HIGH TEMPERTURE CORROSION OF SILICON CARBIDE AND SILICON NITRIDE IN WATER VAPOR

Elizabeth J. Opila, Cleveland State University, Raymond C. Robinson, QSS Group. Inc., Michael D. Cuy, QSS Group. Inc., NASA Glenn Research Center, 21000 Brookpark Rd., Cleveland, OH 44135, USA

Silicon carbide (SiC) and silicon nitride (Si_3N_4) are proposed for applications in high temperature combustion environments containing water vapor. Both SiC and Si_3N_4 react with water vapor to form a silica (SiO_2) scale. It is therefore important to understand the durability of SiC, Si_3N_4, and SiO_2 in water vapor. Thermogravimetric analyses, furnace exposures and burner rig results were obtained for these materials in water vapor at temperatures between 1100 and 1450°C and water vapor partial pressures ranging from 0.1 to 3.1 atm. First, the oxidation of SiC and Si_3N_4 in water vapor is considered. The parabolic kinetic rate law, rate dependence on water vapor partial pressure, and oxidation mechanism are discussed. Second, the volatilization of silica to form $Si(OH)_4(g)$ is examined. Mass spectrometric results, the linear kinetic rate law and a volatilization model based on diffusion through a gas boundary layer are discussed. Finally, the combined oxidation and volatilization reactions, which occur when SiC or Si_3N_4 are exposed in a water vapor-containing environment, are presented. Both experimental evidence and a model for the paralinear kinetic rate law are shown for these simultaneous oxidation and volatilization reactions.

1. INTRODUCTION

SiC and Si_3N_4 are proposed for use in a variety of land-based power generation and aerospace propulsion applications that require material durability in combustion environments. These environments are typically complex high temperature gas mixtures that contain about ten percent water vapor as a product of hydrocarbon combustion[1]. The chemical durability of SiC and Si_3N_4 in water vapor is thus a key requirement for application of these materials.

SiC and Si_3N_4 undergo simultaneous oxidation and volatilization reactions in water vapor according to paralinear kinetics. It is important to understand the parametric dependence, (pressure, gas velocity, and temperature) of both oxidation and volatilization in water vapor so that predictions can be made for paralinear kinetics of SiC and Si_3N_4 in complex application environments. This paper reviews the basic mechanisms of oxidation and volatilization for SiC and Si_3N_4 in water vapor in terms of the parameters that describe the application environment. It also shows experimental evidence for these mechanisms and addresses the capability of experimental

techniques to accurately measure the kinetics of oxidation and volatilization for predictive purposes.

1.1 Oxidation of SiC and Si_3N_4 in water vapor

SiC and Si_3N_4 oxidize in water vapor to form a silica scale as given by the following reactions:

$$SiC + 3H_2O(g) = SiO_2 + CO(g) + 3H_2(g) \qquad [1]$$

$$Si_3N_4 + 6H_2O(g) = 3SiO_2 + 2N_2(g) + 6H_2(g) \qquad [2]$$
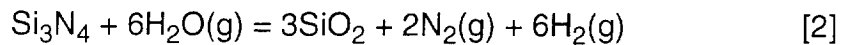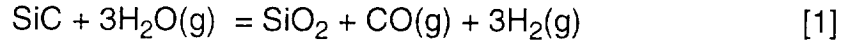
The oxidation of silica formers occurs by a parabolic oxidation process. The oxidation is limited by transport of oxidant through the silica scale so that oxide formation slows as the scale thickness increases. The experimentally determined parabolic oxidation rate, k_p, is given by the following expressions:

$$k_p = (\Delta wt)^2/t \quad or \quad k_p' = x^2/t \qquad [3]$$

where Δwt is the measured weight change, t is time, and x is oxide thickness.

It has been shown for oxidation of silicon that the oxidation rate increases in water vapor relative to oxygen due to the much higher solubility of water vapor in silica[2]. It is also known that the oxidation rate of silicon is limited by the transport of molecular water vapor through the silica scale[2] as described by the following power law:

$$k_p = P(H_2O)^n \qquad [4]$$

Here n is the power law exponent and is equal to 1 for molecular diffusion. This exponent would be less than one for oxidation due to transport of a charged species through an oxide scale. Results for SiC and Si_3N_4 will be discussed in this paper.

