

Paralinear Oxidation of CVD SiC in Simulated Fuel-Rich Combustion

Dennis S. Fox,* Elizabeth J. Opila,*,[†] and Raiford E. Hann*

Glenn Research Center at Lewis Field, National Aeronautics and Space Administration, Cleveland, Ohio 44135; and Department of Chemical Engineering, Cleveland State University, Cleveland, Ohio 44115

The oxidation kinetics of CVD SiC were measured by thermogravimetric analysis (TGA) in a $4H_2\cdot12H_2O\cdot10CO\cdot7CO_2\cdot67N_2$ gas mixture flowing at 0.44 cm/s at temperatures between 1300° and 1450°C in fused quartz furnace tubes at 1 atm total pressure. The SiC was oxidized to form solid SiO₂. At \geq 1350°C, the SiO₂ was in turn volatilized. Volatilization kinetics were consistent with the thermodynamic predictions based on SiO formation. These two simultaneous reactions resulted in overall paralinear kinetics. A curve fitting technique was used to determine the linear and parabolic rate constants from the paralinear kinetic data. Volatilization of the protective SiO₂ scale resulted in accelerated consumption of SiC. Recession rates under conditions more representative of actual combustors were estimated from the furnace data.

I. Introduction

THE low-density and high-temperature capabilities of SiC in both monolithic and composite forms make it a candidate material for aircraft turbine engine combustion applications. In order for SiC-based materials to be feasible in combustion environments, their behavior under fuel-lean and fuel-rich conditions must be determined. The equivalence ratio (ϕ) is the amount of fuel used in a combustion application expressed as a fraction of the stoichiometrically exact amount of fuel at which complete combustion occurs to form only CO2 and H2O. Many applications operate under fuel-lean conditions ($\phi < 1$). Some advanced designs also incorporate fuel-rich operation ($\phi > 1$). Jacobson¹ has calculated equilibrium products for Jet A aviation fuel $(CH_{1.9185})$ as a function of ϕ . At $\phi = 1.4$ (fuel-rich) and a temperature of 1400°C, the resulting gas composition is $\sim 4H_2 \cdot 13H_2 \circ 10C \circ 7C \circ 2 \cdot 66 \circ N_2$. The mole fraction of oxygen is $\sim 1.5 \times 10^{-9}$. In this fuel-rich environment, active oxidation is not expected, because the oxidants H2O and CO₂ are present. As is shown, SiC exhibits paralinear kinetics in the fuel-rich gas. This results from the formation of SiO₂ and simultaneous volatilization of the oxide.

(1) Chemical Reactions

The reaction of SiC with oxygen to form SiO₂ is welldocumented and discussed in detail in Ref. 1. However, oxygen is not present in the reaction gas in this study. The gas mixture does contain, however, the oxidants $H_2O(g)$ and CO_2 . SiC oxidizes according to the following reactions:

$$SiC(s) + 3H_2O(g) = SiO_2(s) + CO(g) + 3H_2(g)$$
 (1)

$$\operatorname{SiC}(s) + 3\operatorname{CO}_2(g) = \operatorname{SiO}_2(s) + 4\operatorname{CO}(g)$$
(2)

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The formation of SiO_2 via Eq. (1) is well-documented.^{2–7} Antill and Warburton,² as well as Opila and Nguyen,⁸ have determined that SiO_2 formation from Eq. (2) is negligible compared with Eq. (1).

In a gas that contains H₂ and/or CO, reduction of SiO₂ is anticipated.⁹⁻¹⁵ Tso and Pask¹³ observed linear weight losses from the reaction of fused SiO₂ with H₂ at 1300° and 1400°C. This weight loss was attributed to the formation of SiO(g), with the apparent activation energy for the reaction being 343 kJ/mol. Misra¹⁵ determined the chemical stability of SiO₂ in H₂ and H₂/H₂O(g) at 100 kPa system pressure using thermochemical analysis/equilibrium calculations. Below 1100 K (827°C), SiH₄(g) formation was expected from the reaction of H₂ with SiO₂, although the equilibrium partial pressures were quite low (<10⁻² Pa). Above 1100 K, SiO(g) formation was favored, with partial pressures of 10⁻¹ Pa at 1300°C and 1 Pa at 1450°C calculated. In H₂ + H₂O atmospheres, SiO(g) was the predominant gaseous species at temperatures >1200 K (927°C). The equilibrium partial pressure of SiO(g) decreased with increased moisture content and increased with increased temperature.

Two SiO_2 reduction reactions that are possible in the fuel-rich gas composition used in this study are

$$\operatorname{SiO}_2(s) + \operatorname{H}_2(g) = \operatorname{SiO}(g) + \operatorname{H}_2\operatorname{O}(g)$$
(3)

$$\operatorname{SiO}_2(s) + \operatorname{CO}(g) = \operatorname{SiO}(g) + \operatorname{CO}_2(g)$$
(4)

These reactions result in a linear weight loss, with the linear rate constant (k_1) reported in oxide thickness with time $(\mu m/h)$ or specific weight with time $(mg/(cm^2 \cdot h))$.

