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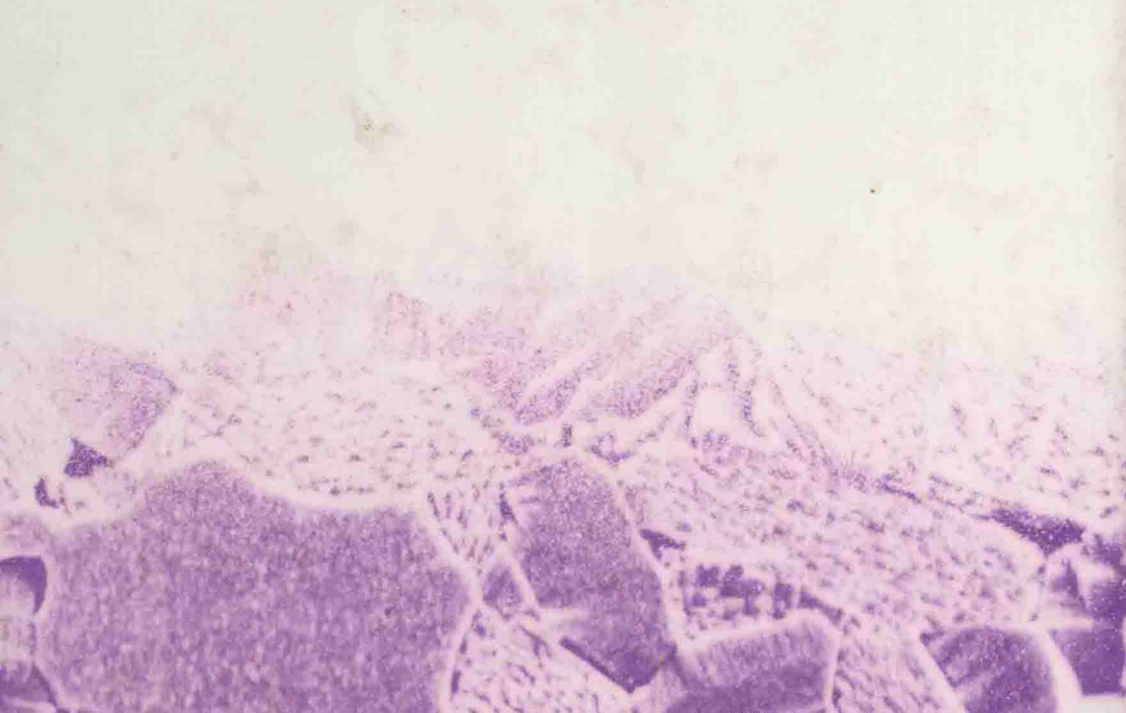
Ceramic Transactions

CORROSION AND CORROSIVE DEGRADATION OF CERAMICS

Richard E. Tressler • Michael McNallan



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CORROSION AND CORROSIVE DEGRADATION OF CERAMICS

Edited by Richard E. Tressler, The Pennsylvania State University
and
Michael McNallan, University of Illinois

The American Ceramic Society, Inc.
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Preface

This volume on "Corrosion and Corrosive Degradation of Ceramics" constitutes the proceedings of an international symposium held as part of the First Ceramic Science and Technology Congress at Anaheim, CA, on November 1 and 2, 1989. The need for an international symposium on this topic was emphatically identified during a workshop on corrosion of ceramics sponsored by the Gas Research Institute and held at Penn State on November 12–13, 1987. GRI graciously agreed to cosponsor the symposium, and we thank Dr. Max Klein and Mr. Michael Lukasiewicz of GRI for their encouragement and support.

In this symposium we attempted to cover all of the current research thrusts in this emerging field of research by inviting internationally-known authorities in the various subfields of this general topic. The major emphasis became the high temperature corrosion behavior in corrosive gases and molten liquids largely because it is this regime of behavior which often defines the safe use envelope in applications. Some papers dealt with the coupled effects of corrosive environment and applied stress on the performance of ceramics which represent an important new research thrust in structural ceramics. A paper entitled "Water Corrosion of $YBa_2Cu_3O_{7-\delta}$ Superconductors" by L. D. Fitch and V. L. Burdick, presented at the meeting, has been published elsewhere (*J. Am. Ceram. Soc.*, **72** (10) 2020–2023 (1989)). This collection of papers represents the state-of-the-art in our understanding of the corrosion and corrosive degradation of ceramics, and it is the first comprehensive book to review the whole field.

We are grateful to the many invited speakers and contributors, particularly the international contingent who form a major resource in this field. We thank the American Ceramic Society for cosponsoring the symposium. We are grateful to Ms. Pam Achter and her staff for promptly editing and compiling this volume. Thanks are due to our staff of Ms. Carol Fee, Ms. Naomi McNulty, and Ms. Lynn Kile for assistance in organizing the program and the manuscript.