The parabolic oxidation rate constant is expected to be independent of gas velocity. The temperature dependence of SiC and Si_3N_4 oxidation in water vapor arises from the enthalpy of solid state diffusion of the oxidizing species in the oxide scale.

1.2 Silica volatility in water vapor

Silica volatility in water vapor is known to occur by the following reaction under conditions typical of many combustion environments[3,4]:

$$SiO_2 + 2H_2O(g) = Si(OH)_4(g) \qquad [5]$$
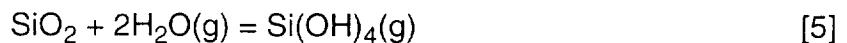
The weight loss of silica in water vapor due to volatility occurs by a linear rate process. The volatility is limited by transport of the volatile hydroxide through a gas boundary layer of constant thickness with time. The experimentally determined linear volatility rate, k_l, is given by the following expressions:

$$k_l = -\Delta w/t \qquad k_l' = -\Delta x/t \qquad [6]$$

The linear volatility rate can be readily modeled for a flat plate geometry using equations for transport of species through a laminar gas boundary layer[5]:

$$k_l = 0.664 \left(\frac{\rho'vL}{\eta} \right)^{1/2} \left(\frac{\eta}{\rho'D} \right)^{1/3} \frac{D\rho}{L} \qquad [7]$$

where ρ' is the density of gas in the boundary layer, v is the linear gas velocity, L is a characteristic length, η is the boundary layer gas viscosity, D is the interdiffusion coefficient of volatile Si-O-H species in the boundary layer, and ρ is the gas density of the Si-O-H species. Equation 7 can be reduced to a simpler relationship in terms of pressure, gas velocity and temperature as follows:

$$k_l \propto \frac{P_{Si-O-H}}{(P_{total})^{1/2}} v^{1/2} \qquad [8]$$

where P_{Si-O-H} is the partial pressure of the volatile Si-O-H species and P_{total} is the total system pressure. The temperature dependence arises from the reaction enthalpy of SiO_2 and water vapor to form volatile Si-O-H species. If the volatile species is $Si(OH)_4$, Equation 8 can be further simplified:

$$k_l \propto \frac{P_{H_2O}^2}{(P_{total})^{1/2}} v^{1/2} \propto (P_{total})^{3/2} v^{1/2} \qquad [9]$$

where P_{H_2O} is the water vapor partial pressure. The final simplification can be made since water vapor partial pressure in a combustion environment scales with the total pressure.

1.3 Paralinear oxidation/volatilization of SiC and Si_3N_4 in water vapor

In water vapor environments SiC or Si_3N_4 will simultaneously undergo oxidation reactions to form silica and volatilization reactions which remove silica. The combined oxidation and volatilization reactions are modeled by paralinear kinetics. This kinetic model was developed by Tedmon for chromia-formers[6] but is directly applicable to SiC or Si_3N_4 reaction kinetics in water vapor:

