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Oxidation Kinetics of Silicon Carbide in Steam at Temperature Range of 1400 to 1800ºC Studied by Laser Heating

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As expected for accident tolerant fuels, the investigation of steam oxidation for silicon carbide under beyond design basis accident scenarios is needed. Many studies focused on steam oxidation of SiC at temperatures up 1600ºC have been reported in the literature. However, behavior of SiC in steam at temperatures above 1600ºC still remains unclear. To complete this task, we have designed and manufactured a laser heating facility for steam oxidation at extreme temperatures. With the facility, we report the first results on the steam oxidation behavior of SiC in the temperature range of 1400-1800ºC for short term exposure of 1-7 h under atmospheric pressure. Based on the mass change of SiC samples, parabolic oxidation rate and linear volatilization rate were calculated to be $k_\mathrm{p} = \exp(1.44 \pm 1.8 + \frac{-96\pm 30\ [\mathrm{kJmol}^{-1}]}{RT[\mathrm{K}]})$, and $k_\mathrm{l} = \exp(4.7 \pm 0.6 + \frac{-95\pm 10\ [\mathrm{kJmol}^{-1}]}{RT[\mathrm{K}]})$. The oxidation layer appears to be maintained at 1800°C in steam, but the bubble formation phenomenon suggests other volatilization reactions may limit its life.

Keywords: SiC; steam oxidation; accident tolerant fuels, laser heating

1. Introduction

Since the nuclear disaster in March 2011 at the Fukushima Daiichi Nuclear Power Plant, development of new materials for accident tolerant fuels for light water reactors has become a heavily discussed issue. During severe accidents as at Three Mile Island or Fukushima Daiichi, the peak temperature of fuel rods could reach very high level, beyond melting temperature of current fuel claddings such as Zircaloy-4. In addition, severe degradation of Zircaloys in light water reactors already occurs below its melting temperature by exothermic oxidation in water vapor resulting in brittle and bursting of claddings (loss of barrier effect) as well as hydrogen and heat release. To provide larger safety margins and potentially avoid severe core degradation under beyond-design conditions, one strategy is to develop fuel systems that tolerate severe accident conditions better than the current Zircaloy claddings. Various alternative materials [1] for fuel cladding have been proposed for this application: ceramics such as silicon carbide (SiC) [2], advanced steels, for example Fe-Cr-Al alloys [3] or advanced Zircaloys such as Cr-coating Zircaloy.

SiC has attracted much attention as a high-temperature structural material over the past decades particularly in a composite form (such as SiC fibers in a SiC matrix). The applications of SiC can range from gas turbines blades to heat exchanger tubes for industrial furnaces due to its advantages such as high strength, high thermal shock resistance and excellent oxidation resistance [4]. As it has been proposed for high temperature applications, oxidation of SiC have been extensively studied [4-16]. Oxidation of SiC at high temperatures induces formation of both a condensed phase oxide, SiO_2, and a volatile sub-oxide SiO or hydroxide $Si(OH)_4$, depending on the oxygen potential, oxidizing species and temperature. The condensed phase oxide, SiO_2, forms a protective, surface layer which is termed “passive oxidation”. This is a compact layer that limits oxygen ingress by diffusion across a SiO_2 layer that is thickening with time and therefore gradually slowing the diffusion processes and SiC oxidation, and yielding a parabolic kinetics. Whereas the formation of volatile products, such as SiO which occurs in environment with very low oxygen potentials such as high-CO content CO/CO_2 mixtures, and H_2/H_2O, is termed “active oxidation”. Here the oxidation product SiO volatilizes increasingly with temperatures beyond 1200°C exposing a fresh SiC surface, and typically yields high linear kinetics at constant temperature, until the SiC is exhausted.

Recently, SiC is also being developed as a replacement for Zircaloy cladding in light-water reactors. SiC is known as a high-temperature structural material, and with a considerable improvement in the fabrication technology of SiC components, both monolithic SiC and SiC composites (eg. SiC fibers in SiC matrix). It is also reported to have many features suitable for nuclear industry such as high radiation damage tolerance, high thermal conductivity and high neutron economy [17]. As an alternative for the accident tolerant fuel, the performance of SiC in steam at extreme temperatures up to 1800°C and beyond, for severe accident scenarios, must then be investigated. However, the study of oxidation behavior in steam at temperatures above 1600ºC presents a challenge. Most of the conventional test facilities for steam oxidation require heating the entire test chamber where refractory lining materials such as alumina and/or zirconia may not survive the test. To complete this task, we have designed and developed a new test facility using a laser heating technique where the heat will be localized and focused on the test sample only.

In this study, steam oxidation of monolithic SiC was investigated at temperatures in the range 1400-1800ºC for 1-7h using laser heating facility (LAHF). The oxidation behavior of SiC was then discussed, based on the mass evolution with time.

