Nitrogen as an Ablative Reactant in Dissociated Air

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Introduction

Far from merely playing the role of a diluent for oxygen, there is increasing evidence that nitrogen participates chemically in the high-temperature combustion[1,2] or ablation[3] of condensed phases.‡ A common feature of these recent examples (the combustion of zirconium and aluminum droplets, and ablation of the Apollo heat shield material, respectively) is that the nitrogen effect cannot be anticipated from experiments carried out in pure nitrogen alone, i.e., the nitrogen/oxygen combination is essential. We wish to report here a striking laboratory example of the combined effects of nitrogen with oxygen in determining the ablation rate of an important refractory material (SiC) chemically far simpler than the Apollo heat shield.§

In the course of a kinetic study of the attack of pyrolytic silicon carbide filaments by each of the gases $O(g)$, $O_2(g)$, $N(g)$, and $N_2(g)$ at subatmospheric pressures and surface temperatures above 1800° K, an extremely high collision efficiency for the $N(g) + SiC(s)$ reaction was observed.[6] Consideration of the previously mentioned precedents immediately suggested an examination of the kinetics of $SiC(s)$ attack in $N(g) + O(g)$ mixtures, with the results reported below.

Experimental Technique

$N + O$ gaseous mixtures were generated by the microwave discharge dissociation of 3% N_2/97% Ar mixtures¶ at ≈ 1 torr total pressure, downstream of which controllable amounts of $NO(g)$ were introduced to produce O-atoms via the rapid bimolecular exchange reaction: $N + NO \rightarrow O + N_2$. The accompanying chemiluminescent reactions were used as indicators for determining absolute N-atom concentrations by the light titration technique.[4,10] The silicon carbide specimens were cut from commercially available 0.102-mm (4-mil) o.d. filaments[11] [chemically vapor deposited on a 0.0127-mm (0.5-mil) diam tungsten substrate] and then electrically (resistively) heated. Reaction rates were determined by microscope determinations of the reduction in filament diameter after constant temperature exposures to the $N(g)/O(g)/Ar(g)$ streams for known durations. Filament temperatures reported are taken to be proportional to optical pyrometer brightness temperature, with the proportionality constants fixed in the temperature range 1366°–1644°K using the melting of 4 pyrometric compounds.** Control experiments in which deliberate changes were effected in total gas flow rate, carrier gas identity and means of generating the atomic reactant, demonstrated that the reaction rates reported pertain to the chemically controlled attack of $SiC(s)$ by ground state atomic reactants at the reported surface temperatures.[7]

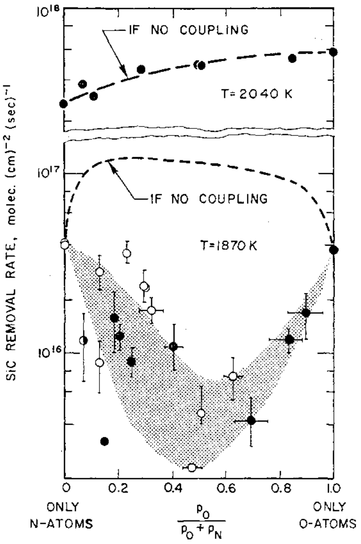

Fig. 1 Kinetics of the attack of silicon carbide[11] by atomic nitrogen/atomic oxygen mixtures [$p_N + p_O = 1.1 \times 10^{-2}$ torr; *p*-(total) = 1 torr; ⊙ white coating, ● no visible coating].

Experimental Results on the $SiC(s)/N(g) + O(g)$ System

Our experiments at a total reactant pressure of 1.1×10^{-2} torr reveal that SiC (*s*) is much less vulnerable to chemical attack by N + O mixtures than expected from our individual N-atom and O-atom data, especially at surface temperatures below about 2000°K. [Above this temperature, nothing seems unusual about the N + O combination, in the sense that the oxygen and nitrogen contributions to Si-atom (or C-atom) removal from the filament appear to be additive.] These trends are clearly seen in Fig. 1, where the abscissa is the fraction of the total reactant pressure (constant at 1.1×10^{-2} torr) comprised by atomic oxygen. Plotted on this figure are the observed adsorbent atom removal rates [silicon or carbon element flux, as inferred from the rate of filament diameter reduction and the nominal density (3.2 g/cm^3) of SiC], as well as the rates that would have been anticipated if the N-atom and O-atom contributions were simply additive (dashed curve,†† marked: if no coupling). Despite the considerable scatter encountered at 1870°K,‡‡ it is clear that the reaction rates observed in nearly equimolar N + 0 mixtures are lower than the additivity prediction by more than one

