High Temperature Steam Oxidation of SiC Coating Layer of TRISO Fuel Particles

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Abstract

High-temperature oxidation behavior of SiC coating layer of TRISO fuel particles in 1500-1700°C steam at 1 atm has been examined inside a zirconia furnace. The SiC coating layers experienced a thickness loss of less than 2.5 μm under these conditions up to 24 h. The thickness of the oxide layer formed under these conditions was consistent with prior steam oxidation tests on high-purity bulk SiC. Upon reducing the presence volatile impurities from the test environment (particularly Al) by conducting the tests inside a zirconia furnace, melting of the silica layer at 1700°C was avoided.

1. Introduction

Since its original application as a coating layer in tristructural isotropic (TRISO) fuel particles of high temperature gas-cooled reactors (HTGRs) [1-2], SiC has been a topic of active research and development for nuclear energy applications [3]. Given today's focus on accident tolerant fuels for light water reactors (LWRs) [4], concepts utilizing SiC as core constituents [5-6] are receiving ample attention. This is the case since high-purity bulk SiC materials have been shown to exhibit exceptional resistance to oxidation in high-temperature steam environments [7-10]. In this study, high-temperature steam oxidation behavior of SiC coating layer of TRISO fuel particles has been examined. The majority of test conditions, consisting of 100% H_2O at elevated temperatures (1500-1700°C), are unique and depart from what is considered applicable for HTGRs under normal and most accident conditions. Under normal operating conditions for HTGRs, only a small partial pressure of water vapor is expected to be present ($< 1.4 \text{ Pa}$ [11]) and under severe accidents the combination of high water vapor partial pressure (10^5 Pa and higher) and elevated temperatures of this study are unlikely [12]. However, for the LWR application of TRISO fuel particles as microencapsulated fuel forms [13], namely fully ceramic microencapsulated (FCM) pellet, severe accidents beyond the design basis can lead to these high temperatures in presence of abundant steam.

FCM fuel consists of TRISO fuel particles embedded inside a sintered SiC matrix. The matrix SiC is consolidated at temperatures $< 1900^\circ\text{C}$ using addition of a small amounts ($\sim 5 \text{ wt\%}$) of sintering aides

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[14]. These sintering aides generally consist of a mixture of yttria-alumina ($Y_2O_3-Al_2O_3$), where the latter compound is more prominent in the mixture. The focus of this study is on the oxidation behavior of the SiC coating layer of the TRISO fuel particle. Although some literature is available on oxidation behavior of sintered SiC [15-17], future studies will focus on determining the steam oxidation behavior of the FCM SiC matrix under similar conditions.

2. Experimental Procedure

For the purposes of oxidation tests, TRISO particles were intentionally produced without the outer pyrocarbon (PyC). The particle coating started with $\sim 520\text{ }\mu\text{m}$ zirconia kernels coated with PyC ($\sim 40\text{ }\mu\text{m}$). These particles were subsequently coated with CVD SiC at ORNL's 50 mm coater using methyl trichlorosilane (MTS), CH_3SiCl_3 . H_2 gas was mixed with the MTS as the fluidization medium (essentially carrier gas that was bubbled through MTS liquid). The coating conditions consisted of a 2 h run time at 1550°C with H_2 and MTS flow at 14800 and 166 sccm. This resulted in formation of a dense SiC layer at the outermost surface with a thickness of $\sim 32\text{ }\mu\text{m}$.

Oxidation testing was carried out in the high-temperature furnace module of ORNL's severe accident test station (SATS). This system, as depicted in Fig. 1(a), has been described in detail previously [10]; however, a fundamental modification to the system was carried out for the tests in this study where all the alumina furnace components have been replaced with zirconia. The zirconia tubes were manufactured by CoorsTek (Golden, CO) with the manufacture specified composition of $ZrO_2+HfO_2 - 9\text{wt}\% Y_2O_3 - 1\text{wt}\% CaO - 1\text{wt}\% SiO_2 - 1\text{wt}\% Al_2O_3$. This modification was carried out since the previous steam oxidation tests [10] in alumina furnace components resulted in alumina volatilization at temperatures above 1500°C (as a result of steam-alumina reaction [18]). Tests carried out in dry oxygen inside alumina tubes have also shown to be affected by the other impurities in these tubes [19]. The volatilized alumina was subsequently incorporated into the oxide scale forming on the SiC materials, changing the chemistry of this layer. By transitioning to zirconia furnace components, this issue was largely mitigated.

The testing on TRISO fuel particles (> 500 particles during each run) was carried out while they were held inside a perforated CVD-SiC tray (Dow Chemical Co., Marlborough, MA with a purity $> 99.999\%$) as shown in Fig. 1(b). Since the outermost layer of the particles consisted of the CVD-SiC coating layer, the particles were only adjacent to each other and the SiC tray; hence no possibility from direct interaction with foreign materials was possible during the tests. Particles without OPyC were intentionally used since it is known that graphite reacts rapidly in presence of water vapor [11] and also to isolate the study to that of SiC coating layer oxidation.