$$\frac{dx}{dt} = \frac{k_p'}{2x} - k_l' \qquad [10]$$

where all terms have been previously defined. A related expression can be developed in terms of weight change[7]. Model dimensional change and weight change paralinear kinetics for SiC in water vapor typical of furnace conditions are shown in Figure 1. At long times or high volatility rates, a steady state oxide thickness develops. Silica is formed at the same rate as it is removed. The SiC or Si_3N_4 recession and weight loss rates are linear in this steady state condition, depend only on the volatility rate of silica, and can be modeled using Equations 6 through 9 alone without considering the
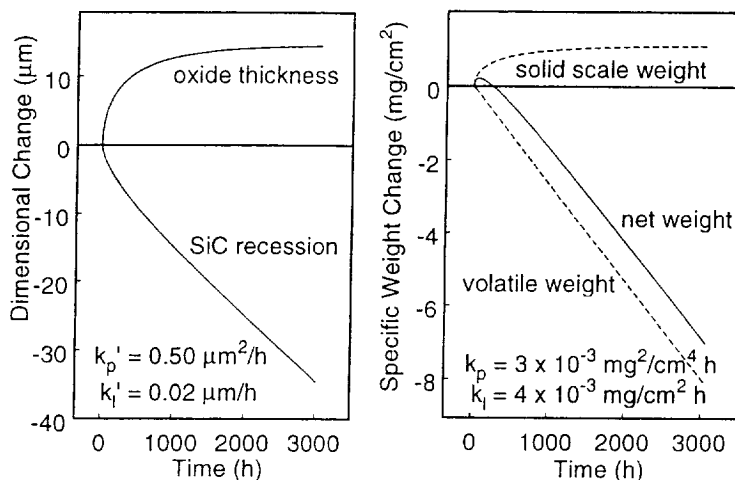
parabolic oxidation rate.

FIGURE 1

Paralinear dimensional change and weight change calculated for SiC in conditions typical of a furnace at 1200°C, 50% H_2O/50% O_2, 1 atm, and 4.4 cm/s gas velocity.

2. EXPERIMENTAL PROCEDURE

A variety of materials have been studied to characterize the oxidation and volatilization of SiC and Si_3N_4 in water vapor environments. These materials include Chemically Vapor Deposited (CVD) SiC (Morton Advanced Materials), sintered alpha SiC, Hexoloy (Carborundum), CVD Si_3N_4 (Advanced Ceramics Corp.), AS800 Si_3N_4 (AlliedSignal Ceramic Components), as well as pure fused silica (Quartz Scientific).

Materials were exposed to water vapor in a variety of test environments: horizontal tube furnace[8], Thermogravimetric Analysis (TGA) furnace[7], Mach 0.3 burner rig at one atm[9,10], and a High Pressure Burner Rig (HPBR)[11]. Test conditions are shown in Table 1. Details of these systems can be found in the references.

TABLE 1

Summary of test conditions for oxidation/volatilization of SiC and Si_3N_4.

	P_{total}, atm	gas	P_{H_2O}, atm	Gas velocity	T, °C
tube furnace	1	$O_2 + H_2O$	0.1-0.9	0.6-1.5 cm/s	1100-1400
TGA	1	$O_2 + H_2O$	0.5	4.4 cm/s	1200-1400
Mach 0.3 burner rig	1	combustion	0.1	100 m/s	1300
HPBR	5-25	combustion	0.5-3.1	5-20 m/s	1150-1450

3. RESULTS AND DISCUSSION

3.1 SiC and Si_3N_4 oxidation in water vapor

Parabolic oxidation rates vary with oxidant vapor pressure and temperature, but are independent of gas velocity. In order to accurately measure oxidation rates for SiC and Si_3N_4 in water vapor several factors must be accounted for. First, the contributions of other oxidants in the gas mixture, such as O_2 and CO_2, must be considered. Previous work has shown that oxidation rates of SiC in water vapor are about an order of magnitude higher than rates observed in dry oxygen[8]. However, when the amount of water vapor in an oxygen carrier gas is low, oxygen transport may contribute significantly to the overall observed oxidation rate. Oxidation rates for SiC in CO_2 are negligible compared to those in water vapor[12].

Second, any silica volatility effects must be suppressed or corrected for. Silica volatility effects can be suppressed by conducting experiments in conditions where an overpressure of $Si(OH)_4$ is established. This can be done by oxidizing in large diameter fused quartz furnace tubes, placing the oxidation sample on the downstream side of a long hot zone in the furnace, and operating at low gas velocities. An alternative for obtaining parabolic oxidation rates where silica volatility occurs is to fit the oxidation data to the paralinear equation using values of k_l calculated with Equation 7[14].