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‡ Considered "lazy" (azote) for more than a century following its isolation/identification, the element nitrogen is now well known to have chemically active forms[4] (e.g., atomic nitrogen) readily produced in electrically discharged or shock-heated gases.

§ The latter has reen reported[3] to be comprised of an epoxy resin, phenolic microballoons, and fiberglass reinforcement in a fiberglass reinforced-phenolic honeycomb matrix. Interestingly enough, both postablation test chemical analysis and thermochemical calculations reveal that silicon carbide is formed in situ and removed during the interaction of the reaction product $SiO_2(c)$ with the carbonaceous char;[3] however, the role of SiC formation/removal in accounting for the observed (total) rate of carbon element removal is unknown. Silicon carbide is also the basis of several promising refractory composites[5] (SiC/B_4C, SiC/HfB_2) for aerospace applications, and (in whisker or filament form) is increasingly used as a reinforcing agent in composites.

¶ Details of our experimental technique are given in Refs. 7–9.

** Produced by the Tempil Corp., N. Y.

†† These were calculated from the partial pressure dependence of the individual reaction rates, independently measured at the reported surface temperatures.[6] The unusual behavior of this no coupling curve at 1870°K is associated with the fact that increased concentrations of O-atoms or N-atoms have been found to suppress the over-all reaction rate slightly at this temperature[6] (i.e., the reaction order is negative).

‡‡ Perhaps associated with the in situ nucleation of visually different surface films observed on the SiC specimens upon cool down (cf. data points shown in Fig. 1: ⊙ white coating, ● no visible coating).

order of magnitude. A similar set of experiments at higher surface temperature (2040°K, cf. top panel of Fig. 1) did not show this strong coupling behavior. Indeed, when the temperature dependence of the heterogeneous reaction in equimolar N + O mixtures was investigated (Fig. 2) it became clear that the N + O coupling effect was marked only below about 2000°K, where the reaction probability§§ drops from its high plateau values ($\approx \frac{1}{4}$–$\frac{1}{2}$) to much lower, strongly temperature-dependent values.

Discussion

By analogy with previous examples of reactant coupling in heterogeneous systems (Refs. 12 and 13), we are immediately led to inquire if new stable reaction products can be synthesized in the SiC/N+O system that could not be synthesized in the SiC/N and SiC/O systems taken individually. In the present case, this is not only a priori likely, but it is found that one (Si_2ON_2) of several possible silicon oxynitride compounds, is already familiar to ceramicists[14] and meteorite analysts.[15]¶¶ While little is yet known of its high-temperature vaporization behavior, Washburn[14] reports that its oxidation resistance (in undissociated air at 1 atm) is superior to that of SiC(*s*) and $Si_3N_4(s)$ at temperatures as high as 2023°K. This background information, combined with our observation that the suppression of SiC oxidation in N + O mixtures takes place in the low temperature-high activation energy-low reaction order regime commonly associated with the existence of rate-limiting condensed product films,[6,9] strongly suggests that we are witnessing the inhibiting effects of in situ silicon oxynitride formation (stoichiometry as yet undetermined) on the steady-state reactivity of our silicon carbide specimens. That this effect should vanish at sufficiently high surface temperatures is qualitatively consistent with the increased desorption rates (and lower steady-state nitrogen and oxygen adatom surface coverages) characterizing the high-temperature plateau region (Fig. 1), and suggests that silicon oxynitride formation ultimately becomes thermodynamically unfavorable under our experimental conditions.