In addition to the above reactions, SiO_2 can also be attacked by the $H_2O(g)$ present in the fuel-rich gas mixture. Brady¹⁶ proposed the following reactions from the reaction of quartz by highpressure steam:

$$\operatorname{SiO}_2(s) + \operatorname{H}_2\operatorname{O}(g) = \operatorname{SiO}(\operatorname{OH})_2(g)$$
(5)

$$\operatorname{SiO}_2(s) + 2\operatorname{H}_2\operatorname{O}(g) = \operatorname{Si}(\operatorname{OH})_4(g)$$
(6)

$$2SiO_{2}(s) + 3H_{2}O(g) = Si_{2}O(OH)_{6}(g)$$
(7)

Hashimoto¹⁷ studied the reaction of SiO₂ and H₂O(g) at 1100°– 1500°C using a transpiration technique at 100 kPa total pressure. Because the amount of volatilization was found to be proportional to the square of the partial pressure of H₂O(g), he concluded that Si(OH)₄(g) was formed (Eq. (6)). Hildenbrand and Lau¹⁸ used effusion-beam mass spectrometry to study the reaction of SiO₂(*l*) and H₂O(g) at 1963–2065 K (~1690°–1790°C) under vacuum conditions. The partial pressure of H₂O(g) was \leq 5 Pa. The gaseous species SiO(OH)₂ (Eq. (5)) and SiO(OH) were detected. The reaction by which the latter formed is

$$\operatorname{SiO}_{2}(s) + \frac{1}{2}\operatorname{H}_{2}\operatorname{O}(g) = \operatorname{SiO}(\operatorname{OH})(g) + \frac{1}{4}\operatorname{O}_{2}(g)$$
 (8)

Opila and Hann¹⁹ found that CVD SiC exhibits paralinear oxidation kinetics in a 0.5 atm $H_2O-0.5$ atm O_2 environment between 1200° and 1400°C. A SiO₂ scale formed via Eq. (1). The volatilization reaction of SiO₂ with H_2O was consistent with Si(OH)₄ formation. Subsequently, Opila *et al.*²⁰ used a unique

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^{*}Resident Research Associate, Cleveland State University, Cleveland, OH.

high-pressure mass spectrometer to determine the volatile species formed from the reaction of $H_2O(g)$ in oxygen and SiO_2 at 100 kPa between 1200° and 1400°C. The primary vapor species was $Si(OH)_4$, with $SiO(OH)_2$ also detected.

In summary, a number of oxidation and volatilization reactions can occur in a fuel-rich environment. Oxidation of SiC by $H_2O(g)$ results in SiO₂ formation. Volatilization of the SiO₂ can occur by reaction with H_2/CO to form SiO and/or by reaction with H_2O to form primarily Si(OH)₄. The combination of these reactions result in paralinear kinetics.

(2) Paralinear Kinetics

Tedmon²¹ developed a mathematical expression for paralinear oxide scale growth kinetics observed in Fe–Cr alloys. In that system, oxidation results in $Cr_2O_3(s)$ formation, with concurrent reaction of the oxide with O_2 to form $CrO_3(g)$. The equation can be used to describe the paralinear kinetics that occur in the SiC–H₂O–O₂ system,¹⁹ as well as the system in this paper. The SiO₂ scale growth kinetics are given by

$$t = \frac{k'_{\rm p}}{2(k_{\rm i}')^2} \left[\frac{-2k'_{\rm i}x}{k'_{\rm p}} - \ln\left(1 - \frac{2k'_{\rm i}x}{k'_{\rm p}}\right) \right]$$
(9)

where *t* is the exposure time, k'_p the oxidation parabolic rate constant (in units of oxide thickness squared versus time, $\mu m^2/h$), k'_1 the volatilization linear rate constant (μ m/h), and *x* the oxide thickness. There is a certain time during the oxidation exposure that the SiO₂ scale reaches a constant equilibrium thickness, $x_1 = k'_p/2k'_1$. This occurs when the rate of oxidation at the interface to form SiO₂ becomes equivalent to the rate of SiO₂ volatilization at the sample surface.

