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Sol–gel derived borosilicate glasses and thin film coatings on SiC substrates: Boron loss and carbon retention due to processing and heat treatment

Bohuslava McFarland [a],*, Elizabeth J. Opila [b]

[a] University of Virginia, Department of Materials Science and Engineering, 395 McCormick Road, Wilsdorf Hall, Charlottesville, VA 22904, United States
[b] University of Virginia, Materials Science and Engineering, 395 McCormick Road, Wilsdorf Hall, Charlottesville, VA 22904, United States

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ABSTRACT

Synthesis of freestanding borosilicate glass and borosilicate thin films (<1 μm thick) applied on silicon carbide substrates was carried out by a sol–gel method for the purpose of determining boria effects on silicon carbide oxidation. Extensive characterization of boron loss, compositional reproducibility, and film quality was carried out through every stage in the gel to glass conversion. Boron loss in the gel synthesis and during heat treatment ranged from 30 to 68 mol% and increased with solvent loading. Hydrolyzed products were evident in glasses heat treated at lower temperatures, but were not present as crystalline phases in the amorphous glass network. Reproducibility of boron concentration in the glass was relatively unaffected by heat treatment conditions, but formation of the borosilicate bond was enhanced in certain gas environments. Carbon retention was characterized for total concentration. Carbon bonding both within the glass network and as a free carbon phase was evident by spectroscopic analysis.

1. Introduction

Ceramic matrix composites (CMCs) are being developed for turbine engine hot section components due to their light weight and high temperature capability [1]. Typically CMCs are comprised of silicon carbide (SiC) fibers coated with a boron nitride (BN) layer embedded in a SiC matrix. When exposed to the high temperature combustion environment, CMC components will oxidize.

1.1. Oxidation reactions

SiC will react with oxygen, forming silica (SiO_2), given by Reaction (1) [2]:

$$SiC + \frac{3}{2}O_2(g) = SiO_2 + CO\ (g). \quad (1)$$

BN will react with oxygen to form boria (B_2O_3) as a liquid and nitrogen is given off as a gas, as given by Reaction (2) [3–5].

$$2BN + \frac{3}{2}O_2(g) = B_2O_3\ (l) + N_2\ (g). \quad (2)$$

Silicon carbide and boron nitride also oxidize in water vapor, given by Reactions (3) [6] and (4) [7]:

$$SiC + 3\ H_2O\ (g) = SiO_2 + 3\ H_2\ (g) + CO\ (g) \quad (3)$$

$$2BN + 3\ H_2O(g) = B_2O_3(l) + N_2(g) + 3\ H_2. \quad (4)$$

The silica oxidation product (Reactions (1), (3)) reacts with the liquid boria oxidation product (Reactions (2), (4)) to form a borosilicate glass, shown by Reaction (5) [2,8]:

$$xSiO_2 + yB_2O_3\ (l) = xSiO_2 : yB_2O_3\ \text{glass}. \quad (5)$$

The presence of a BN layer has been observed to accelerate SiC fiber oxidation at rates greater than observed for SiC oxidation alone [2,3,9]. These reactions can result in the depletion of the BN interphase, formation of excessive borosilicate glass, and rapid recession of the SiC fibers [10]. Currently, little is known about the thermally grown borosilicate glass composition, the conditions under which it forms, or oxidant transport rates through the glass.

The motivation of this work is to facilitate the current understanding of how borosilicate glass affects the SiC oxidation kinetics by applying borosilicate glass coatings of known boria concentration onto SiC substrates to replicate thermally grown borosilicate oxides. The purposes of this work are to 1) identify glass coating methods that reliably produce well-defined and sufficient boria concentration and 2) apply

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* Corresponding author.
E-mail addresses: bm8tt@virginia.edu (B. McFarland), opila@virginia.edu (E.J. Opila).

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<1 μm thin glass layers that represent oxide thickness at early stages of oxidation. The requirement for thin glass layers automatically precludes melt methods with silica and boria powders. Alternatively, sol–gel derived borosilicate glass layers show promise for meeting both aforementioned requirements.

1.2. Previous oxidation study of borosilicate glass coated silicon [11]

Schlichting [11] performed a study to understand oxygen transport in high-temperature oxidizing environments through various borosilicate glass film compositions coated onto silicon substrates, as summarized in Fig. 1A. The coating compositions were prepared by a sol–gel method. The effects of boria concentration in sol–gel derived borosilicate glass coatings on the transport rate of oxygen as compared to oxygen transport in silica glass films on silicon were investigated. The increase in the oxygen diffusion rate was found to be significant: a 1 mol% boria addition to silica increased the oxygen diffusion coefficient by nearly four orders of magnitude (Fig. 1A). The Si oxidation rates determined experimentally for a substrate coated with a pure SiO_2 sol–gel derived glass coating are compared with the classic Deal and Grove results for thermally grown oxides on silicon in Fig. 1B [12]. Despite the steeper slope of the sol–gel derived silica glass layer, results in both studies are within the same order of magnitude. These experimental results validate this approach to understanding oxidation of silicon-based materials through application of sol–gel derived glassy layers as models for thermally grown oxides followed by standard oxidation experiments.

