journal

*J. Am. Ceram. Soc.*, **83** [1] 211–13 (2000)

# Observations of Accelerated Silicon Carbide Recession by Oxidation at High Water-Vapor Pressures

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**A study of the exposure of SiC at 1200°C and high water-vapor pressures (1.5 atm) has shown SiC recession rates that exceed what is predicted based on parabolic oxidation at water-vapor pressures of less than or equal to ~1 atm. After exposure to these conditions, distinct silica-scale structures are observed; thick, porous, nonprotective cristobalite scales form above a thin, dense silica layer. The porous cristobalite thickens with exposure time, while the thickness of the underlying dense layer remains constant. These observations suggest a moving-boundary phenomenon that is controlled by the rapid conversion of dense vitreous silica to a porous, nonprotective crystalline $SiO_2$.**

## I. Introduction

The effect of water ($H_2O$) vapor on silica growth on silicon-based ceramics in air or oxygen at high temperature has been investigated in some detail.[1–6] However, most studies of this effect have been conducted at water-vapor pressures of <1 atm. As part of an effort to characterize and understand the environmental effects on SiC-based composites at the higher system pressures that are encountered under combustion conditions for land-based gas turbines, the oxidation of SiC in air+15% $H_2O$ at 10 atm (~1 MPa) is being studied. This communication reports initial observations of rapid SiC recession via oxidation in a system where the water-vapor pressure is high and the gas velocity is low. The accelerated rate of SiC recession, combined with microstructural observations, suggest a moving-boundary phenomenon that is controlled by the conversion of a constant-thickness, dense vitreous silica layer to a porous, nonprotective crystalline $SiO_2$ layer that thickens with time.

## II. Experimental Conditions

SiC bars (~50 mm × 4 mm × 3 mm) or thin plates (~40 mm × 10 mm × 3 mm) were exposed in a high-pressure, high-temperature facility that has been described elsewhere.[3,7] The SiC materials used in this study were sintered α-SiC (Hexoloy™ SA, The Carborundum Co., Niagara Falls, NY) and high-purity β-SiC that was produced via chemical vapor deposition (CVD). The CVD-SiC was exposed in bulk form (Morton International Advanced Materials, Woburn, MA) or as a thick (>110 μm) seal coat on SiC-fiber-reinforced SiC composites. Exposures were conducted at a temperature of 1200°C and a total pressure of 10 atm in slowly flowing (3 cm/min) air or air+15 vol% $H_2O$, typically in increments of 500 h. $H_2O$ was injected into the gas stream above its condensation point, and the mixture was heated to the exposure temperature. The $H_2O$ in the exit stream was condensed, and its volume was measured as a function of time. Cross-sectional specimens were characterized using backscattered electron imaging and transmission electron microscopy (TEM). The degree of oxidative degradation was obtained from post-test microstructural analysis and measurement of the SiC recession directly from the polished cross sections.

## III. Results

Exposure to high-pressure air+$H_2O$ at a temperature of 1200°C for 500 h resulted in the formation of distinct silica-scale structures on the different SiC materials, as illustrated in Fig. 1 for CVD-β-SiC. A thin, dense silica layer adjacent to the SiC typically was observed under a much-thicker, porous silica scale. Such scale morphologies have been observed under similar exposure conditions for CVD-SiC seal coats that are used to protect SiC-based, fiber-reinforced composites.[7] When no water vapor was present in the gas stream, only a thin, dense vitreous silica layer formed on the surface of the SiC, as shown in Fig. 2 for sintered α-SiC.

X-ray diffractometry (XRD) of numerous specimen surfaces of CVD-SiC and α-SiC, after exposures to the air+15% $H_2O$ environment for ≥500 h, consistently identified the thick, porous surface $SiO_2$ layer as cristobalite. However, the thin, dense underlying scale was vitreous silica, as determined by TEM. This layer (denoted by the arrows in Fig. 1) was typically 4–6 μm thick. Precise thickness determinations were limited by interfacial

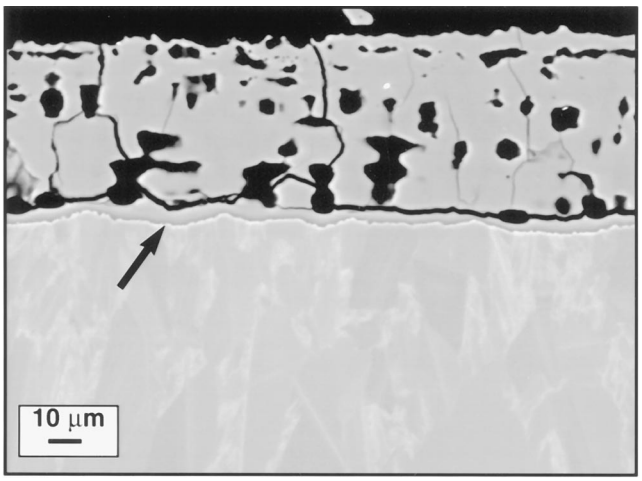


**Fig. 1.** Typical silica-scale morphology observed for bulk CVD-β-SiC after exposure to air+$H_2O$ at 1200°C and 10 atm for 500 h. Arrows show the dense silica layer.