2. Experimental details

Test facility

Fig. 1 shows the Laser Heating Facility (LAHF) which was specifically manufactured for this study. Main features of LAHF are: a controlled oxidizing environment, in situ observation ports, off-gas analysis, extremely fast heating/cooling rate and operational temperature above 2000ºC. The main unit consists of a laser head, two radiation pyrometers, video camera, airtight test vessel, vacuum pump, gas line heaters and flow rate controllers. The test vessel is made of stainless steel. The sample holders inside the test vessel are made of zirconia. Five quartz windows are positioned in the vessel wall for the purposes of laser light transmission, pyrometer temperature measurement and in situ observation. The temperature of the test vessel and gas flow can be controlled in the range of room temperature to 200ºC. The flow rates of steam, Ar carrier gas and hydrogen can be controlled in the range of 0.1~3.0 g/min, 0.1~5.0 l/min and 0.06~3.14 g/min, respectively. The laser module has a maximum power of 2500W which allows the sample to be heated at the rate of 1000K/s. The test program, including gas flow rates, temperatures of gas and vessel can be remotely setup, monitored and logged in the control system. A gas chromatograph is attached to the off-gas system to sample and measure the generation of hydrogen and carbon monoxide. The gas analysis of LAHF can also be implemented with a mass spectrometer if needed.

Experimental procedure

The SiC samples (10x10x1 mm, approx. 0.32 g) used in this study were made of monolithic β-SiC (above 99% theoretical density). After placing the SiC sample into the test vessel (see Fig. 2), the ambient air inside the vessel was evacuated and then purged with Ar gas. After heating the vessel to 150ºC, a pre-heated (150ºC) gas mixture of steam and Ar-carrier was then introduced into the vessel. The entire gas pipe system, and viewing ports were also heated up to 150ºC to keep dry steam conditions (i.e. no condensation). After setting the gas flows and test conditions as described in Table 1, the laser beam was switched on and the beam (approx. 6.5 mm diameter) was focused on the sample surface. Two radiation pyrometers (FTK9S, Japan Sensor Corporation) were used to measure the sample temperature (spot size: 1.5 mm, effective wavelength: 1.95-2.5 μm). The value of the pyrometer reading at the sample center was used to give feedback to the temperature control system. A second pyrometer (with the same specifications), focusing on the sample periphery, was used for reference. The difference between the values from the first and second pyrometer remained 100ºC under the test conditions. During the tests, physical appearance of the sample was observed and recorded by a video camera located on top of the test vessel. The gases (H_2 and CO) generated during the test were analyzed via a gas chromatograph (SGHA-P2, Nissha FIS, Inc.). The sample mass was measured before and after the tests using an analytical balance (XSE205, Mettler Toledo (0-80g scale; reproducibility ≤ 0,02mg). The microstructure of the sample after testing was observed using field-emission scanning electron microscope (JSM-7800, JEOL Ltd.) with energy dispersive x-ray spectroscopy (EDS). Phase identification of sample was carried out using x-ray diffraction (XRD) technique with the CuKα_1 line at an operating voltage of 40 kV, and a current of 30 mA. The step size was 0.02° for 2θ ranging from 3 to 80 ° at a speed of 2 deg/min.

3. Results

Figure 3 shows a typical temperature profile of the oxidation test conducted for monolithic SiC using the laser heating facility. The SiC sample was heated up from room temperature to 1000ºC within 10 s in the first step. From 1000 to 1800ºC, the heating rate was set as 0.5ºC/s to simulate a prototypic loss-of-coolant accident. After reaching the target temperature, the steam oxidation of SiC sample was continued for a fixed interval to investigate the time variation of the interaction. After the dwelling time, the cooling rate was 100ºC/min.

Figure 4 shows photographs of SiC samples before and after steam oxidation tests performed at 1400, 1600, 1700 and 1800ºC for 7 h of dwelling time. Due to the heat loss at the contact points between sample holders and test sample, the oxidation rate at the sample periphery seems to be lower than the rate in the center. Steam oxidation of monolithic SiC at 1400ºC for 7 h appears to be insignificant as its physical appearance did not change much. At 1600ºC, a brightly-contrasting and amorphous-like phase was observed on the sample surface. At 1800ºC, a bubbling phenomenon was observed at the center of the sample during steam oxidation tests. Figure 5 shows an oxide nodule observed from cross sectional view of the SiC sample after steam oxidation at 1800ºC for 7 h and with EDS maps of O, Si and C of the cross-section. The oxide nodule is attributed to the formation of gaseous products such as H_2 and CO at temperatures above 1700ºC where the SiO_2 scale started to melt.

Figure 6 shows the oxide layer formed on the surface of SiC samples after steam oxidation at various temperatures. The formation of an oxide layer on SiC sample after steam oxidation at 1400ºC for 7 h (Fig. 6a) was barely noticeable. For 1600ºC and 1700ºC exposures (Fig. 6b and c), a thin, dense oxide layer approximately 3 μm formed on the SiC substrate. As for steam oxidation at 1800ºC, Fig. 6d shows a dense, thicker oxide layer, approximately 10 μm between nodules. At this temperature, the oxide layer did not form homogeneously on the SiC substrate. According to the XRD patterns as shown in Figure 7, SiO_2 in Cristobalite form was detected on the surface of the SiC samples after exposure high temperature steam.