Several studies have been made to determine the parabolic oxidation rate of silica-formers in water vapor. The validity of the results is discussed as follows. Choi et al.[13] measured the oxidation of Si_3N_4 in water vapor in fused quartz tubes by measuring oxide thickness. The volatility of silica was probably partially suppressed under these conditions by using a quartz tube, but the decrease in apparent oxidation rate at high water vapor contents with an oxygen carrier gas might in part be explained by silica volatility. Very low oxidation rates were observed when inert gases were used as the carrier gas. Only very thin silica scales form, so that transport of oxidant through the silica scale may not limit the oxidation rate. Instead, surface reactions of Si_3N_4 with water vapor may limit the oxidation rate, especially at the low temperatures of 1100 and 1200°C.

The dependence of the oxidation rate of SiC on water vapor partial pressure was measured in a horizontal tube furnace[8]. The reported power law exponents (n, in Equation 4) varied between 0.76 and 0.85 and results are shown in Figure 2. In these furnace experiments volatility of silica was suppressed by the techniques described above, but oxygen was used as a carrier gas. At conditions of 0.1 atm H_2O/0.9 atm O_2, oxygen will contribute significantly to the observed oxidation and should be accounted for. Corrections for the effect of oxygen on reported oxidation rates are now in progress. SiC oxidation experiments at temperatures of 1100°C and below were linear-parabolic in nature indicating that surface reaction rates of water vapor with SiC limit oxidation.

Experiments using argon as a carrier gas for water vapor at temperatures of 1200°C and higher would yield oxidation rate results more readily.
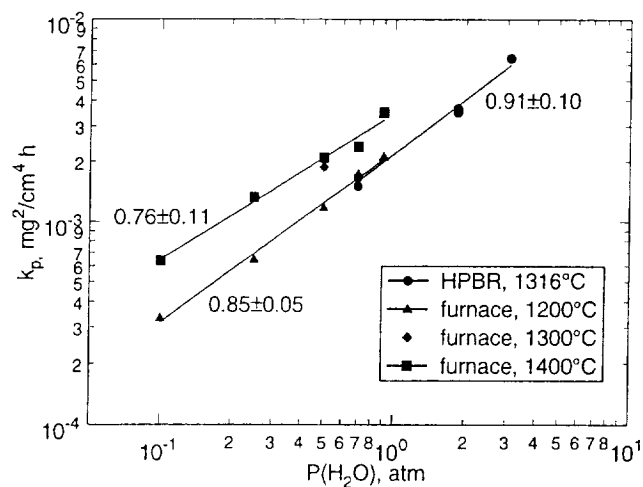

FIGURE 2

The variation of CVD SiC oxidation rate with water vapor partial pressure measured in a furnace with H_2O/O_2 mixed gas and the HPBR with real combustion gases.

Opila and Robinson[14] measured parabolic oxidation rate constants for SiC as a function of water vapor pressure using a high pressure burner rig at 1316°C. A power law exponent (n in Equation 4) of 0.91±0.10 was found, indicating molecular diffusion of water vapor controls the oxidation rate. Results are also reported in Figure 2. The power law exponent from this study is the most accurate to date since both silica volatility and mixed oxidant effects were accounted for. Corrections to the measured oxide thickness for silica volatility were made by fitting the results to paralinear kinetics using calculated values of k_l and solving for k_p. The effects of oxygen in the combustion gas on measured rates in this case are negligible since the oxygen content is approximately the same as the water vapor content, and the water vapor to oxygen ratio remains constant as total pressure is varied.

These three studies[8,13,14] show that the determination of the water vapor pressure dependence of the parabolic oxidation rate is complex due to surface reaction rate limited oxidation, mixed oxidant effects, and silica volatility effects. Interpretation of the above results indicates that molecular permeation of water vapor controls the oxidation rate of SiC at temperatures of 1200°C and higher. More results are needed for Si_3N_4.

