3) The critical heat load Q_c at which value the superfluid breakdown occurs increases proportionally to the wetted perimeter for the film flow for moderate values of D_w.

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Prediction of Recession Rates for Pyrolytic Graphite

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Introduction

A THIN coating of pyrolytic graphite can protect the structure of advanced performance ramjet combustors from oxidation by hot combustion gases for two reasons. First, the dense, nonporous pyrolytic graphite offers fewer sites for attack by oxygen than does ordinary, more porous graphite. Second, by the nature of the deposition process of pyrolytic graphite, it is primarily the relatively nonreactive basal plane that is exposed to attack. However, pyrolytic graphite is subject to oxidation, and recession rates must be used in calculating the proper coating thickness. Excess thickness increases the time and cost of the coating process and results in vehicle performance penalties.

Ramjets typically operate at temperatures near 2000 K and at pressures from 1 to 10 atm. Their exhaust contains 5-15% oxygen. For these conditions, the oxidation of pyrolytic graphite is reaction rate controlled; oxygen diffuses to the surface more rapidly than it can react at the surface. Previous studies of graphite ablation have primarily considered only molecular oxygen. However, it has been observed that at high temperatures atomic oxygen reacts with pyrolytic graphite 50-80 times as fast as molecular oxygen.[1-4]

The surface reaction rate, which is kinetically controlled, proceeds by[5]

$$C + O_2 \rightarrow CO + O \tag{1}$$

and

$$C + O \rightarrow CO \tag{2}$$

Reactions forming CO_2 are neglected because they are much slower. We have also neglected reactions involving gas phase molecules other than oxygen. Although H_2O and CO_2 may actively contribute to graphite oxidation, Schaefer et al.[6] present an equation for the oxidation rate of pyrolytic graphite in the presence of H_2O and CO_2 from which we estimate that the combined mass loss from those two gases is less than 1% of the expected loss from oxygen alone.

This Note compares the recession rates of pyrolytic graphite due to molecular and atomic oxygen over a wide range of ramjet operating conditions. It is concluded that the neglect of atomic oxygen can contribute errors as large as 100% in predicted pyrolytic graphite recession rates.

Molecular Oxygen Recession Rate

Nagel and Strickland-Constable[7] reported rate constants for the oxidation of pyrolytic graphite. They fit their experimental data to a surface reaction mechanism proposed by Blyholder et al.,[8] which involved two different rate equations. At temperatures below 1000 K the oxidation is described by a rate equation with an activation energy of 25 to 30 kcal/gmole. Between 1500 and 2300 K, the rate of oxidation reaches a maximum, then decreases. At still higher temperatures it increases again, following a rate equation with an activation energy between 70 and 90 kcal/gmole.

Blyholder et al. assumed two types of surface active sites to be present on carbon. The more reactive (type A) sites support the oxidation reaction at low temperatures. At higher temperatures, some type A sites are converted to less reactive (type B) sites. This accounts for the temporary decrease in the oxidation rate in the intermediate (1500-2300 K) range of temperatures. The mechanism is described by a set of three elementary reactions

	Reaction	Rate (gram atoms C/cm^2-s)	
(i)	$A + O_2 \rightarrow A + 2CO$	$r_{(i)} = k_A P_{O_2}(x)/(1 + k_z P_{O_2})$	(3)
(ii)	$B + O_2 \rightarrow A + 2CO$	$r_{(ii)} = k_B P_{O_2}(1 - x)$	(4)
(iii)	$A \rightarrow B$	$r_{(iii)} = k_T(x)$	(5)

where (x) is the fraction of surface covered with type A sites; $(1-x)$ the fraction of surface covered with type B sites; P_{O2} the partial pressure of oxygen in atmospheres, and k_A, k_B, k_z, and k_T are reaction rate constants. Applying the stationary state assumption to Eqs. (4) and (5) yields the value of x as

$$x = \left(1 + \frac{k_T}{k_B P_{O_2}}\right)^{-1} \tag{6}$$

The recession rate in cm/s becomes

$$\dot{S}_{O_2} = \left[\frac{k_A P_{O2}}{1 + k_z P_{O2}}(x) + k_B P_{O2}(1 - x)\right] 12/\rho_{pg} \tag{7}$$

using Eqs. (3) and (4), where Eq. (6) defines x. The density of pyrolytic graphite, ρ_{pg}, is assumed to be 2.20 g/cm^3 throughout this study.

Using a best fit to the experimental data, Nagle and Strickland-Constable[7] obtained the following rate constants: $k_A = 20 \exp(-30{,}000/RT_w)$; $k_B = 4.46 \times 10^{-3} \exp(-15{,}200/RT_w)$; $k_T = 1.51 \times 10^5 \exp(-97{,}000/RT_w)$; $k_z = 21.3 \exp(+4100/RT_w)$; where $R = 1.987$ cal/gmole-K and T_w is the surface temperature in K.

The recession rate is shown in Fig. 1 as a function of the wall temperature for several values of molecular oxygen partial pressure.

