WATER VAPOR EFFECTS ON SILICA-FORMING CERAMICS

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Silica-forming ceramics such as SiC and Si_3N_4 are proposed for applications in combustion environments. These environments contain water vapor as a product of combustion. Oxidation of silica-formers is more rapid in water vapor than in oxygen. Parabolic oxidation rates increase with the water vapor partial pressure with a power law exponent value close to one. Molecular water vapor is therefore the mobile species in silica. Rapid oxidation rates and large amounts of gases generated during the oxidation reaction in high water vapor pressures may result in bubble formation in the silica and nonprotective scale formation. It is also shown that silica reacts with water vapor to form $Si(OH)_4(g)$. Silica volatility has been modeled using a laminar flow boundary layer controlled reaction equation. Silica volatility depends on the partial pressure of water vapor, the total pressure, and the gas velocity. Simultaneous oxidation and volatilization reactions have been modeled with paralinear kinetics.

1 Introduction

Silica-forming ceramics have been proposed for many applications in combustion environments. Some of these include Si_3N_4 for land-based power generation turbine blades, SiC fiber-reinforced SiC composites for aeropropulsion combustor liners, and carbon fiber-reinforced SiC composites for space propulsion applications such as nozzles, turbopumps, gas generators, and thrust cells. All of these applications require material durability in high temperature, high pressure, high velocity combustion environments. The amount of water vapor present in hydrocarbon/air combustion environments is in the range of 8-13 mole percent over a wide range of equivalence ratios [1]. In space propulsion applications, oxygen/hydrogen combustion environments can result in water vapor contents between 13 and 68%. Significant instability of water vapor occurs at the stoichiometric oxygen/hydrogen ratio of 8 due to gas temperatures exceeding 3500K. Because of this instability, combustion product mole fractions in the oxygen/hydrogen system vary somewhat with total pressure.

The key reactions for silica-forming ceramics in water vapor are oxidation and volatilization reactions as shown below.

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

$Si_3N_4 + 6H_2O(g) = 3SiO_2 + 2N_2(g) + 6H_2(g)$ (2)

Volatilization: $SiO_2 + 2H_2O(g) = Si(OH)_4(g)$ (3)

The oxidation and volatilization reactions will each be examined separately, and then simultaneous oxidation/volatilization paralinear kinetics will be discussed.

2 Oxidation of silica-formers in water vapor

2.1 Parabolic oxidation kinetics

The oxidation rate of silica-formers at high temperatures (1200°C and higher) follows a parabolic rate law. The parabolic rate constant, k_p, is found experimentally from:

$$k_p = (\Delta wt)^2/t \text{ or } k_p = x^2/t \qquad (4)$$

where Δwt is the specific weight change, x is the oxide thickness, and t is time. It is well known that the oxidation rate of silica-formers in water vapor is higher relative to the rates observed in oxygen. This has been shown for silicon [2], for silicon carbide [3,4], and for silicon nitride [5]. This result has been explained [2] knowing that

$$k_p \propto D_{eff}\, C \qquad (5)$$

where D_{eff} is the effective diffusivity of the oxidant in silica and C is the concentration of the oxidant in silica. Although the effective diffusivity of water in silica is less than that of oxygen, the solubility of water in silica, C, is much greater than solubility of oxygen in silica. The product of D_{eff} and C is thus greater for water vapor.

2.2 Dependence of parabolic rate constant on water vapor partial pressure

The concentration of water vapor in silica, C, can be related to the partial pressure of water vapor at the oxide/gas surface. By varying the partial pressure of water vapor and monitoring the resulting parabolic rate constant, the mobile oxidant species in silica can be identified. Several studies have shown that the parabolic rate constant of silicon and SiC depends on the water vapor partial pressure with a power law exponent value close to one [2,3,6]. This indicates that molecular water vapor rather than a charged species is the mobile species in silica. These results are consistent with the findings for the diffusivity of water in silica glass [7]. Different results were found for the dependence of the oxidation rate of Si_3N_4 on water vapor partial pressure [5], but it is not clear if the volatility of silica was accounted for in this study.