Conclusions

The surprisingly low chemically controlled ablation rate of silicon carbide in O + N mixtures observed here can be qualitatively accounted for by the in situ formation of microscopic silicon oxynitride surface films. These films are apparently more stable (against vaporization) in the present O + N environment than the corresponding $SiO_2(c)$ surface phase in atomic oxygen or $Si_3N_4(c)$ in atomic nitrogen. If this postulate is correct, our work suggests that greater attention should be paid to the possible role of stable oxynitride compounds in future studies of ablation in dissociated air, particularly for silicon-containing materials. More pointedly, ablation analysts should be aware that the absence of such compounds in presently available thermochemical tables[17] provides little assurance that their over-all effects on ablation rate will be negligible.

Added in press: Preliminary x-ray studies indeed reveal the presence of new crystalline phases on the recovered surface of SiC(*s*) filaments exposed to O + N mixtures. The observed patterns, which are more complex than those of stoichiometric Si_2ON_2, are presently under investigation. For a recent experimented study of the equilibrium between $SiO_2(s)$, $Si_2ON_2(s)$, $N_2(g)$, and $O_2(g)$ at 1673°K and 1773°K, see Ref. 18.

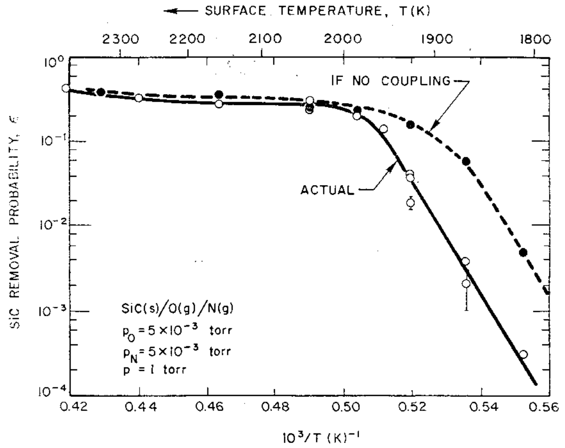

Fig. 2 Temperature dependence of the attack of silicon carbide[11] by an equimolar atomic nitrogen/atomic oxygen mixture. [$p_N = p_O = 0.5 \times 10^{-2}$ torr; p(total) = 1 torr; ⊙ rates observed in N + O mixture, ● rates expected based on independent nitridation and oxidation data[6].]

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§§ The reaction probability presented in Fig. 2 is simply the number of silicon or carbon atoms removed from the filament (regardless of their chemical state of aggregation) per reactant atom strike.

¶¶ Called sinoite,[15] white crystalline $Si_2ON_2(s)$ has a structure in which each silicon atom is tetrahedrally surrounded by one O-atom and three N-atoms.[16] Its prominence among nitrides formed in meteorites suggest that it is among the stablest of condensed nitrides. Interestingly enough, it appears that $Si_2ON_2(s)$ cannot be formed by heating $SiO_2(s)/Si_3N_4(s)$ mixtures, but can be formed in the high-temperature oxidation of $Si_3N_4(s)$.[14]

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A Perturbation Solution for Fins with Conduction, Convection, and Radiation Interaction

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Nomenclature

A = cross-sectional area of fin
E = radiation emittance (total hemispherical value)
h = convective heat-transfer coefficient
k = thermal conductivity
L = length of fin
p = perimeter
T = temperature
X = axial distance, measured from fin base
Z = dimensionless distance = X/L
ϵ = radiation-conduction parameter = $\sigma EpL^2T_b{}^3/kA$
θ = dimensionless temperature = T/T_b
λ^2 = Biot modulus = hpL^2/kA
ν = fin geometry parameter = A/pL
σ = Stefan-Boltzmann constant

Subscripts

b = fin base
e = environment

Introduction

INTEREST in space radiators has stimulated considerable work on conduction problems with surface radiation. Such problems are characterized by nonlinear differential equations as in fins, or nonlinear boundary conditions as in one-dimensional slabs. Because of the nonlinear nature of these systems most exact solutions involve numerical integrations requiring the use of computers.[1–4]

Perturbation techniques have been extensively applied in obtaining approximate solutions to problems in fluid mechanics. However, their utilization in solving heat-transfer problems involving the interaction of conduction with radiation has been limited. Tien and Abu-Romia[5] discuss the analysis of radiation interaction problems using perturbation methods. Dicker and Asnani[6] developed a perturbation technique for determining the transient temperature in a one-dimensional slab that is insulated on one side and subject to radiation on the other side. Mueller and Malmuth[7] applied the techniques of singular perturbation to solve the steady-state conduction problem with surface radiation and aerodynamic heating for a finite fin insulated on both ends.