Paralinear kinetics of SiC can be followed using thermogravimetric analysis (TGA). Weight changes due to both SiO_2 growth and volatilization are measured. Weight-change kinetics can be described by

$$t = \frac{\alpha^2 k_{\rm p}}{2(k_{\rm l})^2} \left[\frac{-2k_{\rm l}\Delta w_{\rm l}}{\alpha k_{\rm p}} - \ln\left(1 - \frac{2k_{\rm l}\Delta w_{\rm l}}{\alpha k_{\rm p}}\right) \right]$$
(10)

$$\Delta w_2 = -\beta k_1 t \tag{11}$$

where $\alpha = MW_{SiO_2}/(MW_{O_2}-MW_C)$ and $\beta = MW_{SiC}/MW_{SiO_2}$ (where MW is molecular weight), k_p is the oxidation parabolic rate constant in units of specific weight squared versus time (mg²/ (cm⁴·h)), k_1 the volatilization linear rate constant (mg/(cm²·h)), Δw_1 the weight gain from SiO₂ growth, and Δw_2 the weight loss from SiO₂ volatilization. At long times, when the constant equilibrium thickness of the SiO₂ scale is achieved, the weight loss is described by Eq. (11) alone.

The purpose of this paper is to assess the paralinear kinetics of CVD SiC in a simulated fuel-rich environment at $1300^{\circ}-1450^{\circ}$ C. Both the parabolic oxidation rate constant (k_p) for SiO₂ formation and the linear volatility rate constant (k_1) for SiO₂ volatilization are determined. Material recession rates are extrapolated from the furnace data to more realistic, high-velocity conditions.

II. Experimental Procedure

The material used in this study is commercially available bulk CVD β -SiC (Bomas Machine Specialties, Somerville, MA). Atomic emission spectrometry shows some trace impurities are present: <0.01% Be, <0.01% Cu. The SiC was slightly siliconrich (Si_{1.03}C). Sample size was ~2.5 cm × 0.7 cm × 0.3 cm. This yielded a surface area of ~5.6 cm². Specimens were cleaned using a detergent solution, distilled water, acetone, and alcohol.

Oxidation experiments were conducted in a vertical tube furnace at four temperatures: 1300°, 1350°, 1400°, and 1450°C. Fused quartz furnace tubes (Quartz Scientific, Fairport Harbor, OH) were used. Samples were suspended from a sapphire hook. The oxidation kinetics were followed using TGA. Weight change was continuously monitored with a recording microbalance (Model C-1000, Cahn Instruments, Inc., Cerritos, CA).

Alumina furnace tubes were not used because impurities (primarily sodium) could significantly enhance oxidation of SiC.²² In using fused quartz with a reactive gas, one should realize that volatilization of the tube material also occurs and could saturate the gas stream with volatile products and influence the reaction kinetics of the oxidized SiC sample. The 2.5 cm long SiC sample was placed in the center of the ~10 cm long hot zone. In retrospect, a position near the upstream edge of the hot zone would have been more prudent. Formation of volatile products from the quartz tube would then occur downstream of the specimen.

A schematic of the experimental apparatus has been published previously.7 It is based on a design by Belton and Richardson.23 Experiments were conducted at 100 kPa (1 atm) total pressure. A gas mixture composed of 5H2·11CO·8CO2·76N2, flowing at 100 cm³/min, was passed through a presaturator containing deionized water held at a temperature of 80°C. The gas was then passed through a saturator and held in a water bath at a temperature of 49.7°C. Condensation of the excess water in the gas stream occurred, resulting in a pH₂O of 12%. This process resulted in a furnace environment of $\sim 4.4 H_2 \cdot 12.0 H_2 O \cdot 9.7 CO \cdot 7.0 CO_2 \cdot 66.9 N_2$. This synthetic fuel-rich composition closely corresponded to that calculated from the combustion of Jet A fuel at $\phi = 1.4$. The 100 cm³/min gas flow rate corresponded to a velocity of 0.44 cm/s in the 2.2 cm ID quartz furnace tube. A counterflow of N₂ in the microbalance chamber (10 cm³/min) was used to protect it from the reaction gas. Experiments were initiated by raising the furnace temperature, already at the desired test temperature, around the sample. Heat lamps were then placed around the lower portion of the quartz furnace tube to keep the $H_2O(g)$ entrained in the gas. Heating tape was used on the glass tubes of the saturation system for the same reason.

One concern is that the gas mixture could further equilibrate and/or change composition in the TGA furnace at $1300^{\circ}-1450^{\circ}$ C. Using a free-energy minimization thermodynamics program (Chemsage, GTT Technologies, Sweden), the inlet fuel rich-gas composition is calculated and found to remain essentially constant across the temperature range of $600^{\circ}-1700^{\circ}$ C. At temperatures $<600^{\circ}$ C, changes in gas composition are expected to be kinetically limited.

Two separate types of TGA experiments were conducted. In the first, as-received SiC was exposed to the fuel-rich gas. Weight change versus time was measured for exposure times of ~100 h. Two or three samples were typically run at each of the four test temperatures. For those samples that exhibited paralinear kinetics, the parabolic and linear rate constants (k_p and k_1) for SiO₂ formation and volatilization were determined. This was done by a best fit of the paralinear kinetic model discussed above using a nonlinear least squares analysis to the TGA data. This model is presented in detail in Ref. 19.