D. P. Butt—contributing editor

Manuscript No. 189206. Received August 9, 1999; approved October 8, 1999.
Sponsored by the U.S. Dept. of Energy, Office of Energy Efficiency and Renewable Energy, Office of Industrial Technologies, as part of the Continuous Fiber Reinforced Ceramic Composite (CFCC) Program, under Contract No. DE-AC05-96OR22464 with Lockheed Martin Energy Research Corp.

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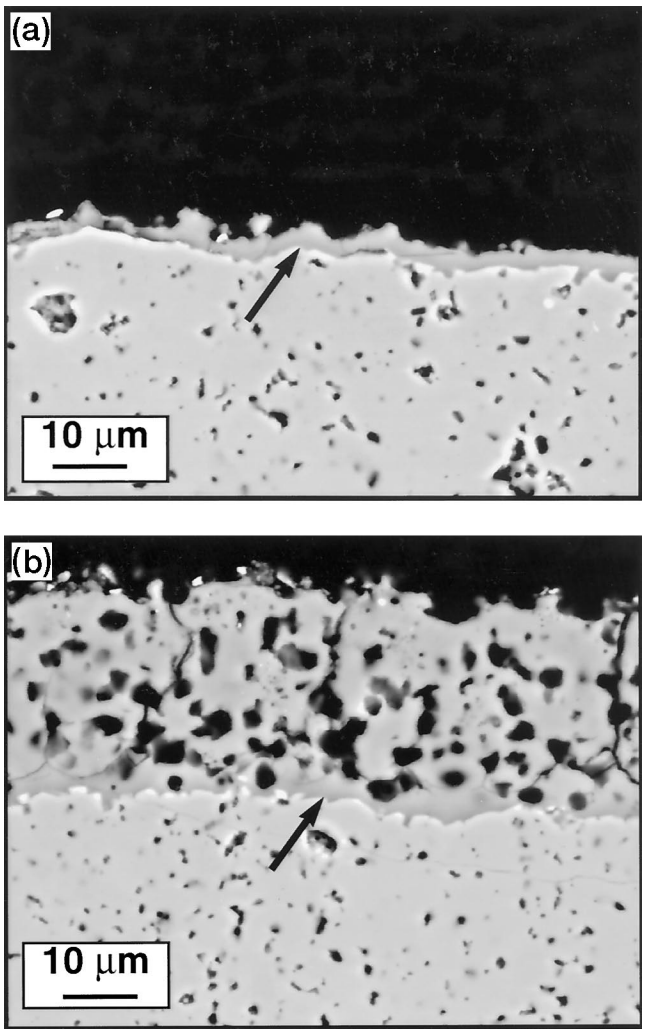


**Fig. 2.** Silica scale on sintered α-SiC after exposure at 1200°C for 100 h at 10 atm in (a) air only and (b) air+$H_2O$. Only a thin, dense silica layer formed when no $H_2O$ was present.

roughness and microstructural differences among the various forms of SiC.[8] For any particular series of exposed SiC specimens, significant changes in the thickness of this dense silica layer, as a function of exposure time (500–4000 h), were not observed.

In contrast to the constant layer thickness of the vitreous silica, the porous cristobalite scale continually thickened with exposure time. Reliable measurements of the thickness of the cristobalite mass were not possible, because of scale spallation during either cooling or handling. Nevertheless, the typical remaining thickness of the silica scale observed on the various exposed SiC specimens was substantially greater than what would be expected for this temperature and more-modest water-vapor pressures[2,6] and was qualitatively indicative of a high rate of SiC oxidation. Scale-thickness measurements are not necessarily a reliable measurement of the amount of oxidation, because of scale spallation, incorporated defects (cracks and voids), and a possible redeposition of silica that results from local gas-phase transport at low gas velocities. Direct microstructural analysis of sequentially exposed cross sections was used and consistently showed up to ~40–50 μm of SiC recession per 500 h of exposure.

## IV. Discussion

It is well-known that the presence of water vapor increases the rate of silica growth on SiC at high temperature (see Opila[6] for a summary of previous investigations). However, the rate of SiC recession observed in the present work is higher than that predicted by the well-established models for SiC oxidation, as a function of the water-vapor pressure and gas velocities.[4,5] Recently, Opila[6] formulated a relationship for the parabolic rate constant for the oxidation of SiC, as a function of water-vapor pressure, based on well-controlled experiments in which SiC was exposed to temperatures of 1000°–1400°C with up to ~0.9 atm (~90 kPa) of $H_2O$. The measured SiC recession at 1200°C and 10 atm of air +15% $H_2O$ is considerably higher than what would be predicted based on the extrapolation of the Opila relationship to this water-vapor pressure (1.5 atm (~150 kPa)).