This Note presents a regular perturbation solution to the fin problem with a constant base temperature and a radiating tip condition. The solution takes into consideration the interaction of conduction with radiation and convection. To examine the accuracy of the perturbation solution, a numerical solution is obtained.

Analysis

The system under consideration is a constant cross-sectional area fin of length L and perimeter p, which is maintained at constant base temperature T_b at $X = 0$ and subject to radiation to an environment at temperature T_e at $X = L$. The fin also exchanges heat with the environment along its length by convection and radiation. The thermal conductivity k, radiation emittance E, and convective heat-transfer coefficient h are assumed constant. Based on these assumptions, the one-dimensional steady-state conduction equation, written in dimensionless form, is

$$d^2\theta/dZ^2 - \epsilon\theta^4 - \lambda^2\theta = -\epsilon\theta_e{}^4 - \lambda^2\theta_e \tag{1}$$

with boundary conditions

$$\theta(0) = 1 \tag{2}$$

$$d\theta(1)/dZ = -\epsilon\nu[\theta^4(1) - \theta_e{}^4] \tag{3}$$

where

$$\epsilon = \sigma EpL^2T_b{}^3/kA \text{ (radiation-conduction parameter)} \tag{4}$$

$$\lambda^2 = hpL^2/kA \text{ (Biot modulus)} \tag{5}$$

$$\nu = A/pL \text{ (geometry parameter)} \tag{6}$$

The case of $\epsilon \ll 1$, which corresponds to weak radiation-conduction interaction, is considered. An asymptotic expansion for θ in the perturbation parameter ϵ is assumed. Considering the first-order approximation in ϵ, gives:

$$\theta(Z;\ \epsilon) = \theta_0(Z) + \epsilon\theta_1(Z) \tag{7}$$

Substituting (7) in Eqs. (1–3) and equating terms of equal powers of ϵ the zero- and first-order problems are obtained. For the zero order, the governing equation and boundary conditions are

$$d^2\theta_0/dZ^2 - \lambda^2\theta_0 = -\lambda^2\theta_e \tag{8a}$$

$$\theta_0(0) = 1 \tag{8b}$$

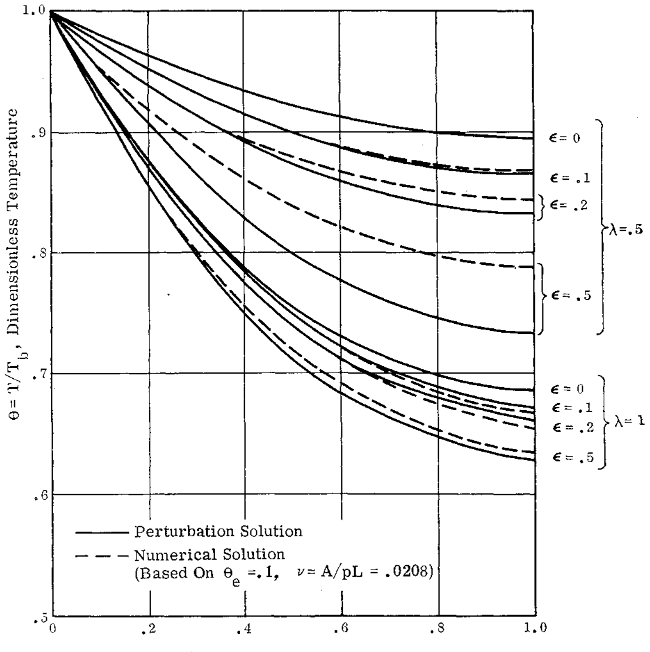

Fig. 1 Conductive fin subject to a radiative and convective environment.

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