanghai 200240, China

² Konca Solar Cells Co., Ltd, Jiangsu 214174, China

³ School of Materials, University of Manchester, Manchester M13 9PL, United Kingdom

* Author to whom correspondence should be addressed.

E-mail: fwguo1984@163.com and xiaofengzhao@sjtu.edu.cn.

Abstract

Steam oxidation of silicon carbide (SiC) layer in nuclear fuel particles were performed in flowing argon–water vapor mixture with a total pressure of 1 bar at 1173–1673 K. Both the phase composition and the microstructure of the oxide scale on the SiC layer varied with the oxidation temperature. Reaction rates of water vapor with the SiC layer were determined by measuring the oxide scale thickness. It was found that the oxidation of SiC layer follows the parabolic law. The activation energy was calculated to be 103 ± 11 kJ/mol. It is proposed that the rate determine step of the oxidation is the diffusion of water vapor molecules in the oxide scale. The fracture strength of SiC shell after steam oxidation was evaluated using a crush test. The fracture strength decreased with the increase of the oxidation temperature due to the thinning of the SiC layer.

Keywords: Fuel particle; Silicon carbide; Steam oxidation; Fracture strength

1. Introduction

High-temperature gas-cooled reactor (HTGR) is one of the most promising candidates for the future generation-IV nuclear system due to its inherently safe design ^[1]. The primary safety assurance comes from the HTGR nuclear fuel element that is based on the tristructural-isotropic (TRISO) type fuel particle. Generally, the spherical fuel kernel in a TRISO particle is coated with four successive layers, namely a porous carbon buffer layer, an inner dense PyC (IPyC) layer, a SiC layer and an outer dense PyC (OPyC) layer ^[2]. The TRISO system is designed not only to retain all fission products during neutron irradiation but also to withstand the thermo-mechanical stresses experienced during service. The SiC layer is a key component for the integrity of TRISO particles and acts as a pressure vessel to accommodate gaseous fission releases.

During operation, the concentration of contaminants in the coolant-helium is maintained at a low level by cycling a certain fraction of the coolant through a purification system. However, the fuel elements may be oxidized by low concentration oxidants (e.g., H₂O, CO₂, O₂) presented in the helium ^[3]. The ingress of steam into the coolant from a damaged heat exchanger is probably the most likely accident which would destroy the integrity of the layers of TRISO particles ^[4]. Once the graphite matrix of the compacts or pebbles has been oxidized away and the SiC shell of the TRISO is exposed, the steam oxidation would cause degradation of the mechanical and thermal properties of the outer layers and increase the failure probability, and in the worst case results in a rapid release of volatile fission products (e.g., Xenon and Krypton) ^[5, 6]. Much more than a cost issue, it can cause disastrous safety problems. On the other hand, the potential application of TRISO particles in other reactors (e.g., light water reactor) has attracted considerable interest ^[7]. Therefore, an investigation of the high temperature steam oxidation of SiC layers in TRISO particles is important for assessing the safety of the reactor.

The steam oxidation of SiC (e.g., sintered α -SiC, high purity β -SiC and SiC-based composites) has attracted tremendous research interest for decades ^[8, 9, 10], since SiC component has been developed for the hot sections in gas turbines, e.g., turbine blades. The water vapor is a major cause for the failure of SiC-based ceramics in combustion environments. Furthermore, the SiC layers on spherical substrates exhibited different microstructure from that of the bulk SiC ^[11]. Some researchers have reported high temperature oxidation behavior of TRISO particles in air or oxygen ^[12]. Recently, the oxidation of the SiC layer in TRISO particles in flowing steam environments at 1737–1973 K was also studied ^[13]. But the effects of oxidation on the mechanical strength of SiC layers in TRISO particles still need to be further clarified.

In the present work, the oxidation of the SiC layers in TRISO particles was investigated in steam at a temperature range of 1173–1673 K. The composition and microstructure of the SiC layers after steam oxidation were characterized and analyzed. The oxidation kinetics of the SiC layer was studied with the aim of predicting the SiC degradation rate in case of a steam ingress accident in operation. The fracture strength of the SiC layer after steam oxidation was further investigated, which is essential for the design and performance analysis of TRISO particles.

2. Experimental procedure

The TRISO particles were provided by the University of Manchester made by fluidised bed chemical vapor deposition using zirconia particles with a diameter about 500 μm as simulated kernels ^[14]. To study the oxidation behavior of SiC layer, the TRISO particles were originally produced without the OPyC layer. The average thickness of the buffer, IPyC and SiC layers were 200 μm , 40 μm and 24 μm , respectively.