The observed rapid conversion of SiC to $SiO_2$ and the accompanying transformation of vitreous silica to cristobalite at 1200°C are uniquely related to the presence of $H_2O$ at high pressures. Opila[6] demonstrated that $H_2O$ is the dominant oxidant when it is present in significant concentrations. In the present study, when oxygen is the major oxidant, only a thin vitreous silica scale is formed at a rate that is comparable to that reported in the literature for low water-vapor pressures (Fig. 2).[9] Furthermore, if $H_2O$ is the sole oxidant present in significant concentrations (1.7 atm (~170 kPa)), an accelerated oxidation process that is similar to what is reported here has been observed for sintered α-SiC.[3]

The presence of cristobalite after exposure at 1200°C in the high-pressure environment used in this work is not unexpected. Studies with silica glasses have indicated that $H_2O$ can significantly enhance the devitrification rate and reduce the crystallization temperature.[10] Consequently, in the present study, the exposure of fused silica in 10 atm of air or air+15% $H_2O$ at a temperature of 1200°C has revealed that a thick layer of cristobalite forms on the fused silica after 100 h, but only in the presence of added water vapor. In this regard, Opila[6] observed some conversion of amorphous silica to cristobalite during exposure of CVD-SiC in 0.9 atm of $H_2O$ at a temperature of 1200°C.

Impurities also can increase both the oxidation rate of SiC and the conversion of vitreous silica to cristobalite, particularly in the presence of water vapor.[2,6] Water vapor will facilitate the delivery of impurities to the specimen surface,[2] which, in turn, accelerates the devitrification process.[6] This process may be a contributing factor to the measurement of SiC recession rates that are higher than those predicted based on the Opila relationship; however, such impurity effects alone cannot explain the high oxidation rate of SiC that is reported here.

The very-thick porous, nonprotective silica scale that formed on the SiC in air+$H_2O$ (Figs. 1 and 2) is consistent with the above-reported rapid SiC recession. Abundant amounts of CO (and other gaseous reaction products that are associated with impurities/additives in the SiC) will be generated during the rapid oxidation of SiC at the high water-vapor pressure that is used in this work. This abundance of gaseous species can lead to a high volume of porosity in the bulk of the silica, rendering it nonprotective. However, despite this high flux of gaseous product(s), the vitreous silica layer that is observed adjacent to the SiC remains microscopically dense (see Figs. 1 and 2.)

Although more-detailed kinetic studies are needed for a definitive analysis, the observation that the thin, dense silica layer does not thicken with time suggests a moving-boundary process.[4,11,12] In the present case, a layer of fixed thickness is maintained when the oxidation front proceeds into the SiC at the same rate at which the dense silica is converted to a porous, crystalline oxide. This type of moving-boundary process would be quite distinct from a model of similar kinetic form that describes the oxidation of SiC at elevated water-vapor pressures and high gas velocities, where the rate-controlling step is the volatilization of the constant-thickness $SiO_2$.[4,5] As such, this latter model, for the low gas-flow rate that has been used in this study, would predict much-less SiC recession than what is reported here.

The present results do not allow determination of the actual mechanism(s) that controls the rapid conversion of dense silica to porous silica. As discussed previously, the process is accompanied by the transformation of vitreous silica to cristobalite, despite a relatively low exposure temperature; however, the relationship to porosity formation is not yet clear. Controlled experiments to more

rigorously determine the oxidation kinetics and examine a mechanistic basis for the rate-controlling step of a moving-boundary process (using specimens of pure silicon, fused silica, and various forms of SiC) currently are being conducted.

## V. Summary

Exposures of SiC in a high-pressure (10 atm), low-flow-velocity, air+15% $H_2O$ environment at a temperature of 1200°C have revealed very rapid SiC recession rates that are not predicted by previous studies that relate (i) parabolic oxidation rate constants to water-vapor pressures or (ii) linear recession rates to gas velocity, based on $SiO_2$ volatility. The present SiC recession data and microstructural observations suggest a moving-boundary phenomenon that is controlled by the rapid conversion of a constant-thickness, dense vitreous silica layer to a porous, nonprotective crystalline $SiO_2$ layer at elevated water-vapor levels.

## Acknowledgments

The authors thank L. R. Walker, M. Howell, and T. S. Geer for technical assistance, M. P. Brady, J. A. Haynes, and P. F. Becher for reviewing the manuscript, and E. J. Opila and J. L. Smialek (NASA—Glenn) for helpful discussions.

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