Steam oxidation tests were conducted under isothermal conditions and during the temperature ramp up and down the specimens were exposed to flowing ultra-high-purity argon. The steam flow velocity in the system was adjusted by the rate of water injection into the boiler. The gas flow velocity was calculated in a simplistic manner using this injection rate, temperature, and the cross-sectional area of the zirconia furnace tube. The exact steam flow velocity past the particles inside the perforated SiC tray is unknown and can vary depending on the location of the particle in the packed bed.

After the oxidation tests, the specimens were cross-sectioned for metallographic examination. The particles were polished to mid-plane to attain a perpendicular view of the oxide-carbide interface. The extent of SiC layer recession was analyzed using a well-developed procedure involving optical microscopy and computer image analysis [20]. Scanning electron microscopy (SEM) studies were conducted with a JEOL 6500 FEG-type microscope operating at 15 kV accelerating potential. X-ray diffraction (XRD) studies were performed using a Rigaku MiniFlex II XRD instrument of 0.45 kW (30 kV and 15 mA) with Cu-K α radiation. For the purposes of the XRD study, the oxidized particles were crushed to remove the zirconia kernels. Subsequently, the coating layers (PyC and SiC) along with the surface oxide were ground in a mortar and pestle with ethanol addition into a fine powder slurry. The slurry was then spread onto a low-background holder for the diffraction experiment. A small amount of Si standard (SRM640b) was added to the spread slurry to be utilized during Rietveld refinement as a reference.

Figure 1. a) Depiction of the high-temperature furnace with zirconia furnace components and b) the state of SiC-coated particles inside the specimen basket during oxidation tests.

3. Results

3.1. Optical microscopy and image analysis

The summary of oxidation test conditions and results on SiC-coated particles is provided in Table 1. The SiC layer thickness prior to and after various oxidation tests was determined via optical microscopy and computer image analysis from roughly 50 particles, an example of which is shown in Fig. 2(a). Fig. 2(b) shows the processed image of the same particle in Fig. 2(a), where the software determined the thickness of coating layers by quantifying the distance of the various interfaces from the center of the particle, as

described in ref [20]. The oxide layer thickness reported in Table 1 was determined from SEM results in Fig. 3, as described in the next subsection.

Table I. Summary of SiC-coated particle oxidation tests. All tests are in 100% H₂O except test #5 that was conducted in flowing air.

ID	Test Temperature [°C]	Test Duration [h]	Gas Flow Velocity [cm/s]	Mean SiC Layer Thickness [μm]	SiC Layer Thickness Std. Dev. [μm]	Oxide Layer Thickness [μm]
1		As fabricated		32.2	0.7	0
2	1500	4	57	30.2	0.9	2.3
3	1600	4	60	30.1	0.9	3.1
4	1600	24	60	29.7	1.0	6.9
5*	1600	24	13*	33.6	1.5	3.1
6	1550	24	58	32.4	1.1	4.4
7	1650	24	62	31.9	0.9	3.7
8	1700	4	63	30.8	1.0	7.2

*Test performed in flowing air.

Figure 2. a) Optical image of the SiC-coated particle after oxidation and polished to the mid-plane and b) computer image analysis of the same particle for determining SiC layer thickness. Essentially, $y=0$ is the center of the particle and the distance from this origin are measured for various layers. The red lines indicate the computer recognized location of the interfaces.

As it is suggested by Table 1, the extent of SiC coating layer recession proved negligible after the various oxidation tests. The starting SiC coating layer thickness varies among the particles after the deposition step; as noted by the standard deviation of $0.7\ \mu\text{m}$ in the SiC layer thickness in the as-fabricated state. Note that the magnitude of SiC layer thickness change is within a few standard deviations of the mean value of the as-fabricated batch. Figure 4(a) shows the distribution in all the thickness measurements using boxplots. Given the small amount of SiC layer thickness recession and the large statistical distribution of the results, no detailed kinetic data could be extracted. However, as shown in Figure 4(b), the average magnitudes of thickness change and the trends (essentially thickness loss in steam and gain in air) are consistent with prior data from SiC oxidation tests in air and steam [10, 21-22]. As expected, Fig. 4(b) also shows that SiC recession increases with time in the flowing steam environment.

3.2. Scanning electron microscopy

The oxide layer thickness was determined from the backscattered SEM images, as shown in Fig. 3. It is possible to predict the oxide layer thickness given the well-developed parabolic oxidation kinetics of SiC in the presence of water vapor [23]. The kinetic data and model of Terrani et. al. [10] have been used for this prediction and compared to the current results. This comparison was performed in Fig. 5 where the data is in sufficient agreement ($\pm 50\%$ of the prediction). Note that the kinetic data from ref. [10] were determined from tests in an alumina furnace and are only applicable up to 1600°C and the results beyond this point in Fig. 5 have been extrapolated. In particular, prior tests at 1700°C inside the alumina furnace resulted in melting of the silica layer [10], however, by transition to the zirconia furnace tube, the oxide layer remained solid. The presence of bubbles at the oxide carbide interface, likely filled with the H_2 and CO reaction byproducts as a result of steam oxidation of SiC, were noted after 1700°C exposure.