In addition to identifying the mobile species, these kinds of studies provide a means for extrapolating oxide growth rates to the higher pressure conditions found in the combustion environments cited in the introduction.

2.3 Bubble formation in the silica scale

Bubbles have been observed to form in the silica scale formed on SiC in water vapor at 1200°C [3,8]. The number of bubbles increases with water vapor partial pressure [3]. While the kinetics follow an apparent parabolic rate law at water vapor partial pressures up to 0.9 atm [3], at 1.5 atm water vapor partial pressure the silica scale is no longer protective and linear oxidation kinetics are observed [8]. These bubbles were not observed for the oxidation of CVD Si_3N_4 or Si at water vapor partial pressures up to 0.9 atm. The bubbles are attributed to the rapid formation of product gases in the oxidation reaction shown in Equation 1. For comparison, the number of moles of gas per mole of silica is less for both Si_3N_4 (Equation 2) and for silicon:

$$Si + 2H_2O(g) = SiO_2 + 2H_2(g) \tag{6}$$

In addition, the oxidation rate of Si_3N_4 is lower than that of SiC due to an inner layer of SiO_xN_y which forms for pure Si_3N_4 oxidized in clean conditions [9].

The conditions for formation of nonprotective silica scales are not fully understood. For example, Opila [3] observed bubbles in the silica scale only in amorphous silica, and not for crystalline silica formed by oxidation of SiC at 1400°C. On the other hand, More et al. [8] found bubbles in the outer crystalline portion of the silica scale formed from the oxidation of SiC at 1200°C at 1.5 atm water vapor partial pressure but not in the inner amorphous portion of the scale. This bubbling phenomenon may not be important, however, for high velocity applications of SiC where the silica scale is volatilized at a rapid rate allowing only thin dense silica scales to exist.

3 Volatility of silica in water vapor

3.1 $Si(OH)_4$ formation

While it was known that silica was volatile in water vapor for many years, the identity of the volatile species had not been established. The volatility of silica can be observed experimentally by a weight loss technique at 1300°C in 1 atmosphere 50% water vapor/50% oxygen at 4.4 cm/s gas velocity [10]. Recent work has shown that $Si(OH)_4$ is the predominant volatile species under conditions of interest for combustion applications of silica-formers. Hashimoto [11] has shown in a careful transpiration study that the silica volatility is proportional to the square of the water vapor partial pressure. Equation 3 shows that this relationship is satisfied by the formation of $Si(OH)_4$. Opila et al. [10] observed the $Si(OH)_4$ molecule by a specialized atmospheric sampling mass spectrometer. SiO(OH) and $SiO(OH)_2$ are other volatile silicon hydroxide species that are important under higher temperature and lower pressure conditions [12].

3.2 Modeling silica volatility using laminar flow boundary layer control equation

Silica volatility can be modeled using laminar flow gas boundary layer theory. This model assumes silica volatility is controlled by diffusion of $Si(OH)_4$ through a gaseous boundary layer. For a flat plate geometry, the linear volatilization rate, k_l, is given by:

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

where ρ' is the density of the boundary layer gas, v is the linear gas velocity, L is a characteristic length, η is the boundary layer gas viscosity, D is the interdiffusion coefficient of $Si(OH)_4$ in the boundary layer, and ρ is the gas density of $Si(OH)_4$. Equation 7 can be reduced to pressure, gas velocity, and temperature terms that describe the combustion environment:

$$k_l \propto \frac{P_{Si(OH)4}}{P_{total}^{1/2}} v^{1/2} \propto \frac{P_{H2O}^{2}}{P_{total}^{1/2}} v^{1/2} \qquad (8)$$

where $P_{Si(OH)4}$ is the partial pressure of $Si(OH)_4$, P_{H2O} is the water vapor partial pressure, and P_{total} is the total pressure. The temperature dependence is found in the $P_{Si(OH)4}$ term and results from the reaction enthalpy of SiO_2 and water vapor to form $Si(OH)_4$. Good agreement is found between calculated and measured volatility rates [10].