As mentioned above, at long times the linear rate loss dominates the paralinear kinetics. However, at temperatures $\leq 1400^{\circ}$ C, the time to reach that point is >100 h. Therefore, a second type of experiment was conducted in which the SiC coupons were first oxidized for 100 h in pure, dry oxygen in the TGA furnace. The gas was then switched over to the fuel-rich composition for a second ~ 100 h exposure. In this way, k_1 could be measured directly. These k_1 values for SiC recession could then be compared with the linear rate constants for SiO₂ volatilization determined in the first type of experiment.

After TGA exposure of the as-received samples, the surface oxide was characterized by XRD. Oxide morphology was then studied using SEM (Model JSM-840A, JEOL, Tokyo, Japan). Polished cross sections on reacted samples were prepared to measure the SiO₂ scale thickness. One of the 2.5 cm \times 0.35 cm edges was polished to 15 µm for these observations. This SEM technique entailed oxide measurements every 1 mm along one of the 25 mm edges. The average thickness for each sample was reported. A National Bureau of Standards calibration standard was used to determine that the measured thickness in this SEM was \sim 5.3% larger than true thickness.

III. Results

(1) As-Received Samples

Thermogravimetric results for the exposure of two as-received CVD SiC samples in 100% oxygen at 1400°C are plotted in Fig. 1. The kinetics are parabolic, with the average $k_p = 1.91 \times 10^{-4}$ mg²/(cm⁴·h). The results for two as-received samples exposed in the fuel-rich gas composition at 1400°C are also plotted. The kinetics for these two samples are paralinear. The difference between the two sets of traces is apparent. Similar weight gains are observed in the first 10–20 h. The weight gain at longer times in the fuel-rich experiment is of lower magnitude compared with the oxygen exposure. This is due to the volatilization of the SiO₂ scale that occurs concurrently with the oxidation. The noise in the kinetic curves is due to the high sensitivity of the microbalance scale required to measure the very small weight changes (~0.1 mg/cm²).

Figure 2 contains representative TGA traces across the temperature range of 1300°–1450°C for single, as-received samples exposed in the fuel-rich gas. The temperature dependence is quite apparent. At 1300°C, the kinetics are parabolic, with the average $k_p \pm 1\sigma = (2.23 \pm 1.53) \times 10^{-4} \text{ mg}^2/(\text{cm}^4\cdot\text{h})$. The kinetics at 1350°–1450°C are paralinear, with the linear rate constant dominating quite early in the reaction at 1450°C. It should be noted that the kinetics for the 1400°C sample in Fig. 2 were measured for 756 h, but only the first 500 h are shown.

Once the paralinear nature of the reaction was established, k_p and k_1 could be determined. An example of the fit of the model to the data is shown in Fig. 3. For this as-received sample exposed to the fuel-rich environment at 1400°C, the rate constants determined from the analysis were k_p of $5.26 \times 10^{-4} \text{ mg}^2/(\text{cm}^4 \text{-h})$, and k_1 from SiO₂ volatility of $2.09 \times 10^{-3} \text{ mg}/(\text{cm}^2 \text{-h})$.

The parabolic and linear rate constants for each as-received sample exhibiting paralinear kinetics are listed in Table I. In addition, the average calculated limiting SiO₂ thickness (x_1) at each temperature is also listed. For cristobalite, this is determined by multiplying $k_p/2k_1$ (mg/cm²) by a factor of 12.9.¹⁹

(2) Preoxidized Samples

As mentioned, a second set of experiments was conducted in the TGA. As-received samples were first exposed in dry oxygen for 100 h in the microbalance furnace. The gas was then switched to the fuel-rich composition. A kinetic trace for one such experiment at 1350°C is shown in Fig. 4. A thick SiO₂ scale (\sim 1.9 µm) was formed in the first 100 h. Note that this thickness was near the limiting SiO₂ thickness, $x_1 (\pm 1\sigma)$ of 2.15 (\pm 0.48) µm, calculated for the three as-received samples exposed at this temperature. Because no further appreciable scale growth should occur, the linear rate constant could be determined from a simple linear regression through the data



Fig. 1. Experimentally determined weight-change kinetics for asreceived CVD SiC at 1400°C: (A) parabolic kinetics in 100% oxygen flowing at 0.44 cm/s, and (B) paralinear kinetics in $4H_2 \cdot 12H_2 O \cdot 10CO \cdot 7CO_2 \cdot 67N_2$ (fuel-rich gas composition) flowing at 0.44 cm/s.



Fig. 2. Experimentally determined weight-change kinetics for single specimens of as-received CVD SiC at 1300° to 1450° C in $4H_2$ · $12H_2$ O·10CO· $7CO_2$ · $67N_2$.



