

STEAM OXIDATION OF SILICON CARBIDE AT TEMPERATURES ABOVE 1600°C

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ABSTRACT

Silicon carbide (SiC) has recently attracted much attention as a potential material for accident tolerant fuel cladding. High-temperature oxidation of SiC at the temperature range approximately lower than 1600°C in steam has been studied by various authors. To evaluate the behaviour under design extension conditions, the knowledge for the higher temperature region is necessary. In this study, we accumulate the high-temperature oxidation data at higher temperatures (1700-1800°C) using a laser heating furnace. The oxidation kinetics is then discussed based on the weight loss and the observation of the cross-sectioned surface of tested samples using a field emission scanning electron microscope. At the investigated conditions, although a dense oxide layer was observed on sample surface, significant mass loss of SiC occurred. Below 1700°C, the oxidation kinetics seems to follow the parabolic laws. The activation energy calculated based on the data of this study is to be 370 kJ/mol. Rapid degradation and bubbling of SiC at 1800°C were observed after 1 h oxidation.

1. Introduction

Silicon carbide (SiC) has been widely applied to high-temperature structural materials due to its advantages such as high strength, high thermal shock resistance and excellent oxidation resistance [1]. Applications of SiC ranges from gas turbines to heat exchanger tubes for industrial furnaces. As used for high temperature applications, oxidation of SiC have been extensively studied [2-4]. Oxidation of SiC at high temperatures induces formations of both a condensed phase oxide, SiO₂, and a volatile sub-oxide, SiO, depending on the oxygen potential and temperature [5]. The condensed phase oxide, SiO₂ forms as a protective layer when oxygen potential is high and the formation of this oxide is termed "passive oxidation". Whereas the formation of volatile products occurs in environments with low oxygen potential such as CO/CO₂, H₂/H₂O, oxygen/inert gas and water vapor. As formation of the volatile products which can lead to rapid material consumption, this phenomenon is termed "active oxidation".

Recently, application of SiC has been proposed for accident tolerant fuel cladding materials. For instance, CVD-SiC can be applied as top coating on SiC/SiC composites clads. The accident that occurred in Fukushima Daiichi nuclear power station is a typical example of design extension conditions. During the accident progression, the temperature of the hottest fuel rod could exceed 2000°C [6]. In this particular use, the interaction of SiC with high temperature steam has to be comprehensively studied. However, previous works [7-8] mainly focused on the interaction at temperatures approximately lower than 1600°C, due to the difficulties of high temperature experiment with steam. In this study, we designed a laser heating test facility and attempted to obtain the high temperature data above 1600°C.

2. Experimental procedure

SiC samples (10x10x1 mm) used in this study were fabricated, using chemical vapor deposition method by IBIDEN. After setting the SiC sample into the chamber (as described in Fig. 1), the ambient air inside the chamber was evacuated. A pre-heated (150°C) gas mixture of steam and Ar-carrier was then purged into the chamber. The entire gas pipes,

chamber and view ports were also heated up to 150°C to keep dry steam. After setting the gas flows and test conditions as described in Table 1, the sample was irradiated by the laser beam focused on the sample surface. Two pyrometers were managed to measure the sample temperature. The value of pyrometer measuring at sample center was used to give feedback to the temperature control system. Whereas, the second pyrometer focusing on the edge of sample was used for reference. The difference between the values from the first pyrometer and the second pyrometer was less than 100°C under the tested conditions. During heating, the sample surface was observed by an in-situ video camera. The off-gases (H₂ and CO) generated during the test were analyzed via a sensor gas chromatograph. Mass of samples was measured before and after the tests by using an analytical balance. Microstructure of the samples after test was observed using field-emission scanning electron microscope (JSM-7800F, JEOL Ltd.) with energy dispersive x-ray spectroscopy (EDS). Phase identification of samples was carried out using X-Ray diffraction (XRD) technique with CuK α operating voltage of 40 kV, current of 30 mA, step size of 0.01°, time per step of 3 s/step and 2 θ scanned area ranging from 3 to 80°.