4 Paralinear oxidation of silica-formers in water vapor

4.1 Modeling paralinear oxidation

In the previous sections, oxidation and volatilization mechanisms of silica-formers were discussed separately. However, in combustion environments these processes occur simultaneously. The combined oxidation and volatilization of silica-formers in water vapor can be described by paralinear kinetics. The paralinear kinetic model developed by Tedmon [13] for chromia-formers can be directly applied to silica-formers:

$$\frac{dx}{dt} = \frac{k_p}{2x} - k_l \qquad (9)$$

where x is oxide thickness, t is time and the rate constants have been previously defined. A related expression can be developed in terms of weight change [14]. Predicted dimensional and weight changes are shown in Figure 1. At long times or high volatility rates, a constant oxide thickness is formed due to the steady state condition in which the formation and volatilization of silica occur at the same rate. Under these conditions, linear recession and weight loss rates of the silica-former are observed which depend only on the silica volatility rate and can thus be predicted using Equations 7 and 8.

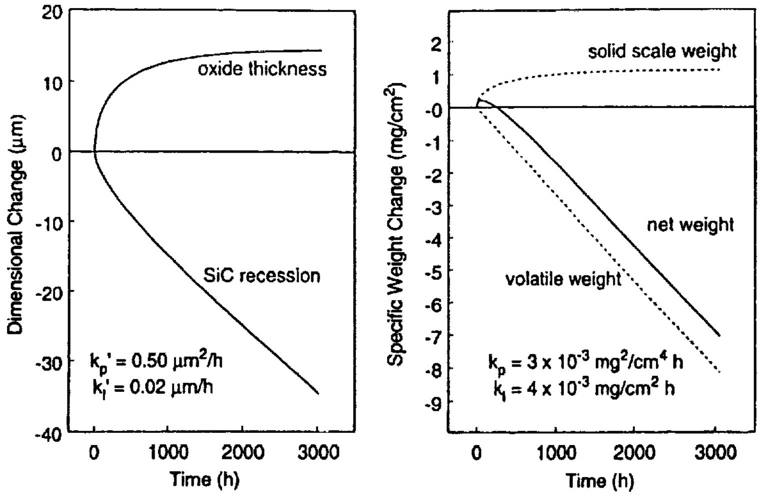

Figure 1. Paralinear dimensional and weight change kinetics calculated for SiC at 1200°C, 1 atm total pressure, 50% H_2O/50% O_2, 4.4 cm/sec.

4.2 Limits of the paralinear oxidation model

The paralinear model has been shown to be valid over a wide range of pressure, gas velocity, and temperature conditions, including laboratory furnaces [14], burner rigs [15], and turbine conditions [16]. However, some limits to this model have been found. At high pressures and low velocities volatility rates are negligible. A thick bubbled non-protective scale will form under such conditions [8] as discussed in section 2.3. At high gas velocities, turbulent flow will occur resulting in a higher velocity dependence than shown in Equations 7 and 8. In addition, at high gas velocities on the order of 600 m/sec, no silica film was found on a Si_3N_4 vane exposed to a 1066-1260°C combustion environment for 815 hours [16]. While the recession rates of this vane were close to those predicted by Equations 7 and 8, the absence of any silica film suggests the possibility that another mechanism could be controlling the recession rates at these and higher velocities. One possible rate limiting mechansim could be the reaction of water vapor with SiC or Si_3N_4 to form silica. As soon as silica is formed it is volatilized. At high temperatures SiO(OH) and $SiO(OH)_2$ are predicted to become more important than $Si(OH)_4$ [12,17]. This would affect both the temperature and pressure dependence of the volatility rates. In addition, at temperatures greater than the melting point of silica, the recession would no longer be described by Equations 7 and 8 due to ablation-type processes.

Deviations of the paralinear model have been observed under certain conditions, though the exact pressure, velocity, and temperature limits of the paralinear model are not yet defined. Additional work is needed to define the transition pressures between protective and non-protective scale formation and the transition velocities between boundary layer controlled volatilization and silica growth limited volatilization. In addition, more thermochemical data for the SiO(OH) and $SiO(OH)_2$ species are needed to accurately predict the pressure and temperature dependence of silica volatility especially at higher temperature combustion conditions.

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