Fig. 3. Paralinear kinetics for CVD SiC exposed in fuel-rich environment at 1400°C ((—) fit of data to paralinear kinetic model by nonlinear least-squares analysis).

acquired during the fuel-rich exposure (second 100 h). The linear rate constants (mg SiC/(cm²·h)) determined from this set of experiments are summarized in Table II. SiO₂ volatility at 1300°C was too low to be accurately measured within the sensitivity limit of the TGA. A comparison of the average k_1 values from the as-received SiC experiments with those from preoxidized SiC experiments is found in Table III. The agreement of the k_1 values between the two techniques is quite good.

(3) XRD and Oxide Measurement

After TGA exposure of the as-received samples, the surface oxide was characterized by XRD. In all cases, the major crystalline phase was cristobalite. Very minor tridymite peaks were also observed with the 1400° and 1450°C samples. Pronounced tridymite peaks were only observed with the 756 h, 1400°C specimen. Tridymite formation likely resulted from the sapphire sample hanger. The surface morphology of a typical SiO₂ scale is shown in Fig. 5(A). The cracks are due to the transformation of β -to- α cristobalite on cooling.²⁴

After X-ray analysis, polished cross sections of each of the exposed as-received samples were then prepared. The SiO₂ scale thicknesses were measured using SEM and the 5.3% calibration correction. An example of such a cross section is shown in Fig. 5(B). The oxide thickness for this sample, exposed at 1400°C for 756 h, was determined to be 2.18 (\pm 0.24) µm. The results for all

 Table I.
 Parabolic and Linear Rate Constants for As-Received Samples

 Exposed to a Fuel-rich Environment

Temperature (°C)	Exposure time (h)	$k_{\rm p} ({\rm mg}^2 { m SiO}_2/({ m cm}^4 { m \cdot h}))$	$(\text{mg SiO}_2/(\text{cm}^2\cdot h))$	Average calculated x_1 (µm)
1350	100 162 175 [‡]	$\begin{array}{c} 2.87 \times 10^{-5} \\ 2.05 \times 10^{-4} \\ 1.08 \times 10^{-4} \end{array}$	$\begin{array}{c} 7.06 \times 10^{-5} \\ 6.05 \times 10^{-4} \\ 4.22 \times 10^{-4} \end{array}$	2.15
1400	$96^{\dagger} \\ 99^{\dagger} \\ 100 \\ 101 \\ 756^{\ddagger}$	$\begin{array}{c} 1.97 \times 10^{-4} \\ 5.26 \times 10^{-4} \\ 1.91 \times 10^{-4} \\ 2.41 \times 10^{-4} \\ 3.56 \times 10^{-5} \end{array}$	$\begin{array}{c} 9.31 \times 10^{-4} \\ 2.09 \times 10^{-3} \\ 1.03 \times 10^{-3} \\ 8.27 \times 10^{-4} \\ 2.31 \times 10^{-4} \end{array}$	1.41
1450		$\begin{array}{c} 1.02 \times 10^{-5} \\ 6.94 \times 10^{-5} \end{array}$	3.00×10^{-3} 3.22×10^{-3}	0.08

Note: Paralinear kinetics for the 1400°C samples are shown in [†]Fig. 1 and [‡]Fig. 2.



Fig. 4. Weight-change kinetics for preoxidation experiment on CVD SiC at 1350° C. Parabolic weight gain is observed from formation of SiO₂ in the first 100 h in 100% O₂. Volatility of SiO₂ is evident from exposure in the fuel-rich gas mixture at t > 100 h.

Table II. Linear Rate Constants from Samples Preoxidized for 100 h in Oxygen and Subsequently Exposed to the Fuel-Rich Environment

Temperature (°C)	Fuel-rich exposure time (h)	$k_1 (mg SiC/(cm^2 h))$
1350	96 96 114	$\begin{array}{c} 1.17 \times 10^{-4} \\ 3.66 \times 10^{-4} \\ 2.35 \times 10^{-4} \end{array}$
1400	65 100 100 140	$\begin{array}{c} 4.31 \times 10^{-4} \\ 5.75 \times 10^{-4} \\ 1.05 \times 10^{-3} \\ 7.50 \times 10^{-4} \end{array}$
1450	95 110 194	$\begin{array}{c} 2.13 \times 10^{-3} \\ 1.01 \times 10^{-3} \\ 9.25 \times 10^{-4} \end{array}$

the oxide measurements made on as-received CVD SiC exposed to the fuel-rich environment are listed in Table IV.