Temperature °C	Duration h	Heating rate °C/s	Steam flow rate g/min	Carrier gas (Ar) L/min	Steam partial pressure atm
1700	0.1 - 3	0.5	3	0.1	0.98
1800	0.25 - 1	0.5	3	0.1	0.98

Table 1. Test conditions for steam oxidation of SiC

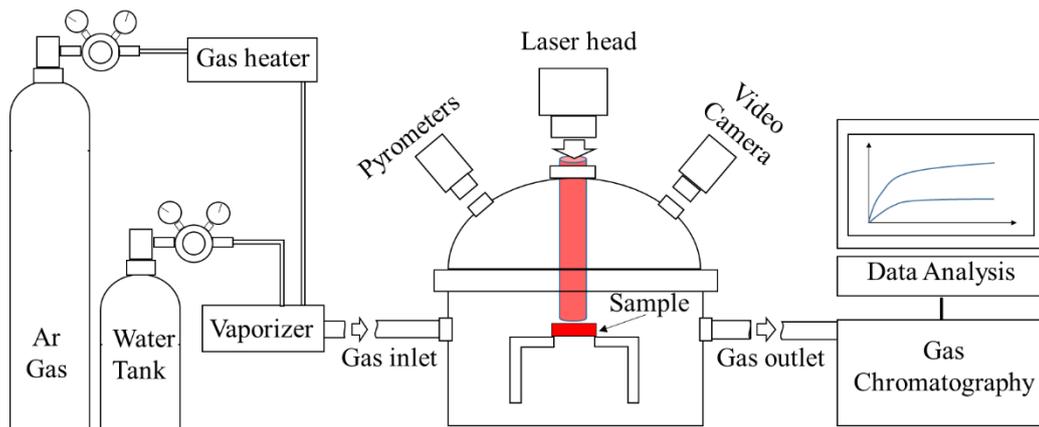


Fig. 1. Schematic diagram of the laser heating furnace

3. Results and discussion

Figure 2 shows a typical temperature profile of the investigation conducted for SiC using laser heating furnace. The sample temperature was raised from room temperature to 1000°C within 10 s in the first step. Then, from 1000 to 1800°C, the heating rate was managed as 0.5 °C /s to simulate a prototypic loss-of-coolant accident condition in the second step. After achieving the targeted temperature, the interaction was continued for fixed times in the third step to investigate the time variation of the interaction.

Figure 3 shows photographs of CVD-SiC sample before and after the test conducted at 1800°C for 45 min dwelling time. Apparently, an oxide layer was

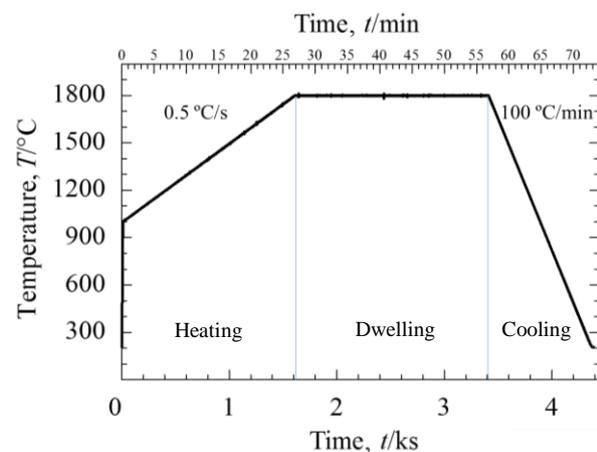


Fig. 2. Temperature profile of steam oxidation of SiC conducted at 1800°C for 30 min using the laser heating facility.

formed on sample surface.

Figure 4 shows a cross-sectional view of CVD-SiC sample exposed in steam at 1700°C for 3 h dwelling time and its corresponding element mapping of O, Si and C. A dense oxide layer was formed on sample surface with a thickness of approximately 10 μm. According to the XRD patterns as shown in Fig. 5, no crystallized silicon oxide phase was detected. This fact indicated that an amorphous SiO₂ layer was formed on sample surface.