3.2 Silica volatility in water vapor

Silica volatility under conditions typical of combustion environments occurs by the reaction of silica with water vapor to form $Si(OH)_4(g)$ as given by Equation 5. This species was identified indirectly by Hashimoto[4]; volatility was found to vary with the

square of the water vapor partial pressure, consistent with Equation 5. Direct identification of this species was made using a high pressure sampling mass spectrometer[3]. The mass spectra for silica in water vapor and oxygen is shown in Figure 3.
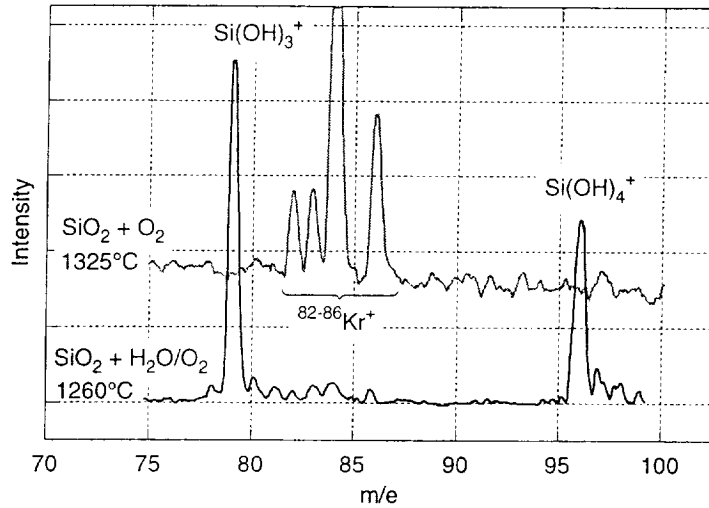

FIGURE 3

Mass spectra for SiO_2 measured in dry O_2 and 90 % H_2O/10% O_2 at one atmosphere. The mass spectrum for krypton, found in the dry O_2 provides an internal calibration of the mass to charge ratio (m/e).

Silica volatility is dependent on water vapor partial pressure, total pressure, and gas velocity. In this laboratory, SiO_2 volatility was measured in a TGA[7]. Typical results are shown in Figure 4. Measured rates were in fair agreement with rates calculated using Equation 7. The pressure and gas velocity dependence of silica volatility were not measured directly, but determined from the variation of k_l for SiC and Si_3N_4 derived from paralinear kinetics. This will be discussed in the next section. In principle the pressure and gas velocity dependence of silica could be measured directly.

3.3 Paralinear oxidation/volatilization of SiC and Si_3N_4 in water vapor

Paralinear oxidation kinetics of CVD SiC, CVD Si_3N_4, and linear volatility of fused silica as measured in a TGA at 1200°C in 50% H_2O/50% O_2 at 4.4 cm/s gas velocity are shown in Figure 4. This figure demonstrates the effect of variation of k_p on the shape of the kinetic curve. Since silica will have the same volatility rate for all samples, the differences in the kinetic curves are attributed to variation in k_p.

Figure 5 shows paralinear kinetics of AS800 and CVD Si_3N_4 determined from weight change in the HPBR as a function of temperature[15]. The oxidation and volatilization rate constants corresponding to the curves in this figure are shown in Table 2. The water vapor partial pressure in the HPBR (0.6 atm) is comparable to that of the TGA

exposures, but the gas velocity is much higher (20 m/s). Here, for AS800, the oxidation rate appears relatively insensitive to temperature over this temperature range, whereas the volatility rate increases with temperature. Since the relative rates of the oxidation and volatilization reactions have different temperature dependencies, the net result is a dramatic change in the shape of the kinetic curve at short times. Large weight gains at short times are observed at 1163°C, whereas a linear weight loss begins almost immediately at 1296°C. CVD Si_3N_4 shows nearly linear weight loss from the start of the exposure for all temperatures since the oxidation rate to form silica is lower than that of AS800 Si_3N_4.
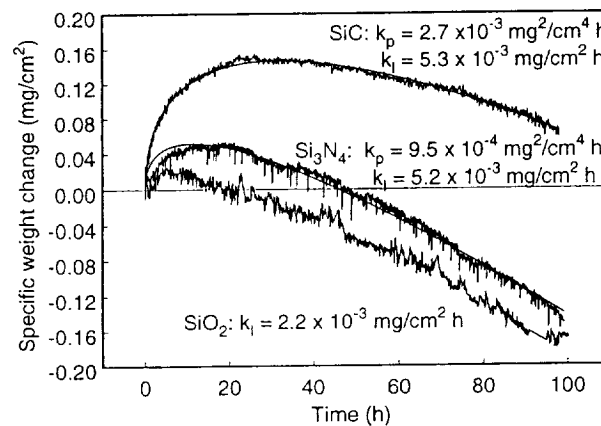

FIGURE 4.