IV. Discussion

(1) Paralinear Behavior

The paralinear nature of the reaction kinetics of as-received SiC with the fuel-rich environment is obvious from Figs. 1–3. Comparison of experimentally measured weight gain (TGA) with that

 Table III.
 Average Linear Rate Constants for As-received and Preoxidized Samples

Temperature	As-received samples	Preoxidized samples
(°C)	(mg SiC/(cm ² ·h)) [†]	(mg SiC/(cm ² ·h))
1350 1400 1450	$\begin{array}{c} (2.45 \pm 1.82) \times 10^{-4} \\ (6.80 \pm 0.47) \times 10^{-4} \\ (2.07 \pm 0.01) \times 10^{-3} \end{array}$	$\begin{array}{c} (2.43 \pm 1.25) \times 10^{-4} \\ (7.15 \pm 2.88) \times 10^{-4} \\ (1.34 \pm 0.08) \times 10^{-3} \end{array}$

[†]Note: For comparison, k_1 values for as-received samples (in mg SiO₂/(cm²-h), Table I) are multiplied by 2/3 (40 g/mol SiC ÷ 60 g/mol SiO₂). Uncertainties reported for k_1 are 1 σ .

calculated from measured oxide thickness (SEM) provides additional evidence (Table IV). For oxidation alone, the weight gain and oxide thickness (x) are related by the expression

$$\Delta \text{wgt} \times 12.9 = x \tag{12}$$

when cristobalite is formed, where Δ wgt is in units of mg/cm², and x in μ m. In all but two cases, the measured oxide thickness is greater than that predicted from the weight gains. It is especially clear from both the long-term 1400°C and the two 1450°C experiments. Although an oxide is continually being formed, reduction of the SiO₂ by H₂ and CO is also occurring. This results in recession of, and weight loss in, the underlying SiC substrate.

The average limiting SiO₂ thickness estimated using $k_{\rm p}/2k_{\rm l}$ (Table I) for each sample is also shown in Table IV. For the samples exposed at 1350° and 1400°C for 100 h, the measured thickness is below the limiting oxide thickness because of the short exposure time. Using the average k_p and k_l at each temperature in Eq. (9), it is estimated to take 3500, 1500, and 7 h at 1350°, 1400°, and 1450°C, respectively, to reach x_1 . Note, however, that SiO₂ thickness on the 756 h specimen is 50% thicker than the calculated x_1 (2.2 versus 1.4 μ m). Also, the measured SiO₂ thickness for the two 1450°C samples is \sim 1.5 μ m, much thicker than the calculated limiting thickness of $\sim 0.1 \ \mu m$. It is believed that the parabolic rate constants are greatly underestimated in the nonlinear least squares analysis of the TGA data at 1450°C and somewhat underestimated at 1400°C (Table I). This is because the volatility of the SiO₂ dominates the kinetics very early in these high-temperature tests, resulting in an inaccurate determination of $k_{\rm p}$. Hence x_1 (= 12.9 × $k_{\rm p}/2k_{\rm l}$) is thought to be underestimated. However, it should be emphasized that the more important parameter derived from the paralinear modeling is k_1 . The recession calculations described below are based on the SiO₂ volatilization kinetics.

(2) Linear Weight Loss Rates

The volatility fluxes determined experimentally are plotted on an Arrhenius diagram in Fig. 6. The activation energy from a fit of all the data points is calculated to be 473 \pm 195 kJ/mol (95% confidence interval). This is in reasonable agreement with the E_a of



Fig. 5. CVD SiC after exposure at 1400°C in fuel-rich environment for 758 h: (A) surface morphology of SiO₂ scale and (B) polished cross section used for SiO₂ thickness measurement.

Temperature (°C)	Time (h)	Δ wgt exp (mg/cm ²)	$x \; (\mu m)^{\dagger}$	$\begin{array}{c} \Delta \text{wgt} \\ \text{from } x \\ (\text{mg/cm}^2)^{\ddagger} \end{array}$	$\Delta wgt \\ exp/\Delta wgt \\ x$
			2.15 µm [§]		
1350	100	0.063	$1.10 \pm 0.27 \ \mu m$	0.085	0.74
1350	162	0.099	$1.19 \pm 0.20 \mu m$	0.092	1.08
1350	175	0.088	$1.26 \pm 0.14 \ \mu m$	0.098	0.93
			1.41 um [§]		
1400	96	0.082	$1.03 \pm 0.15 \mu m$	0.080	1.03
1400	99	0.071	$1.05 \pm 0.14 \mu m$	0.081	0.88
1400	100	0.052	$0.90 \pm 0.07 \mu m$	0.070	0.74
1400	101	0.082	$1.48 \pm 0.31 \mu m$	0.115	0.71
1400	756	0.012	$2.18 \pm 0.24 \mu m$	0.169	0.07
			0.08 um [§]		
1450	80	-0.160	$1.55 \pm 0.23 \mu m$	0.120	-1.33
1450	100	-0.149	$1.50 \pm 0.21 \ \mu m$	0.116	-1.28

Table IV. Comparison of Experimentally Measured Sample Weight Change (TGA) with that Calculated from the Measured SiO₂ Thickness (SEM) for As-received CVD SiC after Exposure in the Fuel-Rich Environment

[†]Uncertainties reported for oxide thickness are 1σ for 25 measurements, spaced 1 mm apart, along the SiC/SiO₂ interface. [‡]Conversion from measured *x* to Δ wgt assumes density of cristobalite (2.32 g/cm³). [§]Indicates average calculated limiting SiO₂ scale thickness at each temperature.