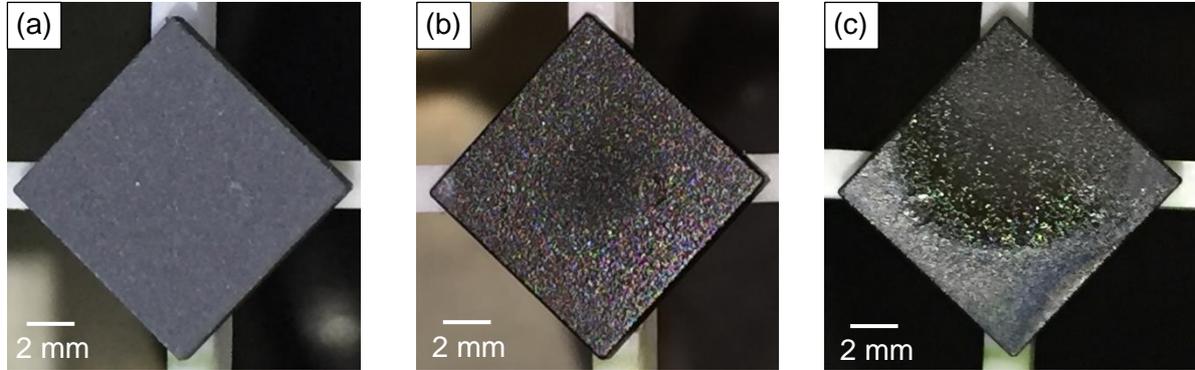


Fig. 3. Appearance of SiC sample (a) before and after exposed in steam at (b) 1800°C for 45 min, (c) 1700°C for 3 h.

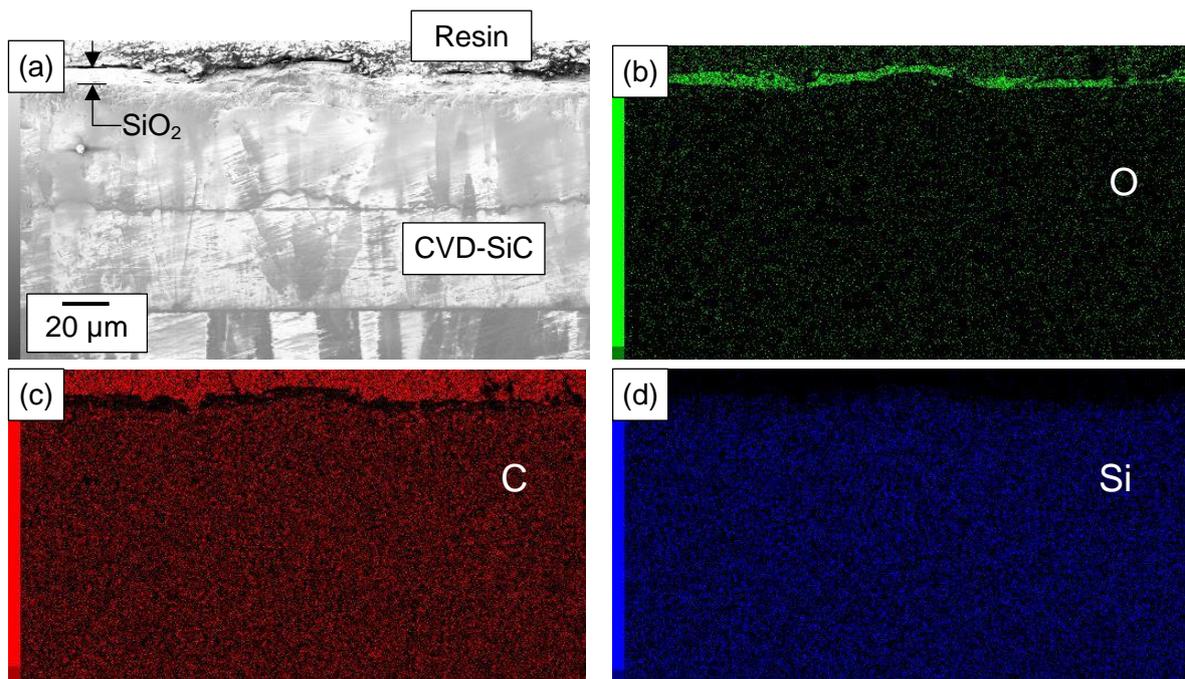
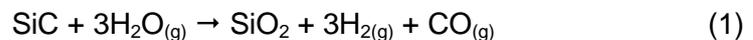


Fig. 4. Field emission scanning electron microscope image (a) shows cross-sectional view of CVD-SiC sample after steam oxidation at 1700°C for 3 h. EDS maps of (b) oxygen, (c) carbon and (d) silicon taken from the same area are also shown.