TGA results for CVD SiC, CVD Si_3N_4, and fused silica measured at 1200°C, 50% H_2O/ 50% O_2, 1 atm, and 4.4 cm/s gas velocity. Lines that show the best fit of the paralinear model to the experimental results are also shown for CVD SiC and Si_3N_4.
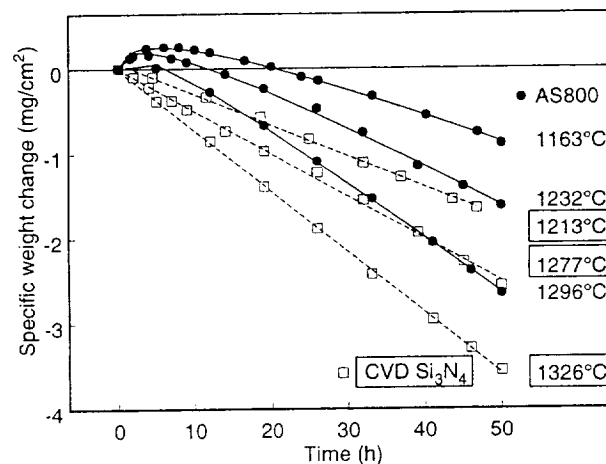

FIGURE 5.

Paralinear weight change kinetics measured for AS800 and CVD Si_3N_4 exposed in the HPBR at 6 atm total pressure and 20 m/s gas velocity. Closed symbols are for AS800 and open symbols are for CVD Si_3N_4. Lines that show the best fit of the paralinear model or simple linear weight loss to the experimental results are also shown for the AS800 and CVD Si_3N_4, respectively.

TABLE 2

Oxidation and volatilization rate constants for Si_3N_4 materials exposed in the HPBR at 6 atm and 20 m/s. These rates correspond to the curves shown in Figure 5.

AS800	k_p (mg^2/cm^4 h)	k_l (mg/cm^2 h)
1163°C	5.0×10^{-2}	3.0×10^{-2}
1232°C	5.1×10^{-2}	4.4×10^{-2}
1296°C	4.8×10^{-2}	6.3×10^{-2}
CVD Si_3N_4		
1213°C	--	3.7×10^{-2}
1277°C	--	5.0×10^{-2}
1326°C	--	7.1×10^{-2}

Figure 6 shows one additional paralinear curve for Hexoloy SiC that was obtained in a one atmosphere, Mach 0.3 burner rig. Previous studies for SiC in this type of burner rig conducted for 3500h[16] did not detect weight losses due to silica volatility. This result shows that, given enough hot surface area (here about 8 cm^2), the one atmosphere, Mach 0.3 burner rig provides conditions that are suitable for detecting silica volatility with more than adequate sensitivity.

The parametric dependence of the volatility rate can be determined from the combined results for SiC exposures in the TGA, HPBR and Mach 0.3 burner rig described above. The temperature dependence for the TGA results[7] and the HPBR results[11] is described elsewhere. The pressure and gas velocity dependence of silica volatility can be seen in Figures 7 and 8, respectively. Both are found to be in agreement with the theory predicted by Equation 9. The velocity dependence uses the average value for the TGA exposures[7]. Both the pressure and velocity dependence include only one data point for the Mach 0.3 burner rig. Further experiments using the Mach 0.3 burner rig are planned to confirm these values.
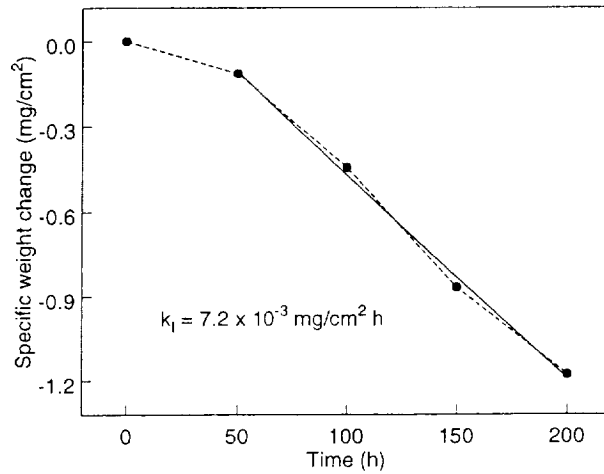
FIGURE 6