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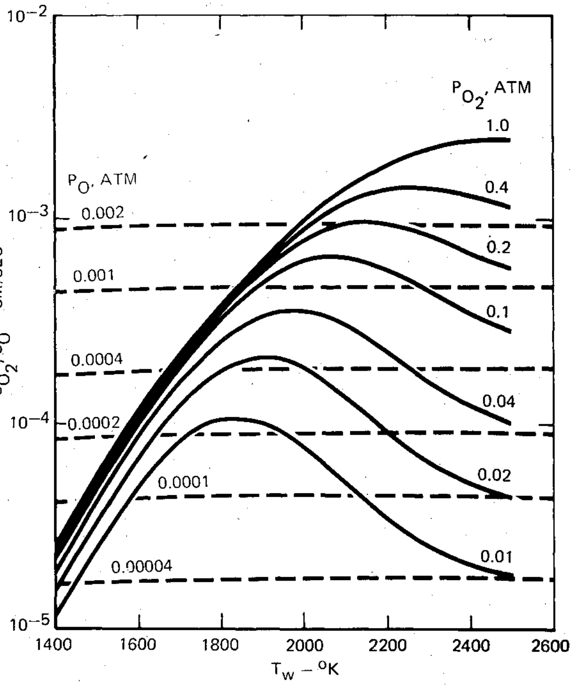

Fig. 1 Variation of pyrolytic graphite recession rates $\dot{S}_{O_2}$ (——) and $\dot{S}_O$ (-----) with wall temperature T_w.

Atomic Oxygen Recession Rate

Reaction (2) is assumed to occur with a reaction probability of ϵ, where ϵ is defined as the ratio of the number of carbon atoms removed from the surface to the total number of atomic oxygen atoms that collide with the surface.[1-3] Park[5] represents the reaction probability as $\epsilon = 0.63 \exp(-1160/T_w)$ by curve-fitting experimental data. There is considerable scatter in the data, especially near temperatures of 2000 K, so that the expression for ϵ is only accurate to about ±50%.

The atomic oxygen reaction rate in g/(cm^2-s) is defined as[1]

$$\dot{m}=0.25\left(\frac{P_O}{kT_w}\right)\left[\frac{8kT_w}{\pi m_O}\right]^{1/2} m_c\epsilon \tag{8}$$

where P_O is the atomic oxygen pressure in atmospheres, m_O the atomic oxygen mass, m_c the atomic carbon mass, and k the Boltzmann constant. The recession rate in cm/s is $\dot{m}/\rho_{pg}$. It can be written as

$$\dot{S}_O=38.08\frac{P_O}{\sqrt{T_w}}\exp\left(\frac{-1160}{T_w}\right) \tag{9}$$

This recession rate is shown in Fig. 1 as a function of the wall temperature for a range of atomic oxygen pressures. Note that the rate is directly proportional to P_O and is insensitive to T_w.

Combined Recession Rate

The total recession rate due to molecular and atomic oxygen is additive. However, $\dot{S}_{O_2}$ and $\dot{S}_O$ are coupled through the relative amounts of O_2 and O in the gas. This, in turn, is related to the thermodynamic state of the gas.

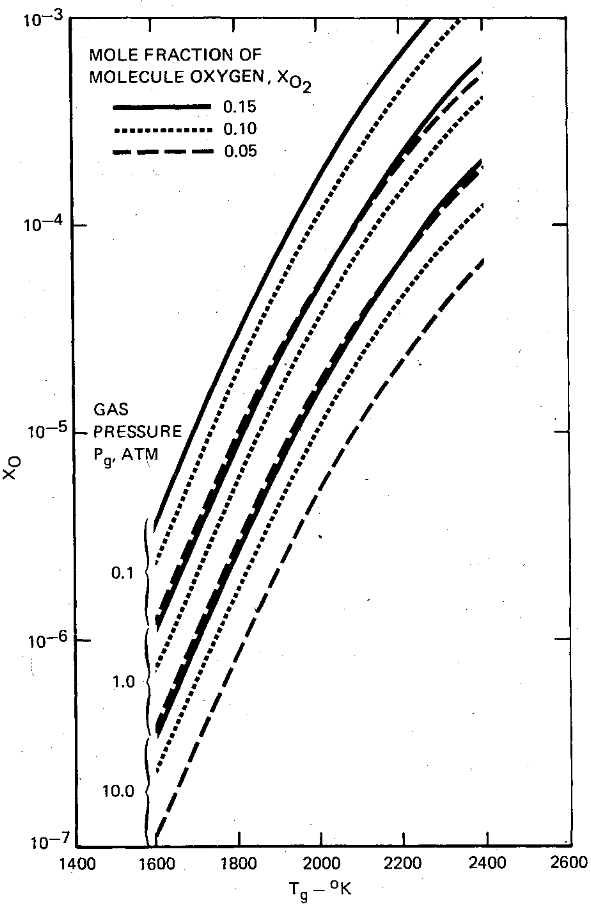

Fig. 2 Variation of mole fraction of atomic oxygen X_O with gas temperature T_g.