Figure 6 plots the mass change of CVD-SiC samples as a function of dwelling time at 1700 and 1800°C. The CVD-SiC samples experience a mass loss under the tested conditions. When exposed to steam at high temperature, silica is formed on the surface of SiC via the following reaction:



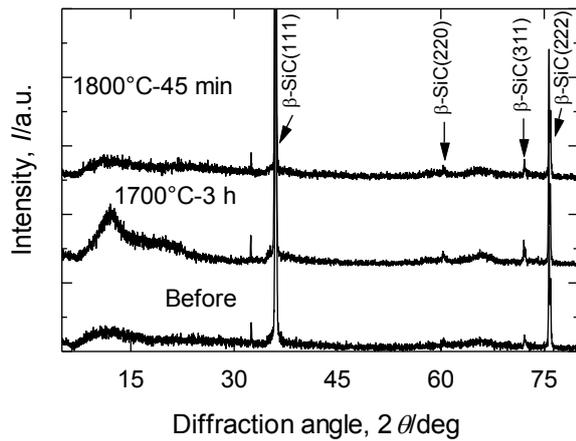


Fig. 5. XRD patterns of CVD-SiC sample before and after steam oxidation at 1700°C for 3 h and 1800°C for 45 min.

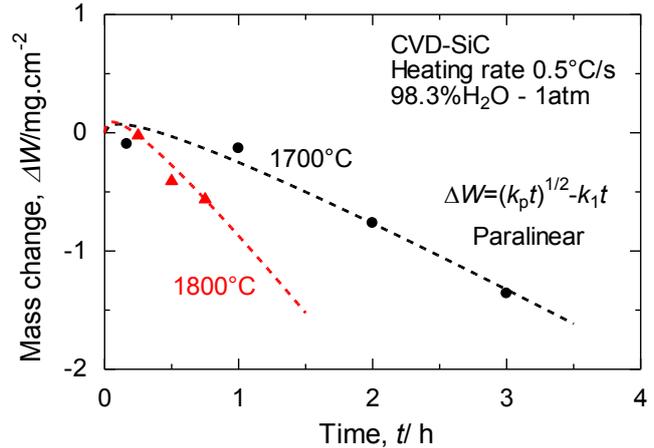
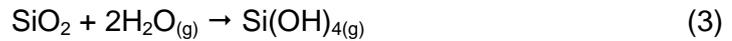


Fig. 6. Mass change of CVD-SiC samples as a function of oxidation time at 1700°C and 1800°C.

The kinetics of SiO_2 growth is controlled by diffusion of oxidizing species through the oxide layer and obeys parabolic laws [9] where the mass gain (Δw_1) is expressed by:

$$\Delta w_1 = (k_p \cdot t)^{1/2} \quad (2)$$

where k_p is the parabolic rate constant and t is time. Fig. 7 shows an oxide nodule formed on the surface of CVD-SiC sample during the test at 1800°C. The formation of the oxide nodule was attributed to the formation of gases (H_2 and CO) at the temperature above 1700°C, where SiO_2 underwent the melting process as its melting point is approximately 1725°C [10]. In the presence of steam, SiO_2 undergoes volatilization via the following reaction:



According to Terrani *et al* [7], the mass loss (Δw_2) caused by the oxide volatilization is given by the following equation:

$$\Delta w_2 = -k_l \cdot t \quad (4)$$

where k_l is linear volatilization rate from the surface. The total mass evolution (Δw) in the sample is the sum of mass gain due to oxide layer formation (Δw_1) and mass loss due to oxide layer volatilization (Δw_2), and expressed as following equation:

$$\Delta w = (k_p \cdot t)^{1/2} - k_l \cdot t \quad (5)$$

Based on the Eqs. (5), the parabolic oxidation and linear volatilization rate constant as shown in Table 2 were calculated to match the obtained data from Fig. 6. The k_p at 1800°C was three times higher than that at 1700°C. Meanwhile, the k_l at 1800°C was two times higher than that at 1700°C.