343 kJ/mol measured by Tso and Pask 13 from the reaction of fused SiO_2 with H_2 at 1300°–1400°C to form SiO.

The measured flux can be compared with the calculated flux. The appropriate relation for the flux of the volatile species from a flat plate through a gaseous boundary layer under laminar flow conditions is:²⁵

$$J = \frac{0.664 \text{ Re}^{1/2} \text{Sc}^{1/3} D\rho}{L}$$
(13)

where *J* is the flux of volatile species from the specimen surface, Re the Reynolds number, Sc the Schmidt number, *D* the interdiffusion coefficient of the volatile species in the boundary layer, ρ the concentration of the diffusing gas species at the solid–gas interface, and *L* the characteristic position along the component length. The Re term is dimensionless; in a tube geometry, flow is laminar for Re < 2000.²⁶ Flow is laminar in the TGA experiments (Re ≈ 2.3). Using the appropriate definitions for Re and Sc, Eq. (13) becomes:

$$J = 0.664 \left(\frac{\rho' \nu L}{\eta}\right)^{1/2} \left(\frac{\eta}{\rho' D}\right)^{1/3} \frac{D\rho}{L}$$
(14)

where ρ' is the concentration of the major gas species and η the gas viscosity. Gas concentration is calculated using the ideal gas law.

When comparing the calculated boundary layer k_1 values with the experimental values, one should recognize that in doing boundary layer calculations, the boundary layer (δ) is defined as:²⁷

$$\delta = \frac{1.5L}{\text{Re}^{1/2}\text{Sc}^{1/3}}$$
(15)

For our sample length and linear gas velocity (0.4 cm/s), the calculated δ is 5.3 cm. However, the furnace tube radius of 1.1 cm fixes δ at <0.5 cm. Correcting the boundary layer calculation (Eq. (13)) for this geometry and gas flow rate results in about a factor of 5 increase in calculated k_1 values. The flux values calculated here have been corrected for the smaller boundary layer.

Measured thermodynamic data are available for SiO.²⁸ Hashimoto¹⁷ has measured data for Si(OH)₄. Krikorian²⁹ and Allendorf *et al.*³⁰ have calculated data for the Si-O-H system. Using these data sets in a free-energy minimization code (Chemsage, GTT Technologies, Sweden), one can calculate vapor pressures of Si-O-H species. For these calculations, SiO₂ (cristobalite) plus an initial gas composition of $4.5H_2 \cdot 10H_2 O \cdot 9.9 CO \cdot 7.2 CO_2 \cdot 68.4 N_2$ are used. The calculated vapor pressures of Si-O-H species are then used in the boundary layer diffusion model, and SiC mass loss rates are determined. The calculated mass loss rates are shown in Fig. 6.

Journal of the American Ceramic Society-Fox et al.



Fig. 6. Arrhenius plot summarizing linear weight-loss rates for CVD SiC under fuel-rich conditions ((---) measured rate and (---) calculated rates).

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The best agreement with the experimental data are for SiO as the primary volatile species ($E_a = 527 \text{ kJ/mol}$). When including JANAF data for SiO, Hashimoto's data for Si(OH)₄, and Allendorf's data for other Si-O-H species, SiO and Si(OH)₄ are predicted to form, with a small contribution of SiO(OH)₂ occurring at the highest temperatures. The calculated mass loss rates agree favorably with the experimental data, but the activation energy is low (220 kJ/mol). When including JANAF data for SiO, Hashimoto's data for Si(OH)₄, and Krikorian's data for other Si-O-H species, SiO(OH)₂ and SiO(OH) are predicted to form, with contributions of Si(OH)₄ at the lowest temperatures. However, calculated mass loss rates are ~10 times larger than those measured experimentally. It should also be noted that calculated thermodynamic data by Allendorf³⁰ find that the species SiO(OH)₂ and SiO(OH) (Fig. 6) are unimportant.

Thus the magnitude and temperature dependence of the measured flux is best described by SiO formation. However, formation of some Si-O-H species under these conditions cannot be ruled out. This is discussed in more detail in another publication.³¹ For the purposes of this paper, additional discussion considers only SiO formation.

(3) Material Recession and Life Prediction

Many combustion applications require components to be used for thousands of hours. If the component is fashioned from SiC and is operating in a fuel-rich environment, some concerns need to be addressed. The SiC is consumed because of continual oxidation by H_2O to form SiO₂. Because of the presence of H_2 and CO, volatilization of the protective SiO₂ also occurs. At times well before the limiting oxide thickness is achieved, the recession rate of the underlying SiC can be approximated by the linear SiO₂ volatility rate alone.