2.1 Steam oxidation

Steam oxidation treatments were performed at a temperature range of 1173–1673 K using argon–water vapor mixtures with a total pressure of 1 bar. The oxidation time varied from 4 h to 48 h. The furnace was horizontally held with an alumina tube and has a 20 mm long hot zone. The alumina tube has an inner cross sectional area of $3.8 \times 10^{-3} \text{ m}^2$, a wall thickness of 5 mm and a length of 1 m. The flow rate of the high-purity argon stream was kept at a constant value, which was calculated to be $8.7 \times 10^{-4} \text{ m/s}$. The import of water vapor was accomplished by bubbling the argon through a bottle of deionized water that was heated in the oil bath thermostat at 363 K. The water content in the mixed gas was controlled by the argon flow rate as well as the water temperature ^[15]. The water content in the gas mixture was measured by flowing the moisturized argon at a rate of $8.7 \times 10^{-4} \text{ m/s}$ through a bottle of concentrated sulfuric acid desiccant for a given time. The weight gain of the desiccant due to the absorption of water could then be converted to the water concentration of the gas mixture. The flow rate of the gas mixture through the alumina tube at room temperature was calculated to be $1.4 \times 10^{-3} \text{ m/s}$. Table 1 summarizes the basic parameters for the steam oxidation setup. During the oxidation experiments, the pipes flowed by saturated gas mixture were kept warmer than the dew point of the water saturated argon ($\sim 325 \text{ K}$) ^[16] to prevent the condensation of water vapor. The alumina tube was purged under steam atmosphere at 1473 K for 48 h before the steam oxidation tests to minimize the effects of impurities. The TRISO particles were placed on the platinum crucible in the middle of the hot zone. The TRISO particle samples which adhered on the platinum crucible especially at high temperature were excluded in the performance characterization in order to avoid any effects of interaction between the platinum and SiC. ^[17, 18] To check if any SiO₂ volatilization occurred during the high temperature steam oxidation, tests were carried out to measure the weight change of the SiO₂ bulk sample (α -cristobalite, 20 mm $\times$ 10 mm $\times$ 5 mm) after steam oxidation using a balance with an accuracy of 0.01 mg. For comparison, parallel experiments were conducted in dry air at 1473 K.

2.2 Characterization

After oxidation, the TRISO particles were embedded in epoxy and ground using the conventional metallographic approach to their middle plane to form a half sphere. Hemispherical samples were retrieved from the epoxy by using acetone to dissolve the epoxy and then heated in air at 1073 K for 8 h to burn off the PyC layers to obtain free-standing hemispherical SiC shells.

The microstructure of the SiC layers in TRISO particles was characterized using a scanning electron microscope (SEM) (Inspect F50, FEI, US), which was equipped with an energy dispersive spectroscopy (EDS). Both the thickness of SiC and oxide scale on the SiC layer after oxidation was measured at approximately twenty points at cross sections of TRISO particles. The phase of reactive products on the surfaces of the TRISO particle were examined by X-ray diffraction (XRD) (Ultima IV, Rigaku, Japan) and by Raman spectroscopy (LabRAM HR Evolution, Horiba, France) with incident laser beam of 532 nm (Nd:YAG).

The fracture load measurements of SiC shells were performed using the modified crush test and the detailed process can be found in the previous study^[19]. The crush test was carried out in a universal material testing machine (Z020, Zwick/Roell, Germany). For each oxidation condition, at least 30 specimens were tested at room temperature with a crosshead speed of 5×10^{-3} m/s. A schematic testing illustration is shown in Fig. 1. The outer radius (r) and thickness (δ) of the SiC shell were measured before testing. The specimen was diametrically loaded between a plunger and a steel base with an annealed brass foil (5 mm $\times$ 5 mm $\times$ 0.5 mm, 68 HV_{0.05}). The brass insert was used to produce a uniform stress distribution under the load contact area. The maximum load before crushing was regarded as the fracture load (F). The radius (r_0) of the load contact area was measured from the impression formed on the brass foil.