February 1990

Richard E. Tressler
Michael McNallan
University Park, PA

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Oxidation of Silicon Carbide Single Crystals and CVD Silicon Nitride*

K. E. SPEAR, R. E. TRESSLER, Z. ZHENG, AND H. DU

Center for Advanced Materials
Ceramic Science and Engineering
The Pennsylvania State University
University Park, PA

The passive oxidation of single crystal silicon carbide and polycrystalline CVD silicon nitride in well-defined oxidizing atmospheres was investigated as a function of temperature, partial pressures, and time to determine the reaction kinetics and scale characteristics for the purest forms of these materials. Parallel experiments using single crystal silicon served as a calibration of these measurements. Parabolic rate behavior was indicated in all cases, as was a dependence of the oxidation rate on the ambient oxygen partial pressure. This evidence indicates that the diffusion of the oxidant through the protective oxide scale was rate controlling. Experimental evidence ruled out the diffusion of product species such as CO or nitrogen as important rate controlling processes. Oxygen isotope studies led to the conclusion that molecular O_2 *is the primary oxidant species transported through the* SiO_2 *scale at temperatures up to 1200°C, but the importance of ionic oxygen diffusion could not be eliminated for temperatures of 1300°C and higher. The marked difference in oxidation behavior of silicon carbide and silicon nitride is explained by the formation of an intermediate oxynitride phase in the nitride system. The diffusion of oxygen through this oxynitride is concluded to be rate controlling. Kinetic and mechanistic models for the oxidation processes were developed to explain the observed results. The developed silicon carbide models appear to adequately represent the experimental results, but for silicon nitride, inconsistencies still exist between the mechanistic model deduced from experimental oxidation data and the partial equilibrium calculations based on this model.*

Introduction

The long term reliability of structural ceramics depends critically on their resistance to environmental corrosion. Developing a basic understanding of the

*This work was funded by the Gas Research Institute under Contract No. 5086-232-1233.

corrosion of silicon carbide and silicon nitride structural parts requires baseline information and models describing the behavior of the pure ceramics in well-defined environments. Investigations of the influence of specific sintering aids and microstructures on the rates and mechanisms of corrosion can then be used to expand these models to engineering ceramic parts.

This paper summarizes research on the oxidation of single crystal SiC and high purity polycrystalline Si_3N_4 CVD coatings in dry oxygen ambients to provide baseline information for these materials. All experiments were performed under temperature-oxygen partial pressure conditions which produced protective SiO_2 product scales on the surface of the samples; i.e., passive oxidation conditions were used in all experiments. The oxidation scales were carefully characterized, and kinetic and thermodynamic models for describing the rates were developed. Single crystal silicon was studied simultaneously to calibrate our experimental measurements. A summary and comparison of our experimental results, conclusions, and models for the oxidation of SiC, Si, and Si_3N_4 are given in this paper. A discussion of the inconsistencies in the thermochemical and mass transport models describing the oxidation of silicon nitride points out the gaps in our understanding of the oxidation behavior of this system.

Comparisons of Experimental Results and Conclusions

The experimental research on the passive oxidation of SiC, Si, and Si_3N_4 included investigations of oxidation kinetics and characterization of the resulting oxide scales. The detailed experimental results on the oxidation of both silicon carbide[1] and silicon nitride[2] have been published elsewhere, so they are only summarized below.

Experimental Materials and Conditions

Silicon carbide single crystal samples were extracted from Acheson furnace clusters of hexagonal alpha-SiC crystal platelets. Both the $(000\bar{1})$ carbon faces and the (0001) silicon faces of the primarily 4H-SiC crystals were examined, although most studies were of the $(000\bar{1})$ carbon faces. The primary impurities were 10 ppm Fe, 50 ppm Ti, and 100 ppm V. The silicon nitride samples were single phase, polycrystalline alpha-Si_3N_4 CVD coatings of high purity furnished by F. S. Galasso, United Technologies Research Center, East Hartford, Connecticut. The sample surfaces were cleaned to remove oxide and other impurities before the oxidation experiments. The oxidizing gaseous ambients were kept free from moisture (<3 ppm).

The kinetics of the process were examined as a function of time, temperature, oxygen pressure, and in the case of silicon nitride, nitrogen pressure. These

Table I. **Experimental Conditions Used in Oxidation Studies**

Parameter	SiC	Si_3N_4
time (min)	60 to 480	60 to 480
T(°C)	1200–1500	1100–1400
$P(O_2)$(atm)	10^{-3}–1	0.05–1
$P(N_2)$ (atm)		0–0.5

experimental parameters are listed in Table I. Argon gas was used when needed to bring the total pressure of the oxidizing ambient to one atmosphere.