While these results suggest increasing oxygen permeation due to changes in the sol–gel derived glass structure [11] with increasing boria concentration, the calculated oxygen diffusivity through silica (Fig. 1A) does not correlate with the experimental oxidation rate results of silica coated Si (Fig. 1B). This discrepancy will be addressed in a future study. For this present study, the utilization of sol–gel derived glasses that are well-defined in composition, bonding, and phase are paramount so that insights into the thermally grown borosilicate glass behavior can be obtained from the effects of sol–gel derived borosilicate glasses on SiC oxidation. These requisites led to several important questions about the sol–gel derived borosilicate glass coatings used in the Schlichting study that were addressed here.

Firstly, Schlichting reported only nominal compositions of sol–gel derived borosilicate glasses, which were synthesized by boria additions to hydrolyzed silane. The problem with reporting nominal concentrations is that the boria concentrations may have been significantly overestimated. Boron loss is a well-known problem associated with borosilicate synthesis procedures, leading to actual glass compositions with >40% to nearly 100 wt.% loss of boria [13–16]. The limited yield of reacting precursors and the concomitant precipitation of boric acid resulting in boron loss in converted glasses were described early on by Nogami and Moriya [14]. Irwin attributed borosiloxane bond instability in gels to hydrolysis by the presence of water, but spectrally observed the integration of hydrolyzed species into borosilicate bonds with the thermal removal of water [17]. The water and silane ratio were additional factors used to limit boric acid precipitation in the gels [18]. Advances in increasing boron retention in the gels were achieved by Soraru (1999) [15], who further pushed the state of the art to decrease boria loss by increasing catalyst pH and by replacing methylated silane with ethyl/vinyl silanes, which seemed to shield the Si–O–B bond from hydrolysis by steric hindrance. Recent synthesis procedures by Grandi advanced boron retention in borosiloxane gels by replacing trialkylborate with trimethoxyboroxine and by substituting a portion of the methylated silicon alkoxide with aminopropyltriethoxysilane, leading to boron concentrations in the xerogel that approached nominal values [13]. While these works provided gainful insight into chemistries that led to increasing boron retention in sol–gel derived borosilicate systems, studies on boron concentration reproducibility and its stability in glasses are needed.

Secondly, Schlichting utilized coating film thicknesses of ~10 μm, determined by scanning electron microscopy (SEM) or from coating weight estimates. This film thickness is problematic because it is difficult to get a crack-free, adherent coating at thicknesses above 1 μm [19]. A 10 μm silica coating thickness is a long diffusion pathway for oxygen ingress for further oxidation, and is representative of thermally grown silica thicknesses exposed to an oxidation environment for 500 h at 1100 °C, the upper temperature limit reported by Schlichting for oxidation experiments. Schlichting's oxidation exposures for the coated Si were 20 h in duration, which are short times to measure significant weight changes with such thick films.

Thirdly, carbon retention from organic volatilization during the gel-to-glass conversion is common to sol–gel derived silica and borosilicate glasses, particularly when heat-treated in an inert atmosphere [20,21]. Although a dark appearance to the glass layers, indicative of carbon retention, was not mentioned in Schlichting's study, retained carbon oxidation has since been shown to occur in bulk sol–gel derived and crosslinked polysiloxane SiOC specimens at elevated temperature in air [22]. Carbon minimization in the sol–gel derived glass layers is sought in this study so that boria effects on SiC oxidation are not overshadowed by retained carbon oxidation from the sol–gel derived glass layers expected to occur during oxidation studies. Volatilization

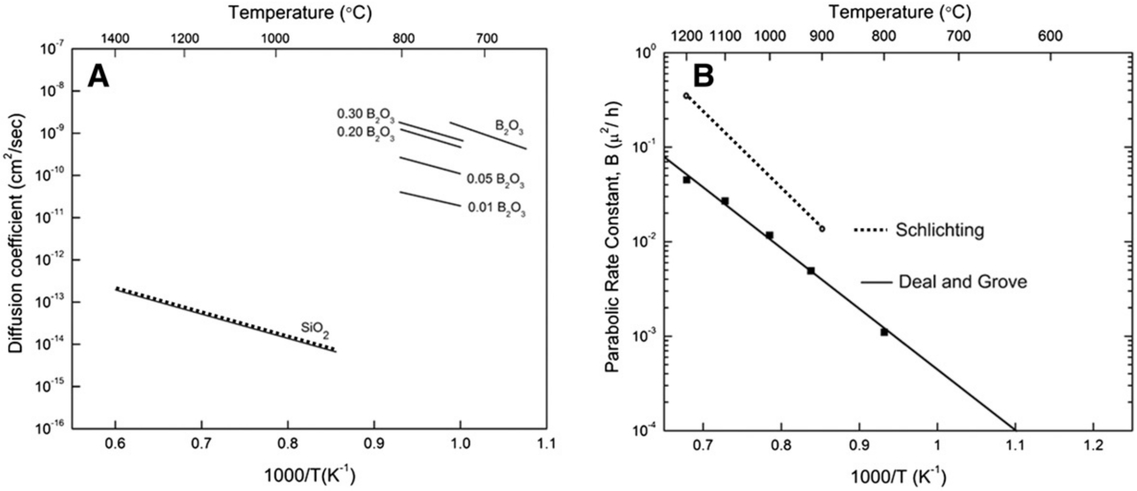

Fig. 1. A) Oxygen diffusivity through glass layers with initial (boro) silicate oxide layer derived from sol–gel method (re-plotted from Schlichting [11]). B) Comparison of silicon parabolic oxidation rates for thermally grown silica (Deal and Grove [12]) and sol - gel derived silica (Schlichting [11]).