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Feature article

Thermodynamic modeling of the silica volatilization in steam related to silicon carbide oxidation

Valentina Angelici Avincola*, Damian Cupid, Hans Jürgen Seifert

Karlsruhe Institute of Technology, Germany

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ABSTRACT

In this paper, the volatilization of the silica scale which can form at the surface of silicon carbide was modeled by means of computational thermodynamics. Using experimentally determined equilibrium reaction constants available in the literature, the Gibbs energy descriptions of $Si(OH)_4$ and $SiO(OH)_2$ silicon hydroxide gas species were developed using the CALPHAD method and included into an existing thermodynamic description of the Si–O–H–C–Ar system. Thermodynamic equilibrium calculations performed with the new descriptions for $Si(OH)_4$ and $SiO(OH)_2$ were carried out in order to calculate the equilibrium vapor pressures of gas species. These were then used to model the weight loss of silicon carbide due to the interaction of silicon carbide with steam. The influence of parameters such as temperature, total pressure, and the ratio of the reactants on silica volatilization were studied in relation to the effective mass loss of silicon carbide.

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1. Introduction

The reaction of silica with water vapor is a fundamental process in different fields, such as geology and astrophysics [1] and it is of increasing importance for understanding the behavior of silica-based coatings and silica-forming ceramics such as silicon carbide [2]. In corrosive atmospheres, the capability of producing compact SiO_2 layers at the solid–gas interface is often employed as a protection to prevent further oxidation of the underlying material. However, deterioration of the protective coating can occur in conditions which are favorable to the volatilization of SiO_2. In case of silica reaction with water vapor, volatile silica hydroxide species can be produced. This phenomenon directly leads to degradation of the SiO_2 scale. The present work focuses on modeling the volatilization of the silica, the material that can be formed at the surface of any silicon based material.

Among the silicon-based materials, this work will focus on silicon carbide. Silicon carbide has outstanding properties such as irradiation tolerance [3] and oxidation resistance [4–6] at high temperatures and in corrosive environments. Its good performance in corrosive atmospheres is mainly due to the so-called passive oxidation, which occurs during oxidation at high H_2O partial pressures (>10 Pa at 1700 K [7]). The passive oxidation consists in the development of a dense SiO_2 scale at the interface between the SiC and the oxidative fluid. Despite the formation of the silica protective layer, SiC degradation can occur mainly in two ways: through active oxidation of SiC, which results in the production of SiO and CO gas species, or by volatilization of the protective silica layer which has formed during passive oxidation of SiC. In both cases, SiC regression occurs. The exact nature of the degradation process depends on the conditions to which SiC is exposed, such as composition of the gas atmosphere, temperature, total and partial pressures of the gas species, and thermo-hydraulic conditions.

Thermodynamic calculations and kinetic simulations, which can be performed using thermodynamic descriptions and kinetic models of the multi-component and heterogeneous systems, are important tools that can be used to understand and predict degradation mechanisms under different conditions. The aim of this work is to calculate erosion of the SiO_2 scale by volatilization, which occurs through the formation of silicon-hydroxide gas species such as $Si(OH)_4$ and $SiO(OH)_2$. In order to calculate the SiO_2 erosion rates, analytical expressions of the Gibbs free energies of the volatile silicon-hydroxides were developed using the CALPHAD method. Thereafter, thermodynamic calculations using the new descriptions were performed. Since previous experimental work [8] has shown that $Si(OH)_4$ and $SiO(OH)_2$ species are formed during the reaction of SiO_2 with water vapor at high temperatures, these two species have been considered in this work. It must be mentioned that although Zhang [9] recently developed thermodynamic descriptions of the Gibbs energy functions of $Si(OH)_4$, $SiO(OH)$, and $SiO(OH)_2$, a comprehensive review of the experimental data which

* Corresponding author.

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were selected to optimize the thermodynamic parameters of the free energy functions was not presented and the analytical expressions themselves were not published.

The present manuscript is structured as follows. First, the available literature data on the equilibrium constants for silicon hydroxide gas species are presented. Next, the thermodynamic optimization of the Gibbs free energy functions of the $Si(OH)_4$ and $SiO(OH)_2$ gas species is described. Finally, calculations performed using a thermodynamic description of the multi-component Si–O–H–C–Ar system including the Gibbs energy functions of $Si(OH)_4$ and $SiO(OH)_2$ are presented and discussed.

2. Literature data

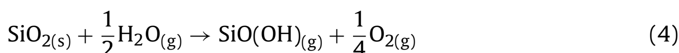
Thermodynamic descriptions of the gaseous products of the volatilization of SiO_2 in steam atmospheres are required to be able to model the thermodynamics and kinetics of SiC oxidation. At high steam partial pressures ($P > 10^{-4}$ bar at 1700 K [7]), passive oxidation of silicon carbide occurs, resulting in the formation of a protective silica scale (Eq. (1)):

$$SiC + 3H_2O \rightarrow SiO_2 + CO + 3H_2 \quad (1)$$

Simultaneously, the SiO_2 scale undergoes volatilization due to the reaction of SiO_2 with H_2O. According to Opila [10], the volatilization of silica at atmospheric pressure in water vapor occurs mainly through the following reactions:

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

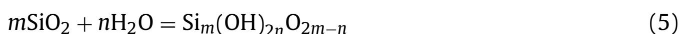
$$SiO_{2(s)+}H_2O_{(g)} \rightarrow SiO(OH)_{2(g)} \quad (3)$$



$$SiO_{2(s)} + \frac{1}{2}H_2O_{(g)} \rightarrow SiO(OH)_{(g)} + \frac{1}{4}O_{2(g)} \quad (4)$$

Both experimentally determined and theoretical estimates of the equilibrium constants for the Si-containing hydroxide species are available in the literature [1,11–13] and are analyzed in the following section.