Figure 8 plots the mass change of monolithic SiC samples as a function of dwelling time after steam oxidation at temperatures of 1400-1800ºC. It appears that the SiC samples underwent a mass loss that steadily increased with temperature. The mass evolution at each temperature seemed to obey near-linear or paralinear laws. At high temperatures, SiC reacts with water vapor to form SiO_2 on the sample surface via the following reaction:

$$\mathrm{SiC} + 3\mathrm{H_2O_{(g)}} \rightarrow \mathrm{SiO_2} + 3\mathrm{H_{2(g)}} + \mathrm{CO_{(g)}} \quad (1)$$

The formation of the SiO_2 layer is controlled by diffusion of oxidizing species through the protective oxide layer which obeys parabolic laws [5-10] . The mass gain (Δw_1) due to the formation of oxide layer is then expressed by:

$$\Delta w_1 = m_{\mathrm{SiO_2 formed}} - m_{SiC\ \mathrm{reacted}} = (k_\mathrm{p}.t)^{1/2} \quad (2)$$

where k_p is the parabolic rate constant and t is time. In the presence of water vapor at high temperatures, the oxide layer reacts with steam and undergoes volatilization process via the following reaction:

$$SiO_2 + 2H_2O_{(g)} \rightarrow Si(OH)_{4(g)} \quad (3)$$

The mass loss (Δw_2) caused by the volatilization of oxide layer in steam is given by the following equation:

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

Where k_l is the linear weight loss rate of SiO_2 (equivalent to the volatilization rate of $Si(OH)_4$) and t is time. The total mass evolution of SiC samples when exposed to water vapor at high temperatures is the sum of mass gain due to oxide layer formation (Δw_1) and the mass loss due to oxide layer volatilization (Δw_2). The total mass evolution is then expressed as following:

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

Based on the Eq. (5) and the mass change of SiC samples in Fig. 8, the parabolic oxidation rate, k_p, and the linear volatilization rate, k_l, were calculated and are shown in Table 2.

4. Discussion

4.1 Oxidation kinetics of SiC

Figure 9 shows the parabolic oxidation rate constant as function of temperature for steam oxidation of SiC in comparison with previous reports. The apparent activation energy of the parabolic oxidation rate constant based on this data was calculated to be 96±30 $kJmol^{-1}$. Depending on the permeation behavior and diffusing species, the activation energy can range from 28 to 527 kJ/mol and has been discussed comprehensively elsewhere [6,7]. For example, Opila [6] reported the activation energy of 28-156 $kJmol^{-1}$ for steam oxidation of SiC under various H_2O/O_2 conditions at temperatures up to 1400ºC. In another work, Terrani [5] reported the activation energy of 238 kJmol^{-1} in a study of pure steam oxidation for SiC at temperatures up to 1600ºC. No activation energy value for k_p of SiC in steam-inert gas mixtures at temperatures up to 1800ºC has been found in the literature. In comparison to the previous reports, the activation energy derived from this study was slightly higher than that of Opila for oxidation of SiC in 90%H_2O/O_2 but lower than that of Terrani conducted under 100% steam environment. Based on the data-fitting in Fig. 9, the Arrhenius relationship is as follows:

$$k_\mathrm{p} = \exp(1.44 \pm 1.8 + \frac{-96 \pm 30\ [\mathrm{kJmol^{-1}}]}{RT[\mathrm{K}]}) \tag{6}$$

Figure 10 shows the linear volatilization rates calculated from mass change data at their corresponding temperatures. The activation energy for the linear volatilization rate constant in this study was 95±10 kJmol^{-1}. The Arrhenius relationship for the linear volatilization rate is as follows:

$$k_\mathrm{l} = \exp(4.7 \pm 0.6 + \frac{-95 \pm 10\ [\mathrm{kJmol^{-1}}]}{RT[\mathrm{K}]}) \tag{7}$$

Terrani [5] discussed that the activation energy for k_l should be comparable to the enthalpy of formation of the volatile species at the gas-solid interface under the relevant test temperatures. The activation energy for linear volatilization rate constant calculated in this study appears to be higher than the enthalpy of formation of $Si(OH)_{4(g)}$ which is approximately 57 kJmol^{-1} at 1500ºC [5].

In consideration of the paralinear behavior of SiC in steam at high temperatures, the formation rate of SiO_2, v_f [mg/cm^2/h], according to the parabolic oxidation rate, is as follows:

$$v_\mathrm{f} = \frac{\mathrm{d}(\mathrm{m}_{SiO2}\mathrm{formed})}{\mathrm{d}t} = \frac{\mathrm{d}(3\Delta w1)}{\mathrm{d}t} = \frac{\mathrm{d}(3\sqrt{k_\mathrm{p}t})}{\mathrm{d}t} = 3/2\sqrt{k_\mathrm{p}/t} \quad (8)$$

In the meantime, the volatilization rate of SiO_2, v_v [$\mathrm{mg/cm^2/h}$], was the linear volatilization rate constant:

$$v_\mathrm{v} = \frac{\mathrm{d}(\mathrm{m}_{SiO2}\mathrm{volatilized})}{\mathrm{d}t} = \frac{\mathrm{d}\Delta w2}{\mathrm{d}t} = \frac{\mathrm{d}(k_\mathrm{l}t)}{\mathrm{d}t} = k_\mathrm{l} \quad (9)$$

In a steady state, the formation rate of SiO_2 is equivalent to its volatilization rate as shown in Fig. 11. From Eq. 8 and Eq. 9, the time to reach the steady state, t_s, is then given by:

$$t_\mathrm{s} = \frac{9k_\mathrm{p}}{4k_\mathrm{l}^2} \quad (10)$$

Based on the Eq. (10), the time to achieve a steady state of SiC in steam under the investigated conditions was calculated and is presented in Table.3. After the achieving a steady state, the loss of SiC is directly proportional to the volatilization rate of SiO_2.