3. Results

3.1 The microstructure of the SiC layers

Figure 2 shows the microstructure of the SiC layer before and after the steam oxidation at different temperature for 24 h. The as-deposited SiC layer exhibits faceted morphology on the outer surface and columnar grains on the cross section (Fig. 2a). No significant variation in the morphology was observed after steam oxidation at 1173 K, while a mosaic oxide layer appeared at 1273 K (Fig. 2b). This means that for an oxidation time of 24 h, the SiC layer has a good steam oxidation resistance below 1173 K and apparent oxidation occurs at 1273 K. After steam oxidation at 1373 K, the surface morphology changed from multifaceted to smooth with the formation of a thin oxide layer. When the oxidation temperature was further increased to 1473 K, the surface of the oxide scale appeared a spherulitic structure (Fig. 2c), which is characteristic for the cristobalite formation ^[9]. The elements C, O and Si were detected by the EDS (inset of Fig. 2c). The samples steam oxidized at 1673 K showed that the SiO₂ grains grew from elongated grains to uniformly spherical grains (Fig. 2d). The spallation of the SiO₂ scale was also observed (inset of Fig. 2d). It was found that most of the pores exhibited an elliptical shape, which tended to line up parallel to the surface of the SiC layer. As comparison, only a thin SiO₂ film was formed on the surface of SiC layer for samples oxidized in dry air at 1473 K (Fig. 2e). Impurities in the SiO₂ scale of all the samples were not detectable by EDS. Therefore, it can be inferred that the presence of water vapor promoted the crystallization of the amorphous SiO₂ and the oxidation rate of SiC layer.

3.2 Phase composition of SiC layers

Figure 3 shows the effect of oxidation temperature on the XRD patterns of TRISO particles after oxidized for 24 h under different conditions. Three typical phases could be identified in the XRD

pattern of the as-deposited sample, namely the ZrO_2 kernel, the PyC layer and SiC layer. At temperatures below 1373 K, no oxide phase was observed. After oxidation at 1473 K, diffraction peaks corresponding to the SiO_2 phase could be detected with weak intensity. To amplify the small peaks, the Y axis was plotted to the $\sqrt{\text{Intensity}}$ (Fig. 3b). The relative intensity of the diffraction peaks of the SiO_2 phase tended to increase with the increase of the oxidation temperature. Combined with Fig. 2, the results showed that the SiO_2 scale formed was amorphous at 1273–1373 K and gradually crystalized at temperatures above 1473 K. The major crystalline SiO_2 phase was detected to be α -cristobalite, which then partially transformed to tridymite after oxidation at 1673 K. The literature report that impurities could promote the transformation of cristobalite to tridymite at 1473 K in steam oxidation ^[19]. However, this effect was not observed in this study. In contrast, no SiO_2 phase was detected in the samples oxidized in dry air at 1473 K. It indicates that the crystallization of amorphous SiO_2 is accelerated by the presence of water vapor ^[20], which might further account for the accelerated oxidation rate.

Raman spectra were also used to characterize the phase composition of TRISO particles after steam oxidation. Significant differences in the Raman spectra at ranges of 100–550 cm^{-1} and 1200–1850 cm^{-1} were observed, as shown in Fig. 4. The peaks at 110 cm^{-1} , 230 cm^{-1} and 417 cm^{-1} correspond to the existence of SiO_2 . The SiO_2 peaks varied from broad peaks to sharp peaks as the oxidation temperature increased above 1373 K. The intensities of the oxide peaks increased consistently with the increase of the oxide layer thickness ^[21]. The bands of SiC (796 and 972 cm^{-1}) were visible (Fig. 4a), so the laser should have penetrated the full thickness of the oxide scale (>5 μm at 1673 K) after oxidation. No obvious SiO_2 phase was detected in the samples oxidized in dry air at 1473 K by Raman spectroscopy. These results are consistent with the XRD analyses. In addition, the D (1350 cm^{-1}) and G band (1600 cm^{-1}) which are the first order peaks of carbon also

appeared with the increase of oxidation temperature above 1473 K. Though the G band is somewhat overlapping with the second order band of SiC that is between 1400 cm^{-1} and 1800 cm^{-1} , the obvious D band confirms the presence of amorphous carbon ^[22]. The low intensity of the D and G band indicates a small proportion of carbon at the interface of the SiC/SiO₂ after high temperature oxidation of SiC, which was identified in previous research by other methods (e.g., Auger electron spectroscopy) ^[23, 24, 25]. However, no more carbon band was observed in the samples after oxidation at 1673 K, at which temperature any carbon formed at the interface of SiC/SiO₂ was likely oxidized after the spallation of the external oxide layer.

3.3 Steam oxidation of SiC layers

To study the oxidation behavior of the SiC layers in TRISO particles, oxidation tests were further performed at different temperatures with different time. The oxide layer thickness as a function of the oxidation time is shown in Fig. 5. When the temperature was below 1173 K, the changes of the surface morphology of the SiC layer were barely noticeable. It appears no measurable oxidation occurred at 1273 K and 24 h exposure, due to slow kinetics. At 1373 K, the SiO₂ layer was thin and the thickness increased slowly. But the thickness of the oxide layer increased significantly with the increase of oxidation time at temperatures above 1473 K. It was found that the oxidation exhibited significant difference in terms of the morphology and the crystalline phase of the oxide scale between in dry air and in steam at the same temperature (e.g., 1473 K). This observation further supported the hypothesis that water vapor can effectively accelerate the oxidation of SiC layer.