General Comparisons

Figure 1 is a schematic diagram illustrating the similarities and differences in the passive oxidation of silicon metal, silicon carbide, and silicon nitride. The oxidation of Si with oxygen produces only one product phase, solid SiO_2. In addition to the solid product of SiO_2, the oxidation of SiC also produces gaseous CO at the SiC interface. As the CO diffuses outward toward the more oxidizing SiO_2/gas interface, it must be oxidized to CO_2. Solid carbon would also form at the SiC/SiO_2 interface if the removal of the CO oxidation product from this interface were slow.

The passive oxidation of silicon nitride results in a solid SiO_2 scale at the gas/oxide interface, an intermediate oxynitride between the SiO_2 and Si_3N_4, and gaseous nitrogen which must diffuse outward through this duplex oxide scale. Thus, two oxidation processes occur in the nitride system: the Si_3N_4 is first oxidized to the oxynitride, and then the oxynitride phase is fully oxidized to SiO_2. Nitrogen is a product in both of these processes.

In all systems, the oxidant must first diffuse through an outer scale of SiO_2. In the case of the silicon nitride, the oxidant must then diffuse through a silicon oxynitride phase before reaching the Si_3N_4 surface.

Table II lists typical results obtained from oxidizing SiC, Si_3N_4, and Si in 1 atm O_2 at 1300°C for 5 hours.[3,4] Figure 2 provides a comparison of the oxidation of these three materials with an Arrhenius plot of the logarithm of the parabolic rate constants versus the reciprocal temperature for the passive oxidation of these three materials. This figure clearly shows the similarities in the Si and SiC oxidation behavior, and their differences with the Si_3N_4 behavior.

Oxide Scale Characterization

In all experiments, a protective oxide scale formed so that oxidation occurred under passive conditions (loss of material by SiO(g) was negligible). The

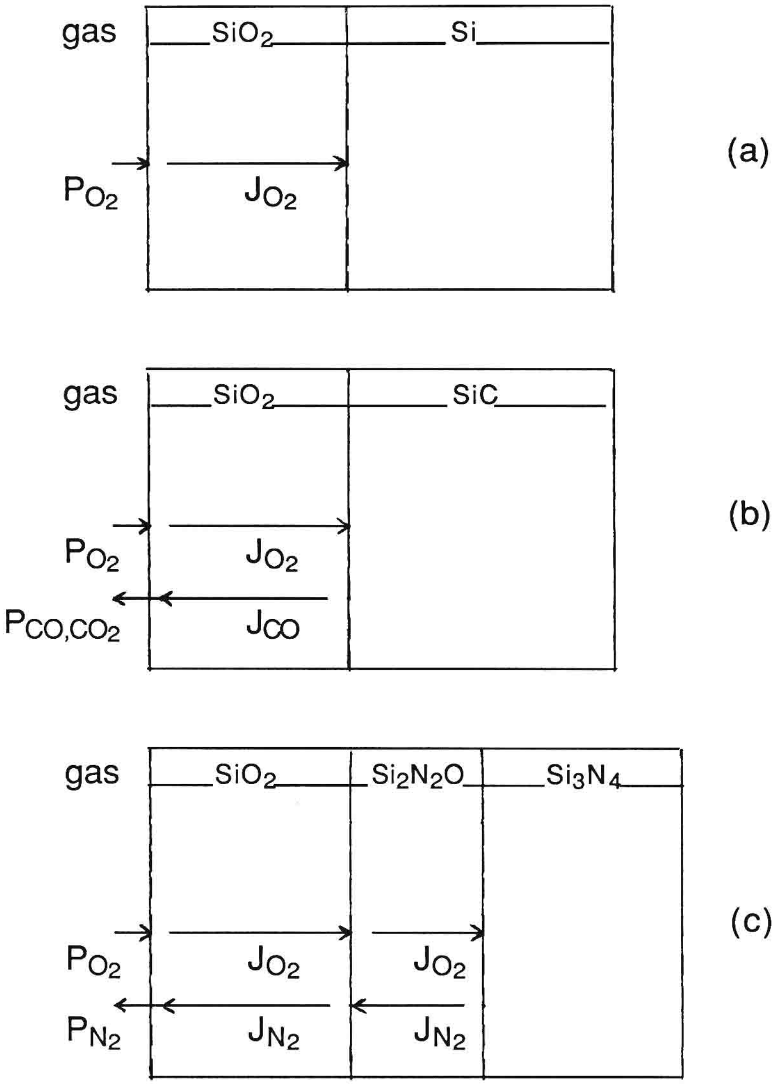

Fig. 1. **Schematic diagram showing the flux of oxygen in and product species out through the oxide scale during the oxidation of (*a*) Si, (*b*), SiC, and (*c*) Si_3N_4.**