4.2 Formation of bubbles on SiC samples

Bubble formation was only observed on SiC sample surface from in-situ video camera during steam oxidation tests at 1800°C. Figure 5 shows small gas bubbles attached to the SiO_2 droplet-SiC interface at 1800°C; while video shots (Fig. 12) demonstrate the rapid bubbling of the plastic SiO_2 film. During the steam oxidation tests at lower temperatures (1400-1700°C), bubble formation was not observed (although the macroscopy of the 1700°C sample (Fig. 4d) shows a roughened surface). It implies that the temperature range of 1700-1800°C was a critical region for the bubble formation of SiC in the steam environment. As depicted in Fig. 13, oxidation of SiC can be explained by chemical reactions at the top surface and the interface between SiC substrate and SiO_2 scale. On the top surface, silicon dioxide reacts with water vapor to form volatile $Si(OH)_4$. In the meantime, at the interface, SiC reacts to form SiO_2, with H_2O or oxidizing OH• or

H• radicals. The radicals can diffuse through the oxide scale generating gaseous products (CO & H_2) at the interface and creating a certain level of pressure. When the temperature of the oxide layer reaches its melting point or becomes viscous, bubbles of SiO_2 emerge, which grow and burst. The gas chromatograph was able to detect the oxidation products of SiC (ie. CO & H_2) at the higher temperatures, unfortunately the limits of detection were reached and these results were purely qualitative. The chromatographic equipment is being updated and a publication concentrating on these aspects for kinetic measurements of the SiC oxidation is intended in the near future.

Similar phenomena of SiO_2 bubbles formation on SiC samples in various environments have been reported elsewhere [5,11,18,19]. Depending on the fabrication method and impurities, formation of SiO_2 bubbles during oxidation of SiC occurred at 1300-1800°C with different bubble sizes going up to several millimeters [18]. In general, the melting point of pure silica is higher than that of silicates. Thus the lower the impurities of SiC, the higher the temperature of bubble formation. As for chemical vapor-deposited SiC, formation of SiO_2 bubbles mostly occurred at 1700-1800°C which is the same temperature range observed for bubble formation as in this study. The melting temperature of SiO_2 is given as 1726°C and a softening range of 1675-1800°C [20].

Although bubble formation was observed at 1800°C in this study, no significant influence on the overall mass evolution of samples was found. When SiO_2 bubbles form on SiC surface, the oxide layer is no longer protective which leads to significant degradation of SiC. It implies that the parabolic oxidation rate of SiC may become linear at longer durations. However, data on the mass change of samples oxidized at 1800°C and the thicker scale 10µm as opposed to 3µm at lower temperatures did not reflect a breakaway phenomenon.

This investigation of monolithic SiC is only a first step on the way to qualify SiC-based as materials since cladding tubes will be SiCfiber-SiC ceramic-matrix composites of different designs. Further investigations will be conducted in the near future with an upgraded gas chromatograph to confirm the kinetics of SiC oxidation and clarify for what durations the protective behavior (or passive oxide layer) can be maintained at 1700°C and 1800°C. Moreover, SiC (monolithic) should be tested at higher temperatures (e.g. 1900°C) to see how much the surface liquid SiO_2 persists and what is its effect on oxidation resistance. A further option is to examine protective coatings if the passive oxidation of SiC is limited to 1800°C in steam.

5. Conclusions

Investigation of steam oxidation for monolithic SiC was conducted at a temperature range of 1400-1800ºC for 1-7 h in a mixture of steam and argon gas containing 97% of water vapor under atmospheric pressure. Although a dense oxide layer was observed on sample surface, SiC samples experience an oxidation to SiO_2 and a mass loss under the investigated conditions (due to SiO volatilization). The oxidation kinetics of SiC followed paralinear laws. Based on the mass change of SiC samples, parabolic oxidation rate and linear volatilization rate at corresponding temperatures were calculated to be $k_\mathrm{p} = \exp(1.44 \pm 1.8 + \frac{-96\pm30\ [\mathrm{kJmol^{-1}}]}{RT[\mathrm{K}]})$, and $k_\mathrm{l} = \exp(4.7 \pm 0.6 + \frac{-95\pm10\ [\mathrm{kJmol^{-1}}]}{RT[\mathrm{K}]})$. These equations appear to be closer to the values of Opila [6] than Terrani [5], although they only go to a maximum temperature 1600°C in one case [5]. Bubbling phenomenon of SiC at 1800ºC was clearly observed with large bubbles forming in a near molten SiO_2 layer; small bubbles were observed to initiate at the interface. Although the microscopy indicated a thicker SiO_2 film formation at 1800°C, the mass change data did not reflex any change of the oxidation mechanism. More extensive investigation is needed to clarify this behavior in the temperature range of 1700-1800°C.

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Table 1. Test conditions for steam oxidation of SiC samples.

Temp. ºC	Duration h	Heating rate ºC/s	Steam g/min	Carrier gas (Ar) L/min	Steam partial pressure atm
1400 1600 1700 1800	1~7	0.5	3	0.2	0.97

Table 2. Calculated parabolic oxidation rate and linear volatilization rate constant from the mass change data based on Eq. 3.

Temperature, T/ºC	1400	1600	1700	1800
Parabolic rate constant k_p/mg^{-2}cm^{-4}h^{-1}	0.004±0.002	0.009±0.003	0.012±0.002	0.015±0.003
Linear rate constant k_l/mgcm^{-2}h^{-1}	0.12±0.01	0.255±0.005	0.335±0.005	0.45±0.005

Table 3. The time to achieve steady state determined by k_p and k_l.

Temperature, T/ºC	1400	1600	1700	1800
Time to achieve steady state $t_s = \frac{9k_p}{4k_l^2}$ [h]	0.63±0.2	0.3±0.07	0.24±0.03	0.17±0.03

Figure 1. Illustration of the Laser Heating Facility (LAHF).