Numerical Calculations

The recession rate due to atomic oxygen was calculated for typical combustor exhaust thermodynamic conditions. Knowing the fuel/air ratio and the gas total pressure and total temperature, we can calculate the mole fraction of molecular oxygen. The mole fraction of atomic oxygen is calculated assuming that the O_2 in the combustion gas partially dissociates to form atomic oxygen. The reaction can be written as

$$nG+O_2\rightarrow(1-a)O_2+2aO+nG \tag{10}$$

where n is the number of moles of inert species G. The O_2 and O are assumed to exist in equilibrium at the gas pressure and temperature. The final mole fractions are related to the parameter a by $X_{O_2}=(1-a)/(1+a+n)$ and $X_O=2a/(1+a+n)$. The magnitude of a is determined from the equilibrium constant for the reaction $O_2 \rightleftharpoons 2O$. Thus,

$$K_P(T_g)=X_O^2P_g/X_{O_2} \tag{11}$$

where P_g is the gas pressure in atmospheres and $K_p(T_g)$ is the equilibrium constant, which is tabulated as a function of gas temperature in Ref. 9. Solutions of Eq. (11) for specific values of n at the thermodynamic conditions of interest indicate that the mole fraction of O_2 does not change significantly due to dissociation.

Figure 2 shows the mole fraction of atomic oxygen as a function of the gas temperature and pressure. For each gas pressure, results are shown for mole fractions of molecular oxygen of 0.05, 0.10, and 0.15. The mole fraction of atomic oxygen is quite sensitive to gas temperature and is much smaller than the mole fraction of molecular oxygen in this temperature-pressure range.

The recession rate for a given set of thermodynamic conditions can be calculated as follows. Assume $T_g = 2200$ K; $T_w = 1800$ K; $P_g = 1$ atm; and $X_{O_2} = 0.10$. At these conditions, $P_{O_2} = 0.1$ atm; and from Fig. 2, $X_O = 1.33\times10^{-4}$. This yields $P_O = 1.33\times10^{-4}$ atm. From Fig. 1, at $T_w = 1800$ K, we get $\dot{S}_{O_2} = 3.1\times10^{-4}$ and $\dot{S}_O = 0.63\times10^{-4}$ cm/s. Adding $\dot{S}_{O_2}$ and $\dot{S}_O$ gives a total recession rate of 3.7×10^{-4} cm/s, of which 17% is due to atomic oxygen.

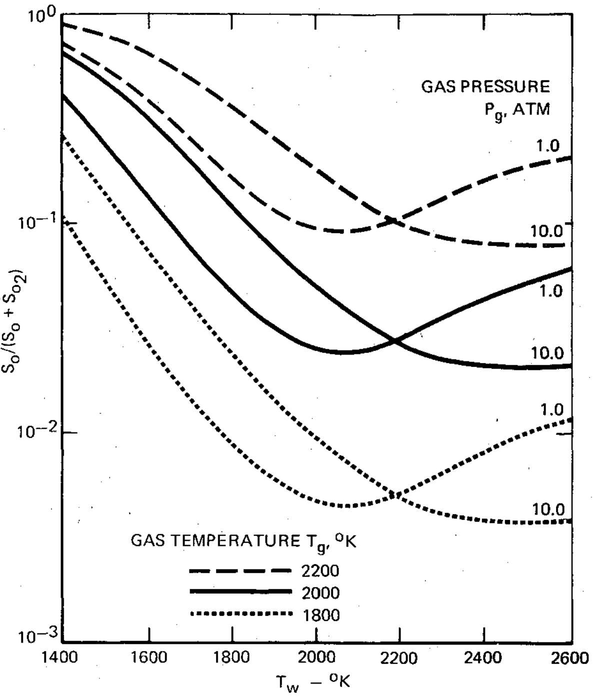

Fig. 3 Variation of the ratio of pyrolytic graphite recession rate due to atomic oxygen to the total recession rate $\dot{S}_O/(\dot{S}_O+\dot{S}_{O_2})$ with wall temperature T_w for a molecular oxygen mole fraction X_{O_2} of 0.10.

Figure 3 shows the ratio of the atomic oxygen recession rate ($\dot{S}_O$) to the total recession rate as a function of wall temperature, gas pressure, and gas temperature for $X_{O_2}=0.10$. In general, $\dot{S}_O$ is important for low values of T_w and high values of the gas temperature and pressure. This occurs because $\dot{S}_{O_2}$ becomes small at low values of T_w, whereas $\dot{S}_O$ is insensitive to the value of T_w. In addition, $\dot{S}_O$ depends directly on P_O, which increases as the gas pressure and temperature increase (for constant oxygen mole fraction). At large values of T_w, $\dot{S}_O$ becomes important mainly because $\dot{S}_{O_2}$ decreases while $\dot{S}_O$ remains constant. Lower gas temperatures greatly reduce the atomic oxygen contribution to the oxidation rate, through the corresponding reduction in P_O.

These atomic recession rates will allow more accurate calculation of the necessary thickness for ablative pyrolytic graphite coatings. Such calculations will be slightly conservative, because some of the atomic oxygen will recombine as it passes through the boundary layer to the cooler wall. However, recombination involves three-body collisions, which occur infrequently compared to the two-body collisions that dissociate molecular oxygen. The assumption of constant atomic oxygen concentration across the boundary layer is thus reasonable.

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