Paralinear weight change kinetics measured for Hexoloy SiC measured in a one atmosphere, Mach 0.3 burner rig at 1316°C and 100 m/s gas velocity. A line representing the linear regression of the last four data points shows the good agreement with linear weight loss kinetics.
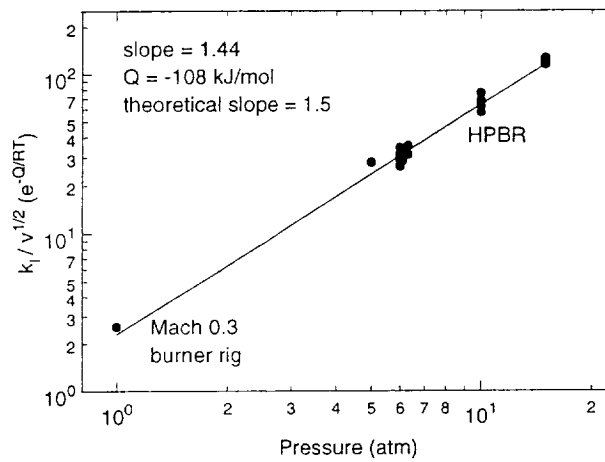

FIGURE 7

The pressure dependence of silica volatility determined for Hexoloy and CVD SiC in both the Mach 0.3 burner rig and the HPBR. The power law exponent of 1.44, determined from the volatility rate normalized for different temperatures and gas velocities, agrees with the theoretical exponent of 1.5.
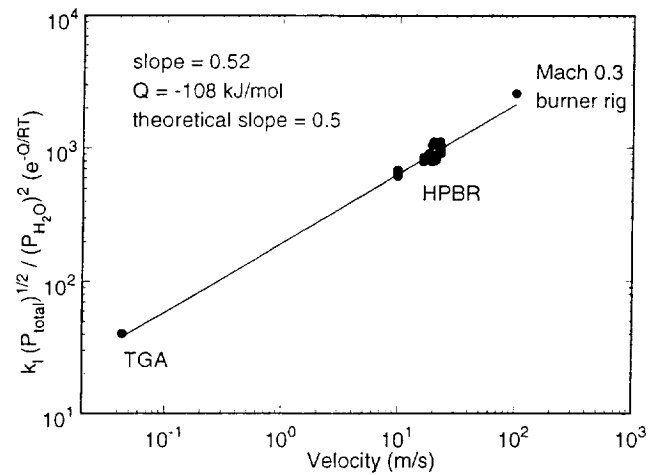
FIGURE 8

The gas velocity dependence of silica volatility determined for CVD and Hexoloy SiC in the TGA, HPBR, and Mach 0.3 burner rig. The power law exponent of 0.52, determined from the volatility rate normalized for different temperatures and pressures, agrees with the theoretical exponent of 0.5.

4. SUMMARY AND CONCLUSIONS

Models for oxidation, volatilization and the combined paralinear kinetics for SiC and Si_3N_4 exposed in water vapor were reviewed. Oxidation occurs by molecular transport of water vapor through the growing silica scale and therefore depends on the water vapor partial pressure but is independent of gas velocity. Silica volatility occurs by $Si(OH)_4(g)$ formation. Volatility depends on the water vapor partial pressure as well as the gas velocity. Reaction kinetics results for oxidation and volatilization measured in both furnace and burner rig exposures were combined and shown to verify these models for corrosion of SiC and Si_3N_4 in water vapor over a wide range of pressures and gas velocities.

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