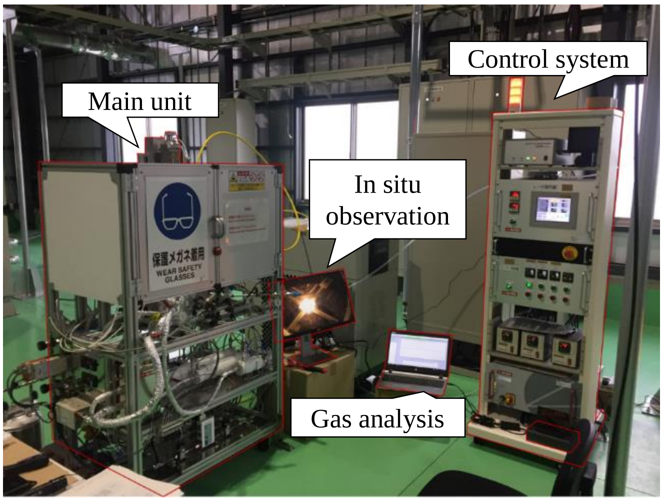

Figure 2. Schematic diagram of the laser heating facility (LAHF).

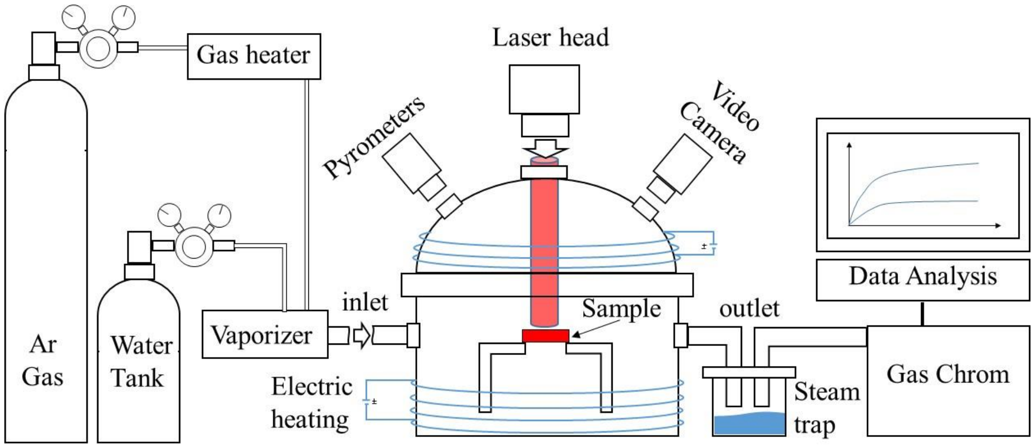

Figure 3. Temperature profile of steam oxidation of monolithic SiC conducted at 1800ºC for 1 h using the laser heating facility.

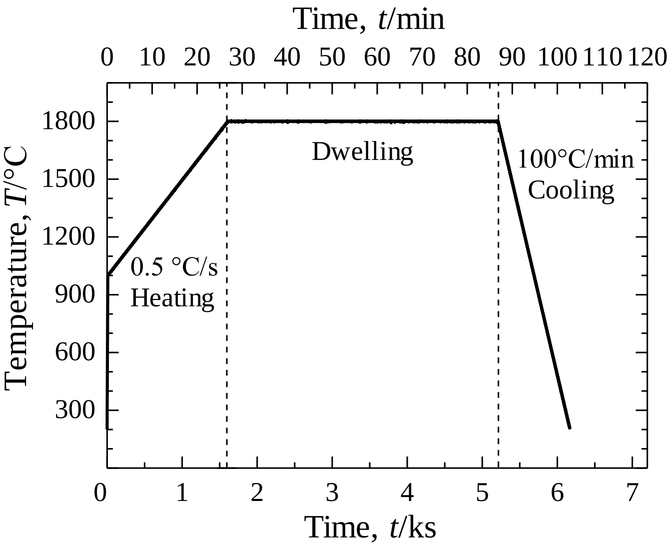

Figure 4. Photographs of SiC samples (a) before and after being exposed to steam at (b) 1400, (c) 1600, (d) 1700 and (e) 1800ºC for 7 h.