3.4 Fracture strength of SiC shells

Figure 6 shows the measured fracture load in the form of Weibull plots. It can be found that there was significant variation in the fracture load for individual particle for the same batch of samples.

The mean fracture loads were in the range of 3.7–4.9 N and slightly decreased with the increase of the oxidation temperature, which could be attributed to the thinning of SiC shells. The Weibull modulus determined from the fracture load plots were in the range of 2.3–2.6, which also decreased with the increase of the oxidation temperature. The relation of the SiC layer thickness to the fracture load of TRISO particles is shown in Fig. 7 in comparison with the previous study using annealed aluminium as inset metal ^[26]. In contrast, crush test using brass in this study resulted in a significantly lower fracture load than that using aluminium (20 HV) ^[26], which could be attributed to the hardness of the insert metal. Finite element analysis has predicted that a small conical volume of highly stressed zone at the inner surface of SiC would be produced with a hard insert metal ^[27].

Furthermore, it is also important to calculate the fracture strength of SiC layer, since it is an important parameter used in the modelling of the failure of TRISO particles. The detailed calculation procedures of the fracture strength were reported in previous study ^[28]. Due to the complexity of the solutions, it was traditionally expressed by using following equations ^[19]. A brief summary is shown in Eq. (1)–(10) ^[18, 28]:

$$C_1 = 0.2205 - 0.04\mu - 0.0115\mu^2 \quad (1)$$

$$C_2 = 1.2044e^{(-1.2703\mu)} \quad (2)$$

$$\mu = r_0 \left[\frac{12(1 - \nu^2)}{r^2 \delta^2} \right]^{\frac{1}{4}} \quad (3)$$

$$\sigma_{membrane} = -C_1 \frac{F\sqrt{1 - \nu^2}}{\delta^2} \quad (4)$$

$$\sigma_{bending} = -C_2 \frac{F\sqrt{1 + \nu}}{\delta^2} \quad (5)$$

$$\sigma_f^L = \sigma_{membrane} - \sigma_{bending} \quad (6)$$

where C_1 and C_2 are the intermediate coefficients, μ is the intermediate variable, ν is the Poisson ratio, r is the outer diameter of shell, δ is the thickness of shell, F is the applied load, r_0 is the radius of the circular contact area, $\sigma_{membrane}$ is the maximum membrane stress, $\sigma_{bending}$ is the maximum bending stress and σ_f^L is the local fracture strength of the specimen, which presents the maximum tensile stress at the inner surface of the shell.

For brittle materials, the fracture strength is best considered as a probability distribution value rather than a fixed value. The distribution of local fracture strength is generally analyzed by the Weibull distribution function. Using Weibull's two-parameter distribution, the cumulative probability of failure (P) is presented by^[19, 28]:

$$P = 1 - \exp \left[-S_E \left(\frac{\sigma_f}{\sigma_0} \right)^m \right] \quad (7)$$

where σ_f is the fracture strength; m is the Weibull modulus; σ_0 is the characteristic strength and S_E is the size effect factor, respectively. The size effect factor is presented as: $S_E = \pi r_0^2$ ^[19, 28]. By taking the logarithm twice, Eq. (7) can be rewritten in a linear form^[19, 28]:

$$\ln(\ln(\frac{1}{1-P})) = m \cdot \ln \sigma_f + \ln(\frac{S_E}{\sigma_0^m}) \quad (8)$$

The Weibull modulus and scale parameter can be obtained from the slope and intercept parameters in Eq. (8). And a conservative probability estimator of the following equation was selected^[19, 28]:

$$P_i = \frac{i}{N + 1} \quad (9)$$

where P_i is the probability of failure for the i th-ranked strength, and N is the sample size. The calculation of the fracture strength for the full spherical shell (σ_f^F) is based on the mean cross-sectional divot area and the mean total inner surface area, which is given as ^[19, 28]:

$$\sigma_f^F = \left[\frac{\pi r_0^2}{4\pi(r - \delta)^2} \right]^{\frac{1}{m}} \sigma_f^L \quad (10)$$

Therefore, the local fracture stress is converted to the value for a full-size spherical shell, which is regarded as the fracture stress representing the whole shell under uniform internal pressurization. Also, the coefficient $\pi r_0^2 / 4\pi(r - \delta)^2$ can be called the scaling factor for size effect between the localized loading and the uniform internal pressurization ^[19, 28].