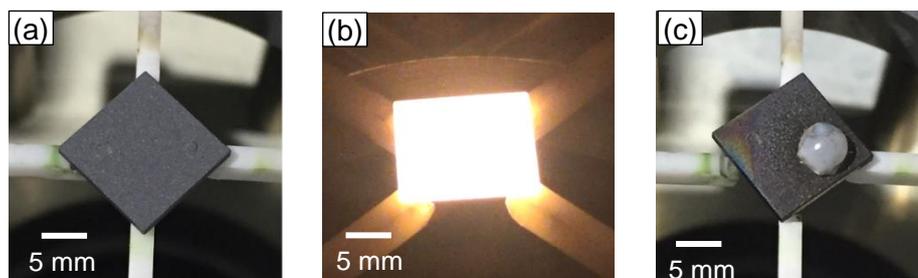


Fig. 7. Appearance of SiC sample (a) before, (b) during and (c) after steam oxidation at 1800°C for 30 min.

Temperature, T/°C	$k_p/$ mg ² .cm ⁻⁴ .h ⁻¹	$k_l/$ mg.cm ⁻² .h ⁻¹
1700	0.21±0.16	0.70±0.08
1800	0.61±0.13	1.65±0.08

Table 2. Calculated parabolic oxidation and linear volatilization rate constant based on the Eqs. (5) to match the obtained data from Fig. 6

Figure 8 plots the common logarithm of the parabolic rate constant versus the reciprocal of oxidation temperature for CVD-SiC that provides the Arrhenius relationship. The apparent activation energy was calculated based on the data of this study to be 370 kJ/mol. *Opila* [9] discussed that the activation energy for oxidation can give information about the diffusion species. Depending on the permeation behaviour and diffusing species such O²⁻ and OH⁻, the activation energy can be ranging from 28 to 527 kJ/mol. In comparison with the activation energy reported by *Terrani* [7] and *Opila* [9] conducted at lower temperatures, the activation energy derived from this study was slightly higher, but still in good agreement with the others.

4. Conclusions

High temperature interaction of chemical vapor deposition SiC with steam was investigated at 1700-1800°C for 0.1-3 h in a mixture of steam and argon gas containing 98% of steam at 1 atm. At the investigated conditions, although a dense oxide layer was observed on sample surface, significant mass loss of SiC occurred. Below 1700°C, the oxidation kinetics seems to follow the parabolic laws. The apparent activation calculated based on the data of this study is to be 370 kJ/mol. Rapid degradation and bubbling of SiC at 1800°C were observed after 1 h oxidation. This suggested that chemical interaction behaviours above 1700°C might be changed due to the liquefaction of silica.

Acknowledgements

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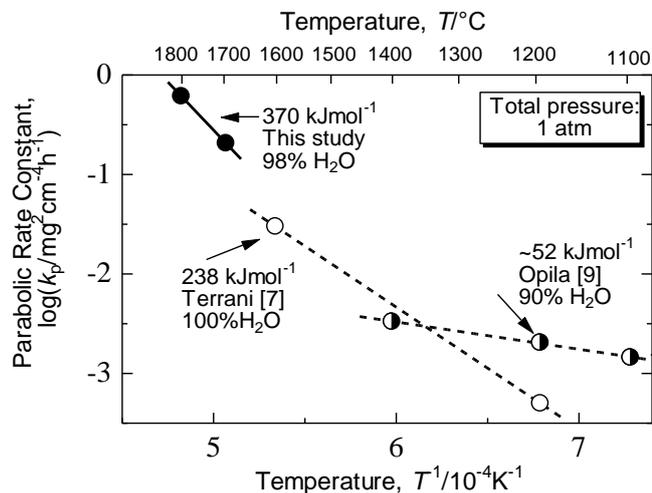


Fig. 8. Temperature dependence of parabolic rate constant on steam oxidation of CVD-SiC samples in comparison with previous reports.

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