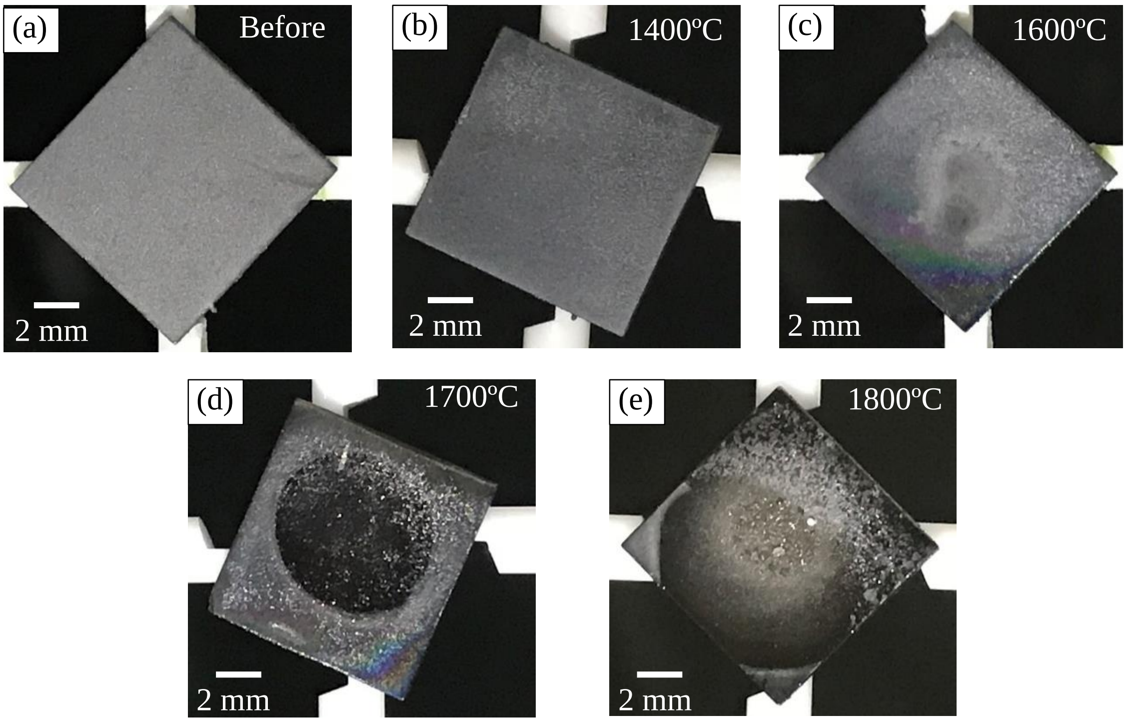

Figure 5. SEM images from a cross-sectional view of monolithic SiC samples after steam oxidation at 1800ºC for 7 h showing bubble formation (see arrows) that are nucleating at the SiC/SiO$_2$ interface and EDS maps of O, Si and C, of the same area.

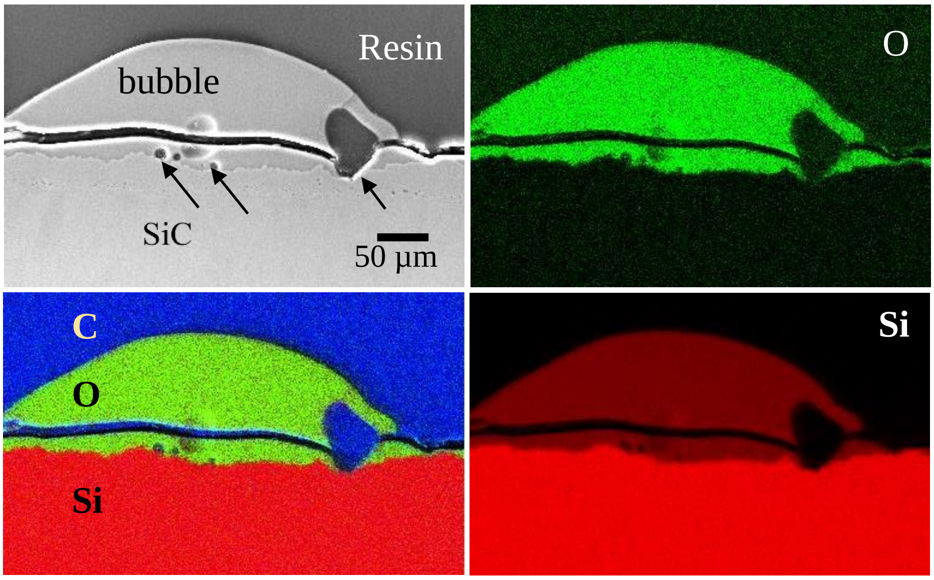

Figure 6. SEM images from a cross-sectional view of monolithic SiC samples showing the oxide layer formed after steam oxidation at (a) 1400, (b) 1600, (c) 1700 and (d) 1800ºC for 7 h.

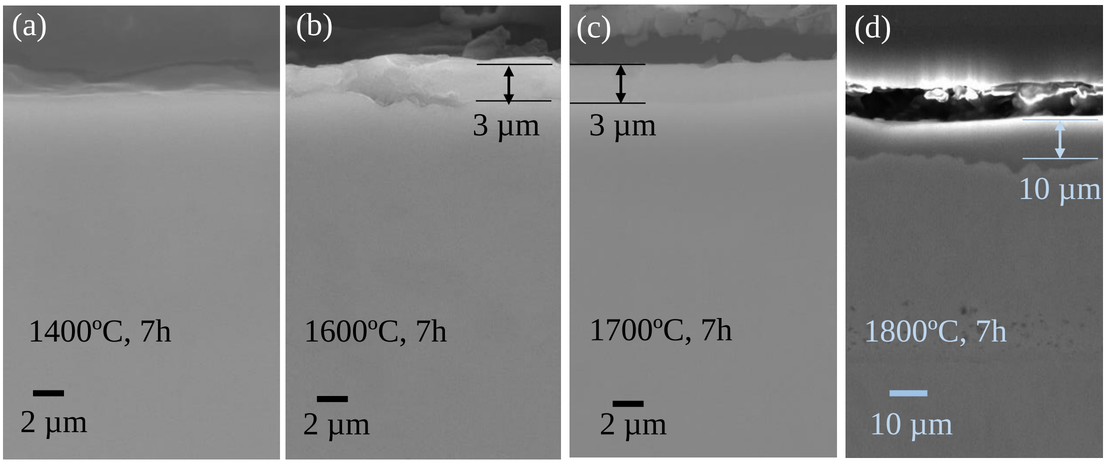

Figure 7. XRD patterns of monolithic SiC samples before and after steam oxidation at 1400-1800°C for 7 h.