Figures 8 and 9 present the calculation results for the local fracture stress (σ_f^L) and the fracture stress for full spherical shells (σ_f^F). The Weibull modulus was obtained by linearly fitting the spots, which shows the width and magnitude of the strength distribution. Table 2 summarizes all the relevant results of the crush tests. The local fracture stress data (Fig. 8) were converted to the fracture stresses for full spherical shells (Fig. 9) using the size effect Eq. (10). The mean values of the local fracture stress were in the range 1501–1638 MPa, while those for the full-size shells under internal pressurization were in the range 553–729 MPa. As listed in Table 2, the scaling factors for size effect between the locally loaded area and the whole inner surface area of the full spherical shell were in range of 2.3–2.7. Both the fracture strength and Weibull modulus tended to decrease with the increase of the oxidation temperature.

4. Discussion

4.1 Oxidation kinetics of SiC layers

Thermodynamic calculations show that the oxidation of SiC in water vapor occurs primarily via the reactions ^[29, 30]:

The SiO₂ scale formed on the surface of SiC may simultaneously volatilize with the presence of water vapor under certain conditions particularly with a high gas flow rate (e.g., 15-30 m/s ^[31]) by forming silicon hydroxide or silicon oxyhydroxide species ^[31, 32]. In this study, the possibility of SiO₂ scale volatility in water vapor can be assumed to be negligible, which is mainly based on the following three observations.

First, the weight loss rate of the SiO₂ bulk sample after steam oxidation exposure were 5.8×10^{-8} g/(m²·s) for 144 h at 1473 K. It was neglected as being roughly two orders of magnitude smaller than the values reported previously ^[17, 31, 32]. Second, the oxide thickness as a function of oxidation time fits well with the parabolic kinetics equation (Fig. 5), which indicates that volatilization of the SiO₂ scale was negligible. And third, the volatilization of the SiO₂ scale would result in the parabolic kinetics, showing a stabilized thickness of the oxide layer (e.g., 30–50 h in 50 vol% H₂O/O₂ mixtures with a rate of 4.4×10^{-2} m/s at 1473–1673 K) ^[32], which is not the case in the present study, as shown in Fig. 5. In addition, the parabolic kinetics predicts that the linear volatilization rate of SiO₂ (k_l) has the following parameter dependence ^[32, 33]:

$$k_l \propto p_{H_2O}^2 \frac{v^{1/2}}{P_{total}^{1/2}} \quad (13)$$

where p_{H_2O} is the partial pressure of water vapor; the p_{total} is the total pressure of gas mixture and v is the gas flow rate. A previous study had reported that the volatility effect of SiO_2 was barely discernible for a gas flow rate of 4×10^{-2} m/s (50 % water vapor/1 bar total pressure/1473–1673 K)^[33]. In this study, the total pressure of gas mixture was 1 bar with 38 vol% water vapor at a low gas flow rate of 1.4×10^{-3} m/s. Therefore, the volatilization of SiO_2 in this study can be neglected.

Ignoring early stages that could be chemical reaction rate-controlling for a very short period (<1 h^[8, 34] ^[35], the SiC oxidation is reported to be determined by two mechanisms: parabolic oxidation and linear SiO_2 volatilization, respectively^[17, 30]. In this study, the SiO_2 volatilization can be negligible. Then the oxidation of SiC was expected to follow the parabolic law, which is expressed as^[16, 18]:

$$x^2 = k_p t \quad (14)$$

where x is the oxide thickness; t is the oxidation time; k_p is the parabolic rate. By fitting the SiO_2 thickness with the oxidation time using Eq. (14), the parabolic rates were obtained and summarized in Table 3. The oxidation parabolic rate of SiC significantly increased with the increase of temperature. And the oxidization rate was about four times of that obtained in dry air at 1473 K (Table 3). Previous investigations had proposed that water vapor can destroy the SiO_2 network by replacing the strong [Si–O–Si] bond with a weaker [Si–OH OH–Si] bond, resulting in a decrease in the viscosity and density of the SiO_2 scale^[18, 32]. Thereby, the process can accelerate the permeation and diffusion of the water vapor in SiO_2 scale as well as accelerate the crystallization of the

amorphous SiO₂ and consequently promote the SiC oxidation. Table 3 compares the parabolic oxidation rates in this study with those in the previous study which also neglected the volatilization and followed the parabolic law ^[16]. The parabolic oxidation rate at 1473 K in the study is close to that in the previous study and then become much smaller than that in the previous study at above 1573 K ^[16]. The difference can be explained by that in the previous study there were contamination effects of sodium and aluminum as detected by EDS, which would highly accelerate the crystallization of the oxide scale and increase the oxidation rate ^[16, 36]. And the effects of impurities become more significant at higher temperature, as the parabolic oxidation rate in this study was less than half of that in the previous study at 1673 K.