Krikorian [13] reviewed the experimental work in the silica-steam system up to 1970 K. The equilibrium constants for reactions between SiO_2 and H_2O at the given temperatures were used to identify the complex Si–O–H gas species ($Si_m(OH)_{2n}O_{2m-n}$). According to this method, the reaction between SiO_2 and H_2O is written as:



$$mSiO_2 + nH_2O = Si_m(OH)_{2n}O_{2m-n} \quad (5)$$

with the equilibrium constant expressed as:

$$K_{eq} = -\frac{f_{complex}}{(a_{s,1})^m (f_{H_2O})^n} \quad (6)$$

where $f_{complex}$ is the fugacity of the different Si–O–H gas species, $a_{s,l}$ is the activity of the solid or liquid condensed phase, and f_{H_2O} is the fugacity of water. Krikorian also used the third law method to calculate the free energy functions of different species from estimation of the vibrational frequencies. $Si(OH)_4$ was found to be the dominant gas species at ambient pressure up to 1970 K.

Hashimoto [1] used the transpiration method to study the reaction of water vapor with crystalline SiO_2 (transparent alpha quartz) at temperatures between 1373 K and 1773 K. In these experiments, mixtures of O_2 and H_2O were allowed to react with crystalline SiO_2 in a noble-metal reaction cell, saturating the atmosphere with silicon hydroxide species. According to the Si-content of the condensate from the gas, the main product of the reaction was $Si(OH)_4$. From these measurements, the equilibrium partial pressure of $Si(OH)_4$ could be calculated assuming ideal gas behavior. The enthalpy of formation of the hydroxide gas species was also calculated using data from the JANAF tables [14].

Hildenbrand and Lau [11,12] measured the partial pressure of $SiO(OH)_2$ and SiO(OH) from the reaction of silica and H_2O at 1963, 2041 and 2065 K using a Knudsen effusion cell source. The gas species were identified by means of a magnetic deflection spectrometer. The enthalpies of formation of $SiO(OH)_2$ and SiO(OH) from SiO and OH gas species were calculated using the third law method, in which thermodynamic data for $SiO(OH)_2$ and SiO(OH) available in the literature [13] were used to calculate the free energy functions. In contrast to other works, the $Si(OH)_4$ species was not detected.

Allendorf [15] combined ab initio electronic structure calculations and empirical correlations to derive the enthalpies of formation at 0 and 298 K and the Gibbs energy of formation from 298 to 2500 K for many gas species, including $Si(OH)_4$, SiO(OH), $SiO(OH)_2$. In particular, electronic structure calculations were performed to calculate the equilibrium geometries and harmonic vibrational frequencies of the gas species [16]. Calculations of electron correlation effects coupled with empirical bond additivity corrections for the equilibrium geometries were subsequently performed in order to accurately determine the heats of formation at 0 K. Thermodynamic properties such as entropies, heat capacities, and heat of formation at other temperatures were further calculated using the heat of formation data at 0 K, the calculated geometries and scaled frequencies and equations derived from statistical-mechanics.

Opila [17] investigated the formation of volatile species from the reaction of fused quartz frit in an oxygen stream saturated with water vapor at ambient pressure using high pressure sampling (supersonic sampling) mass spectrometry. Since the most intense peak was observed for the $Si(OH)_3^+$ species, it was concluded that the $Si(OH)_4$ was the dominant silicon hydroxide gas species in accordance with Hashimoto [1]. A small peak was also observed for $SiO(OH)^+$, suggesting the presence of $SiO(OH)_2$. SiO(OH) could not be measured because its partial pressures were below the detection limit of the instrument (10^{-6} bar).

The work of Opila [17] was followed by that of Jacobson [8,18], in which the transpiration method was used to study the interaction of SiO_2 (cristobalite) with water vapor at temperatures between 1073 and 1728 K. At temperatures below 1673 K, formation of $Si(OH)_4$ was confirmed since the slope of the graph of logP(Si–OH) against logP(H_2O) was 2, as expected for the reaction according to Eq. (2). At higher temperatures, formation of mixtures of $Si(OH)_4$ and SiO(OH) or $SiO(OH)_2$ was detected since the slope of the graph of logP(Si–OH) against logP(H_2O) was less than 2. In order to clearly identify the other gas species, experiments with two different oxygen partial pressures in the reaction chamber were performed. Using this method, the specific gas species could be identified since formation of SiO(OH) is suppressed by oxygen (Eq. (4)), whereas the amount of $SiO(OH)_2$ is independent of the oxygen partial pressure, remaining constant at different oxygen partial pressures (Eq. (3)). The results did not show any oxygen partial pressure dependency, so that the formation of SiO(OH) could be ruled out. The enthalpies and entropies of formation of $Si(OH)_4$ were determined using the second law method. Additionally, the enthalpies of formation of $Si(OH)_4$ and $SiO(OH)_2$ at 298 K were calculated with the third law method using free energy functions from the data of Allendorf [15]. Moreover, Jacobson performed third law calculations employing the experimental data from Hashimoto at 1673 K and the data at reference temperature from Allendorf [15].

Recently, Plyasunov [19] analyzed the available experimental data for the reaction of SiO_2 with H_2O to produce $Si(OH)_4$. In Plyasunoví's work, 102 data points from seven literature sources were analyzed and the assessed thermodynamic functions for $Si(OH)_4$ are given in Table 1 of this work [19].

Rutz and Bockhorn [20] used ab initio calculation and density functional theory calculations to derive the standard enthalpy of

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