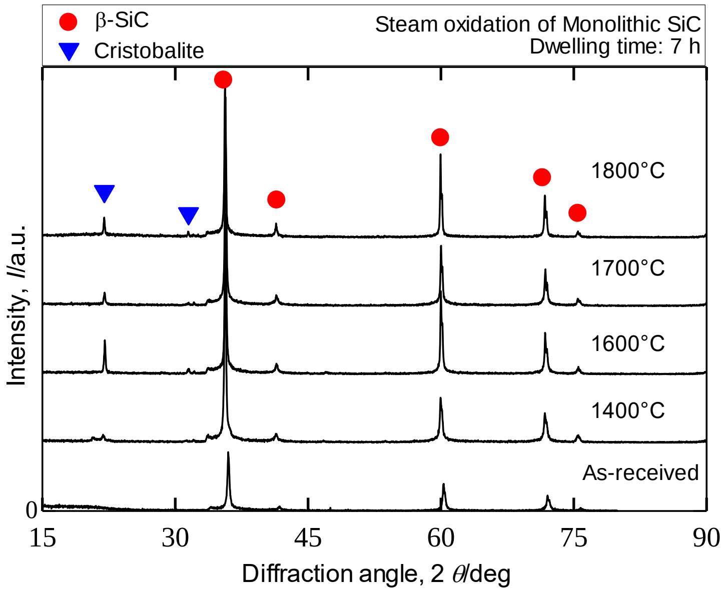

Figure 8. Mass change of monolithic SiC samples as a function of exposure time in steam in the temperature range of 1400-1800°C. The error bars on the points below are smaller than the dots used in the graph

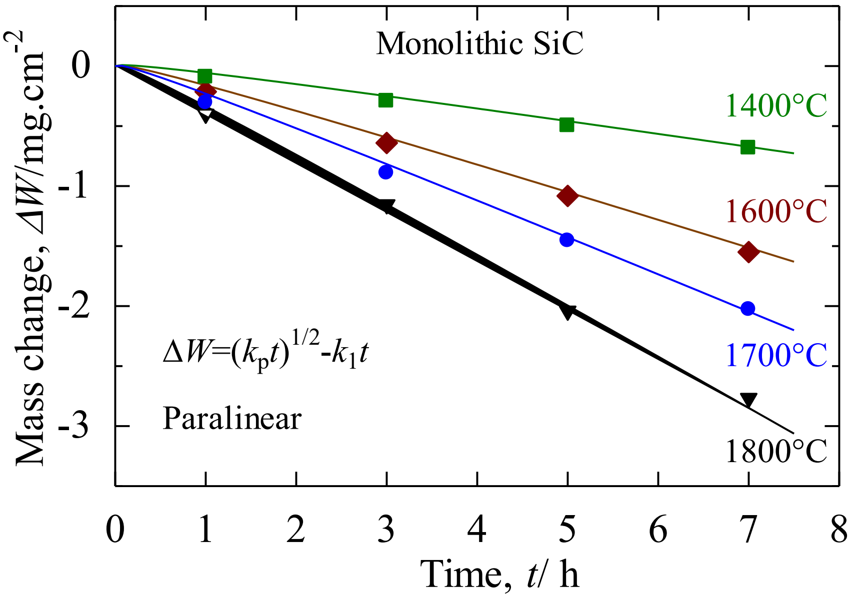

Figure 9. Temperature dependence of parabolic rate constants for steam oxidation of SiC in comparison with previous reports.

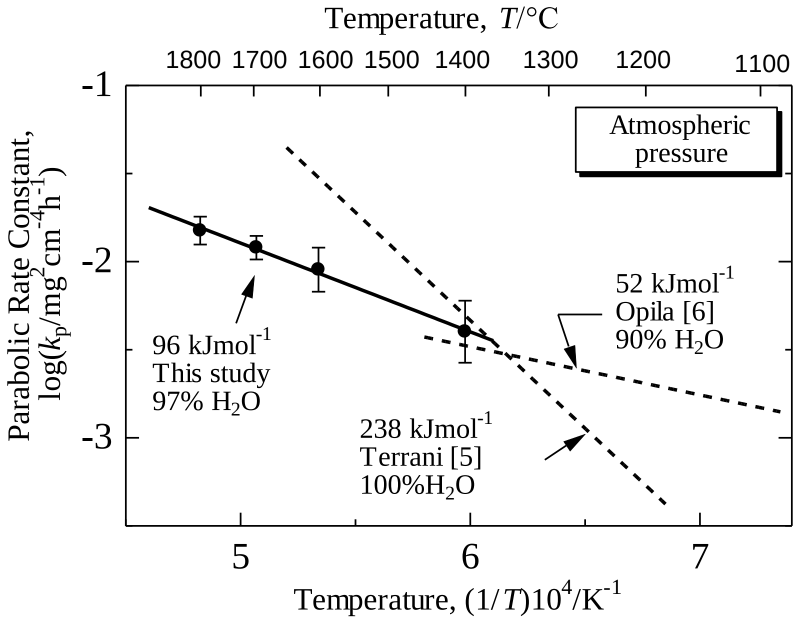

Figure 10. Linear volatilization rate constant derived from this study in comparison with the data reported by Terrani [5] in a study using thermogravimetry and high-temperature furnace tests conducted at lower temperatures.