The temperature dependence of the rate constants can be described using the Arrhenius law ^[37]:

$$k = K_0 \cdot \exp\left(\frac{-E_a}{RT}\right) \quad (15)$$

where k is the rate constant, which is corresponding to the parabolic oxidation rate in this study, K_0 is the frequency factor, E_a is the activation energy, R is the ideal gas constant ($R=8.314 \times 10^{-3}$ kJ/(mol·K)), and T is temperature. Using Eq. (15) to fit the experimental data, the activation energy (E_a) can be estimated. Figure 10 shows the Arrhenius plot of the obtained parabolic rate constant (k_p) versus temperature. The activation energy of the parabolic rate constants above 1373 K was calculated to be 103 ± 11 kJ/mol. This value is much smaller than the value of 428 kJ/mol reported in the previous study, which value was suggested to correspond to the chemical reaction at the SiC surface ^[9]. The oxidation mechanism of the rate-controlling diffusion of SiO or CO molecules was also excluded, which was previously reported for higher activation energies at higher temperatures ^[34]. In this study, a smaller activation energy (103 ± 11 kJ/mol) was derived, which is close to the activation energy for the diffusion of water vapor in amorphous SiO₂ (75 kJ/mol) ^[9]. Therefore, it is

likely that the rate-controlling step is the diffusion of water vapor in SiO₂ scale. The activation energy obtained in this study also falls into the range of the activation energies of 28–156 kJ/mol reported for SiC at up to 1473 K for wet oxygen oxidation, which was controlled by the diffusion of oxidant ^[30]. Nevertheless, the less temperature dependence of SiC oxidation in water vapor indicates that the molecular permeation mechanism is more predominant than a diffusion mechanism that involves charged species ^[30]. The calculated activation energy in this work is smaller than that of the oxidation of SiC at 1473–1673 K in air (about 145 kJ/mol) ^[12], in which the rate-controlling step is the diffusion of oxygen in SiO₂. The difference in the activation energy may be due to a higher diffusion rate and solubility for water than for oxygen in the SiO₂ scale ^[9, 30].

4.2 Effect of steam oxidation on the microstructure of SiC layers

Under oxidative condition, the integrity of the SiO₂ layer is an important factor for the oxidation resistance of the SiC layer. However, above 1473 K, cracks in the oxide layer and even spallation of the oxide layer were observed, which were probably caused by the following reasons: First, the linear thermal expansion coefficient of the cristobalite ($21 \times 10^{-6}/\text{K}$) is higher than that of the SiC ($4.7 \times 10^{-6}/\text{K}$) ^[38], thus the cristobalite SiO₂ scale is in under tensile stress during the cooling procedure, which leads to the cracking of SiO₂ scale. Second, the SiO₂ phase transformed from β -cristobalite (cubic) to α -cristobalite (tetragonal) during the cooling process at around 573 K and had a volume contraction of 6% ^[18], which will also cause tensile stress in the SiO₂ scale. When crack networks formed in the oxide layer after steam oxidation at 1673 K, together with the spherical structure of SiC layer, the oxide scale could not maintain a good adhesion with the SiC. As a result, the SiO₂ layer spalled off from the SiC layer (Fig. 2d3). Meanwhile, the cracks further provided diffusion paths of the gas, resulting in an acceleration of the oxidation rate.

In addition, pores in the SiO₂ scale were also observed after steam oxidation at high temperature (>1473 K), which can be attributed to the gaseous products (i.e., CO and H₂) accumulated during the oxidation process ^[20]. For relatively thick oxides at high temperature steam oxidation, the inward diffusion of water vapor to react with SiC would be hindered. As reported in previous studies, the reaction at the SiC/SiO₂ interface might occur, following the equation ^[12, 37]:

Including the gaseous products (i.e., CO and H₂) from Eq. (11), the as-formed SiO and CO gases diffused outwards and made contributions to the formation of pores ^[34], resulting in more pores at a higher temperature (Fig. 2d). Meanwhile, water vapor can decrease the viscosity and density of the SiO₂ scale, which was beneficial to the outward diffusion of gas products ^[18, 32]. Therefore, pores away from the SiC/SiO₂ interface were observed, especially at a higher oxidation temperature (Fig. 2d).