The measured fluxes from TGA experiments are much lower than one would expect in actual combustion applications. This is because of the low gas flow rate (0.44 cm/s) and the low system pressure (100 kPa). At higher flow rates and system pressures, flux estimates can be made by using a simplified form of Eq. (14).¹⁹ For this approximation, the diffusion coefficient (*D*) is proportional to $1/p_{total}$, and ρ' is proportional to p_{total} . Assuming that SiO(g) is the only volatile species and is formed by the reaction

$$2SiO_{2}(s) + H_{2}(g) + CO(g)$$

= 2SiO(g) + H_{2}O(g) + CO_{2}(g) (16)

then ρ is proportional to p_{SiO} , which can be calculated from the equilibrium constant

$$p_{\rm SiO} = K_{\rm EQ}^{1/2} \left(\frac{p_{\rm CO} p_{\rm H_2}}{p_{\rm CO_2} p_{\rm H_2O}} \right)^{1/2} \tag{17}$$

The variation of k_1 can then be shown as (from Eq. (14))

$$v_1 \propto \frac{v^{1/2}}{p_{\text{total}}^{1/2}} \left(\frac{p_{\text{CO}} p_{H_2}}{p_{\text{CO}2} p_{\text{H}20}} \right)^{1/2}$$
(18)

Now assume that SiC is used under the following combustion conditions: $T = 1400^{\circ}$ C, $p_{total} = 1000$ kPa (10 atm), $\phi = 1.4$, and gas velocity = 20 m/s. Under these conditions, and assuming SiO is the only volatile species, the volatility rate would be about 67 times greater than that under the TGA conditions (1400°C, 100 kPa, $\phi = 1.4$, $v = 4.4 \times 10^{-3}$ m/s). This increase is because of much higher gas velocity ($v^{1/2}$ component in Eq. (18)). In doing such an estimation, one must keep in mind the significant temperature dependence of k_1 .

Once a mass flux is known, a calculation of SiC recession can be made. At 1400°C in the TGA experiments, the average k_1 is $\sim 1 \times 10^{-3}$ mg/(cm²·h). Extrapolating that value to the combustion conditions above, using a density value for SiC of 3.2 g/cm³, and again assuming SiO is the only volatile species, the resulting recession rate of SiC is calculated to be 2.1×10^{-5} cm/h (or 210 μ m in 1000 h). This rate is for laminar flow conditions. Under turbulent flow conditions, recession would be even greater.

A comparison can be made with the results of high-pressure burner rig (HPBR) testing of CVD SiC under fuel-rich conditions.^{31,32} Nominal fuel-rich combustion of aviation fuel at $\phi =$ 1.8–2.0 produced sample temperatures from 1200° to 1450°C. Standard operating pressure was 600–1000 kPa (6–10 atm), and gas velocity was 18–25 m/s. Linear SiC weight loss and surface recession rates were observed because of SiO₂ scale volatility. A fuel-rich material recession relationship was developed, applicable to any combination of HPBR conditions. Using the conditions of T = 1400°C, $p_{total} = 1000$ kPa, and gas velocity = 20 m/s, a recession rate of 940 µm/(1000 h) was extrapolated. This rate was 4 times higher than the calculated 210 µm/(1000 h) from the 100 kPa TGA data. It should be mentioned that, at the higher pressure in the burner rig, volatile species other than SiO became important. These included Si(OH)₄, SiO(OH)₂, and SiO(OH).³¹ The flow in the burner rig was complicated with respect to laminar or turbulent July 2000

flow conditions. Turbulent flow would increase the flux and corresponding recession rate.

It is clear that linear SiC weight loss and surface recession results from SiO_2 scale volatility in both the model fuel-rich environment in the TGA experiments, as well as in more realistic burner rig tests. A designer of SiC components for a fuel-rich application must, therefore, be aware that SiO_2 volatility occurs, and that significant amounts of substrate recession can occur after only hundreds of hours of exposure time.

V. Conclusions

SiC exhibits paralinear kinetics at $1350^{\circ}-1450^{\circ}C$ when exposed in a $4H_2 \cdot 12H_2O \cdot 10CO \cdot 7CO_2 \cdot 67N_2$ gas mixture flowing at 0.44 cm/s in a fused quartz furnace tube at 1 atm total pressure. The material is oxidized by $H_2O(g)$ to form solid SiO₂. The protective SiO₂ is in turn volatilized. The primary mechanism of SiO₂ volatilization under these conditions is consistent with SiO(g) formation. At long exposure times, the kinetics can be approximated by the linear rate constants from the volatilization reaction. As a result of this SiO₂ volatility, accelerated consumption of SiC occurs. Recession rates determined from the furnace experiments can be used to estimate SiC recession under more realistic combustion conditions. A SiC component must, therefore, be of a robust design in order for it to exhibit adequate durability for thousands of hours of operation in a fuel-rich combustion application.

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