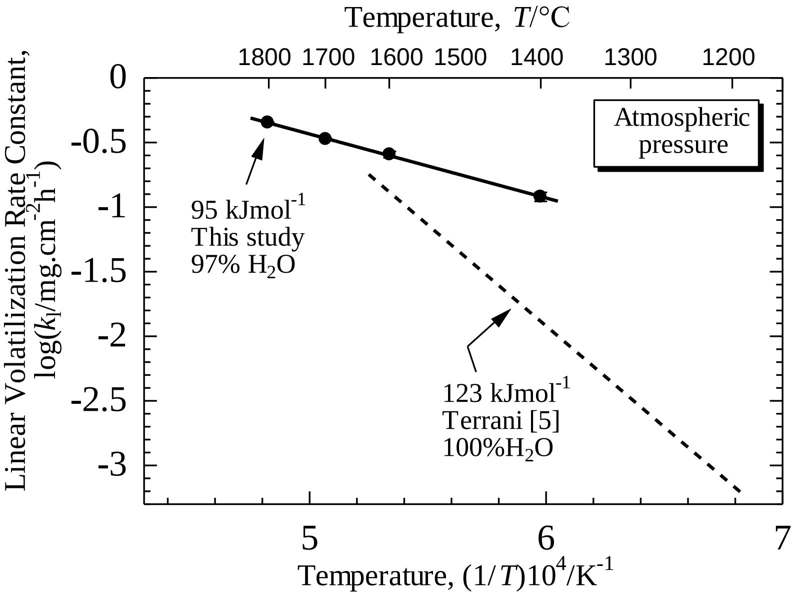

Figure 11. Formation rate and volatilization rate of SiO_2 as a function of time at 1800ºC.

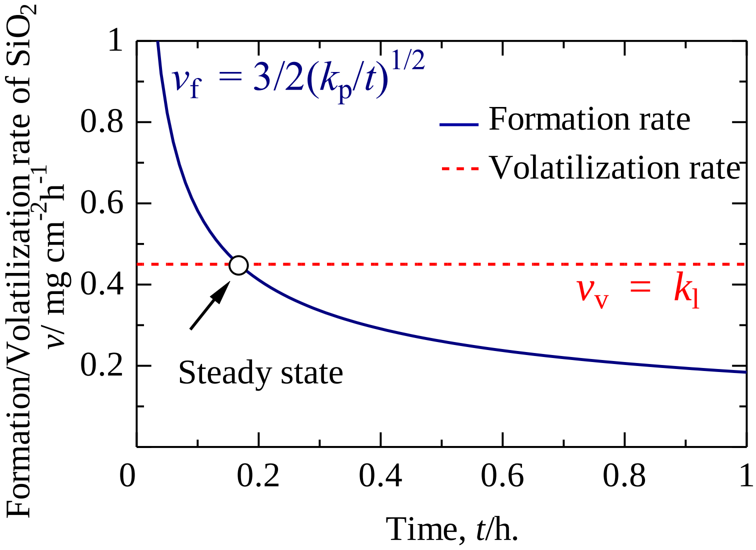

Figure 12. In-situ observation of bubble formation on a SiC sample during a preliminary test at 1800°C in steam atmospheres.

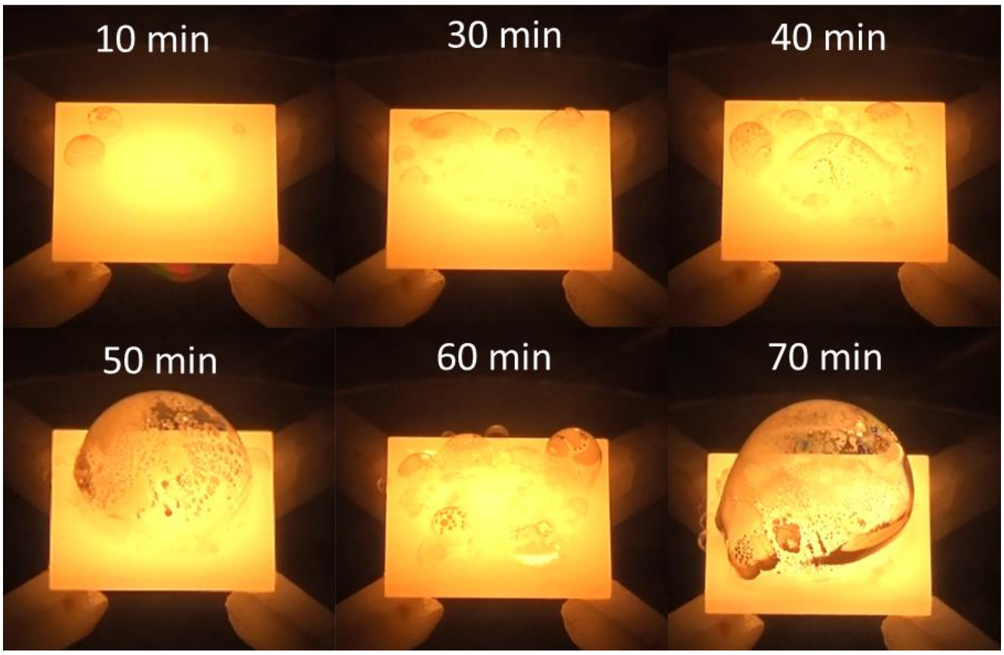

Figure 13. Depiction of bubble formation during steam oxidation of SiC at temperatures below and above SiO_2 melting/softening points between 1700°C and 1800°C.