Surface characteristics of the oxide layers were also documented and are shown in Fig. 6. These results are comparable to what was reported for bulk CVD-SiC [10], excluding the current observation at 1700°C where no sign of oxide layer liquefaction was noted after tests inside the zirconia furnace tube. Crystalline surface oxides undergo cracking upon cooling due to the strong mismatch in CTE with the substrate SiC as discussed in ref [10], and also due to the $\alpha \rightarrow \beta$ phase transformation in cristobalite at low temperatures ($\sim 270^\circ\text{C}$) [24]. Note that the surface features of the silica layer after air exposure at 1600°C appear similar to the original surface topography of the as fabricated SiC shell. This is indicative of the absence of any volatilization in this dry air environment. Also in Fig. 6(b), the thin oxide layer, as seen in Fig. 3(b), resembles the as-fabricated surface and is not smooth. This is likely due to the slow rate of SiO_2 volatilization from the surface.

Energy dispersive x-ray spectroscopy (EDS) was used to characterize the silica layers and to detect presence of any appreciable amount of impurities after $1500\text{-}1700^\circ\text{C}$ exposures, Fig. 7. No sign of Zr incorporation into the oxide layer was observed. However, a small Al impurity may be present in the oxides, the source of which may be the residual amounts of alumina in the zirconia furnace tube.

Figure 3. Backscattered electron image of SiC coating layer cross-section prior and after oxidation.

Figure 4. a) Boxplot representation of the SiC coating layer thickness distribution and b) variation of mean SiC layer thickness with time under high-temperature steam or air environments (error bars are std. dev.).

Figure 5. Comparison between kinetic data prediction of SiO_2 layer thickness from correlations in ref. [10] (contour map) and measured thickness of SiO_2 layer from SEM images in Fig 3 (scatter circles). The prediction assumes steam pressure at 1 atm and steam flow rate at 0.6 m/s.

Figure 6. Backscattered electron image of as-fabricated SiC coating layer surface and the resulting silica layer surface after various oxidation tests in flowing steam, except for (f) that was carried out in dry air.

Figure 7. Characteristic x-ray spectra from oxides formed on the surface of SiC coating layer after 24 h steam exposure between 1550–1700°C. The square root of normalized intensity is plotted to exaggerate minor peaks.

3.2. X-ray diffractometry

Fig. 8 shows a selected portion of the XRD patterns collected from 10–120° 2θ from the coating layers of the particles exposed to air and steam for 24 h at 1600°C and for 4 h to 1700°C steam. The patterns are

complex since the Si standard, multiple phases of silica, SiC, and graphite are all present in these samples. Rietveld refinement on the spectra was performed with the General Structure Analysis System (GSAS) software package [25] over the entire collected spectrum. The important observation here is that under all these oxidation conditions, two polymorphs of silica were detected; the dominant polymorph was α -cristobalite ($P4_12_12$ space group) that forms upon cooling from its high-temperature counterpart, β -cristobalite. Also, minor amounts of α -quartz ($P3_121$ space group) were also detected, likely present after cooling from β -quartz. In our previous steam oxidation study on bulk CVD specimens inside an alumina tube furnace [10], only formation of α -cristobalite was detected after 1400-1600°C exposures. No α -tridymite was detected to be present in these samples.

Figure 8. X-ray diffraction patterns along with the Rietveld refinement fit (solid lines) from oxidized SiC coating layer after 24 h air and steam exposures at 1600°C and 4h steam exposure at 1700°C. The square root of normalized intensity is plotted to exaggerate minor peaks. The different spectra are arbitrarily shifted upward for clarity.

4. Summary

Oxidation of SiC coating layer of TRISO fuel particles in high-temperature (1500-1700°C) flowing steam environments was examined for up to 24 h. The CVD-SiC coating layer exhibits very good steam oxidation resistance where no thickness loss beyond 2.5 μm was observed up to 24 h under these conditions. The thickness of the oxide layer present on the surface of the SiC coating layer under these conditions was consistent with prior steam oxidation tests on bulk high-purity CVD-SiC, indicating similar behavior between these coating layers and the bulk material. Instead of an alumina furnace tube, the zirconia furnace tube that was used in this study largely eliminated deposition of Al impurities into the silica layer during the steam exposure tests. The absence of Al impurities appears to have in turn eliminated melting of the silica at 1700°C. Consistent with prior literature, the major crystalline polymorph of silica present on the surface of SiC coating layers after these exposures was cristobalite. However, a notable extent of quartz was also found to be present.

These results indicate that under postulated severe accident conditions (for a HTGR or a LWR) where water vapor is present at temperatures up to 1700°C, the SiC coating layer of TRISO fuel particles will be effective in retaining fission products up to many hours. The reader should note that this conclusion is derived based on tests on a limited number of particles. Therefore, the statistical nature of defects (e.g. cracks) that could exist in the SiC coating layers may result in release of a small fraction of fission product inventory from susceptible particles.

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