Meanwhile, the formation of carbon at the SiC/SiO₂ interface was observed above 1473 K. The phenomenon was more significant with an increase of the oxidation temperature. It is believed that some carbon was trapped at the interface during the oxidation process due to the kinetically limited formation and removal of volatile CO molecules, especially for relatively thick oxides ^[23, 24, 25]. It was also pointed out that the limited outward diffusion of CO would result in a relatively high CO partial pressure at the SiC/SiO₂ interface, which in turn led to the possibility of carbon formation by increasing the carbon activity at the SiC/SiO₂ interface ^[39]. The reaction for carbon formation at the SiC/SiO₂ interface was reported to follow the equation below ^[12, 37]:

The Eq. (17) was analyzed through thermodynamic simulations with the Gibbs energy data in previous study ^[37], showing the reaction is thermodynamically favorable. The disappearance of graphitization after 1673 K oxidation could be due to the spallation of the partial SiO₂ scale, and the carbon at the interface of SiC/SiO₂ could be easily oxidized above 673 K. It was also suggested that carbon diffused towards the outer surface of the scale and gone away into the atmosphere during oxidation ²³.

4.3 Effect of steam oxidation on the fracture strength of SiC layers

After steam oxidation at above 1473 K, SiO₂ scale with cracks and pores was formed. Gaps between the SiO₂ scale and the SiC layer were observed which indicate a weak interface adhesion. After steam oxidation at 1673 K, the SiO₂ scale eventually spalled from the SiC layer. Therefore, the mechanically weak SiO₂ scale is not supposed to make significant contribution to the fracture strength of the SiC shell under crush test. The fracture patterns of both as-deposited sample and oxidized sample were investigated. For the crush test of brittle material, catastrophic failure generally occurred at the first load instability. Figure 11 shows broken specimens after crush tests, which presented the radiating cracks converging around the apex of the SiC shell. It has been confirmed that the maximum principal stress appeared around the inner-apex of the SiC shell below the loading contact area, where the cracks would initiate ^[19]. Transgranular cracks were observed (Fig. 11a). After steam oxidation at 1473 K, some oxide scale spalled along the cracks and some oxide scale fragments remained overlapping with the cracks (Fig. 11b), which indicates that the cracks did not necessarily propagate from the SiC into the oxide layer. Therefore, it can be assumed that the oxide scale with crack networks formed on the surface had no significant effect on the crush

test.

Previous studies showed that the difference in the fracture strength of the SiC layers in TRISO particles could be attributed to the microstructure features such as the roughness of the IPyC/SiC interface, the porosity and the grain size of the SiC layer^[19, 40]. Because the oxidation temperatures in this study were lower than the SiC deposition temperature (>1773 K), the SiC could maintain its microstructural stability. Thus, the effect of these factors mentioned above on the fracture strength could be assumed negligible. In addition, it has been demonstrated that high temperature thermal treatment (<2273 K) had negligible influence on the strength^[41]. Therefore, the variation of the fracture strength of the SiC layers in this study would be mainly caused by the thickness change of the SiC layer.

Previous study showed that the fracture strength of TRISO particle was proportional to the thickness of the SiC layers, which would decrease with the decrease of the thickness of SiC layer^[26, 42]. In this study, it was found that the samples with relatively thinner layer after high temperature steam oxidation displayed lower fracture loads with a small diameter of impression (Table 2). It has been reported that the size of the indentation impression formed on the brass was almost the same as the size of the stressed area at the inner surface^[19]. Since the fracture stress depends on the area of material stressed, thinner specimens had a smaller effective tested area thus tended to have higher stress concentration at the inner surface of the SiC shell^[19], where failure would initiate, and had both a smaller fracture strength and a smaller Weibull modulus. Previous study pointed out that the ratio (r/δ) of outer radius (r) to the thickness of SiC layers (δ) was a critical dimensional factor for the stress distribution of the SiC shell^[43]. Figure 12a and 12b show the Weibull modulus and the mean fracture strength for the full spherical shell, which decreased linearly with the increase of the ratio (r/δ). The slopes from the linear fitting in Fig. 12 were 0.26 and 33.6 for Weibull modulus and

mean fracture strength with R^2 (goodness of fit) of 94% and 95%, respectively. The results are consistent with the previous results that showed similar values of 0.22 and 28.6 for the Weibull modulus and the mean fracture strength^[43]. The decreased fracture strength of SiC layer after steam oxidation (up to 24% lower at 1673 K) due to the thinning of the SiC layer would increase the failure probability for TRISO particles^[5].

5. Conclusions

The steam oxidation of SiC layers in TRISO particles was investigated at a temperature range of 1173–1673 K in water vapor–argon atmosphere with a total pressure of 1 bar. The oxidation kinetics model of was proposed. The fracture strengths after steam oxidation were also measured.

The presence of water vapor not only increased the crystallization of the amorphous SiO₂ oxide scale, but also increased the oxidation rate of the SiC layer. The SiC layer has a good steam oxidation resistance below 1273 K. Above 1373 K, the oxidation kinetics of SiC follows the parabolic law. The calculated activation energy was 103 ± 11 kJ/mol, suggesting that the rate determine step of the oxidation is the diffusion of water vapor molecules in the oxide scale. The fracture strength decreased with the increase of the oxidation temperature mainly due to the thinning of the SiC layer.

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Figure Captions

Fig. 1 Schematic illustration of the modified crush test system for hemispherical SiC shell.

Fig. 2 SEM images of surface morphology and fracture cross-sections of (a)–(d) steam oxidation for 24 h under different temperatures and (e) oxidation in dry air at 1473 K for 24 h, in which the insert c3 shows EDS results from the surface and d3 shows partial spallation of SiO₂ scale at 1673 K.

Fig. 3 XRD patterns of TRISO particles: (a) includes as-deposited sample, the samples after steam oxidation for 24 h at 1273 K–1673 K and the samples after oxidation in dry air for 24 h at 1473 K and (b) amplifies XRD patterns from 20 degree to 28 degree.

Fig. 4 Raman spectra measured from the surface of SiC layer in TRISO particles: (a) includes as-deposited sample, the samples after steam oxidation for 24 h at 1273 K–1673 K and the samples after oxidation for 24 h in dry air for 24 h at 1473 K and (b) amplifies Raman spectra from 1200 cm⁻¹ to 1850 cm⁻¹.

Fig. 5 The thickness of SiO₂ layer as a function of oxidation time under different temperatures in steam atmosphere.

Fig. 6 Weibull plots for the measured fracture load.

Fig. 7 The measured fracture load as a function of the SiC thickness compared with previous study using different insert metal for the crush test.

Fig. 8 The calculated local fracture strength of SiC shells in the form of Weibull distribution for different steam oxidation treatment samples.

Fig. 9 Weibull distribution of the calculated fracture strength for full spherical shells for different steam oxidation treatment samples.

Fig. 10 Arrhenius plots of parabolic oxidation rate constant (k_p) as a function of temperature for the SiC layer oxidation in steam atmosphere.

Fig. 11 Crack patterns of the broken specimens of (a) as-deposited sample and (b) sample after steam oxidation at 1473 K after crush tests.

Fig. 12 The relationship of (a) the modulus derived from local fracture strength and (b) the mean fracture strength for full spherical shell with the ratio of outer radius to thickness of SiC layer, respectively.

Table Captions

Table 1 Summarized basic parameters for the steam oxidation setup

Table 2 Summarized results of crush tests with the Weibull modulus given in brackets of SiC shells after steam oxidation at different temperatures for 24 h

Table 3 A summary of parabolic oxidation rates of SiC layers at different temperatures

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7

Fig. 8

Fig. 9

Fig. 10

Fig. 11

Table 1 Summarized basic parameters for the steam oxidation setup

	Alumina tube			Hot zone (mm)	The oil bath temperature (K)	The flow rate ($\times 10^{-4}$ m/s)		
	Inner cross sectional area (m^2)	Length (m)	Thickness (mm)			Argon	Water vapor	Gas mixture
Parameters	3.8×10^{-3}	1	5	20	363	8.7	5.2	14

Table 2 Summarized results of crush tests (with the Weibull modulus given in brackets) of SiC shells after steam oxidation at different temperatures for 24 h

Sample	$2r_0$ (μm)	F (N)	σ_f^L (MPa)	Scaling factor for Size effect	σ_f^F (MPa)
As-deposited	120.9	4.8 (2.6)	1638 (7.0)	2.3	729 (6.6)
1373K-24h	119.2	4.6 (2.5)	1624 (6.7)	2.3	699 (6.4)
1473K-24h	114.8	4.4 (2.4)	1573 (6.2)	2.5	627 (7.2)
1573K-24h	112.9	4.2 (2.1)	1551 (5.8)	2.6	588 (6.8)
1673K-24h	107.1	3.7 (2.3)	1501 (5.6)	2.7	553 (4.8)

Table 3 A summary of parabolic oxidation rates of the SiC layers at different temperatures

Oxidation temperature (K)	Parabolic rate (k_p) ($\times 10^{-16}$ m^2/s)	
	This study	Previous study ^[19]
1373	0.56	-
1473	1.31	1.39
1573	1.97	2.73
1673	2.92	6.91
1473 (in air)	0.33	-