

that the magnitude of  $\tau_{yz}$  increases as the beam configuration changes to a plate geometry and as the core thickness increases.

Several points have been considered in the numerical calculations. These relate to rate of convergence of the numerical results and breakdown in usefulness of the developed equations as the geometrical configuration is changed from a beam to a platelike structure. The former problem has been examined by comparing sums of various numbers of terms in the series solution with the required accuracy of the numerical solution at the beam boundary surfaces. It has been found that for geometrical configurations of the type  $a$ ,  $b$ , one and three term summations, respectively, for the core dimensions considered, are sufficient to generate three place numerical accuracy. As noted earlier, the solution for  $\tau_{xz}$  as generated for the thin beam case ( $d/h = 0.2$ ) coincides with that presented in Ref. 1, based upon a two-dimensional elastic solution. In the case of platelike geometries, separate discussion is required in that the rate of numerical convergence for the physical quantities of interest changes with both  $d/h$  and  $a/h$ . As both of these parameters are increased, the required number of terms, to obtain comparable numerical accuracy as described above, requires an increasing number of terms. For example, for the case of  $d/h = 10$  and core dimensions of  $a/h < \frac{1}{2}$ , upwards of sixty terms are required. Larger numbers of terms are required for  $a/h$  ratios  $\geq \frac{1}{2}$ . It is possible, however, to develop numerical techniques, which could provide useful guides for determining the numerical accuracy of the stresses by preselecting a maximum number of cutoff terms to achieve a desired numerical accuracy. The width and core dimensions could be appropriately varied with the number of cutoff terms selected as a parameter. Composite beams with more than three lamina may be solved in the manner indicated previously.

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## Inhibition of the Ablation Rate of Graphite by Gaseous Chlorine

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#### Introduction

**R**ESULTS from a number of laboratory experiments reported in the literature indicate that chlorine gas<sup>1-3</sup> or various chlorinated compounds<sup>3-6</sup> effectively inhibit the oxidation of carbon or graphite in either pure oxygen<sup>1,3</sup> or in air.<sup>2,4-6</sup> The temperature range over which an inhibiting effect has been reported is from 733°K to 2033°K (Ref. 1). The mechanism generally assumed for this inhibition is that chlorine (or the chlorinated compound) is strongly chemisorbed on the surface blocking oxygen from reaching many of the active sites.<sup>1-3,5,6</sup> Experimental evidence offered in support of this mechanism is that the carbon or graphite surface, after oxidation in the presence of chlorine or chlorinated compounds as inhibitors,

has a different character than it does after oxidation in the absence of inhibitors.<sup>1,5,6</sup> Also, it has been reported in other studies<sup>7,8</sup> that chlorine is irreversibly chemisorbed on carbon and graphite at least over the temperature range 77°K to 770°K, with appreciable chlorine remaining on the carbon surface even after heating to 1470°K in vacuum.<sup>7</sup>

If chlorine, in addition to inhibiting the rate of oxidation of graphite, could also be shown to be effective in inhibiting the over-all rate of ablation of graphite in a high-temperature, supersonic environment, this could have significant implications for the design of thermal protection systems in which the rapid ablation rate of carbon or graphite is a serious consideration. Accordingly, the present study was undertaken to investigate the possible inhibiting effect of chlorine on graphite ablation. Of primary interest were the concentration levels of chlorine necessary for inhibition, and the magnitudes of inhibition which might reasonably be attained.

#### Ablation Performance Measurements

Many of the experimental details of the ablation performance measurements are similar to those described in Ref. 9, and therefore will be described only briefly here. The ablation environment consisted of a nominal Mach 2 test stream with a nominal enthalpy of 2.29 Mjoule/kg and a stagnation pressure of 5.7 atm, obtained in an arc-heated air stream. Heating rates were nominally 547 w/cm<sup>2</sup> at the stagnation point; however, due to difficulties encountered in making the heating rate measurements, and also possibly in maintaining constant conditions in the arc heater itself, actual measured heating rates ranged from 517 w/cm<sup>2</sup> to 579 w/cm<sup>2</sup>, and corresponding enthalpies ranged from 2.18 Mjoule/kg to 2.20 Mjoule/kg.

Test specimens were ATJ graphite machined into 1.270-cm-diam hemisphere cylinders, 1.905 cm long, with nose radii of 0.635 cm. The direction of preferred crystallite orientation was normal to the axis of the specimens. The specimens were insulated from their holders during test. Steady-state stagnation-point surface temperatures were measured with a continuous-recording photographic pyrometer, and linear stagnation-point mass loss rates were determined from motion picture film records of the eroding specimens with the aid of a motion analyzer. Representative surface temperature was taken as the steady-state maximum temperature attained during the run; mass loss rate was determined from a least-squares slope of the linear portion of the specimen length decrease with time by multiplying it by the bulk density. Ablation performance measurements were made in pure, dry air, and in mixtures of chlorine in dry air in the concentrations 0.01%, 0.043%, 0.107%, 0.41%, and 1.05% (volume percent). Replicate runs were made at each gas composition.

#### Effects of Chlorine Addition

The results of the ablation performance measurements are shown in Fig. 1 in terms of mass loss rate and surface temperature as functions of the test stream composition. To facilitate comparison, the mass loss rate and surface temperature data obtained in a test stream of pure air (chlorine concentration of 0%) are indicated by the horizontal bounds drawn across the entire figure. Figure 1a illustrates the inhibiting effect of small amounts of chlorine on mass loss rate, indicating that as chlorine concentration increases mass loss rate decreases. At a chlorine concentration of only 1%, mass loss rate is reduced by almost one-third of that in pure air. Figure 1b reveals that small amounts of chlorine depress the surface temperature below that when no chlorine is present. Such surface temperature depression due to chlorine addition has been previously reported,<sup>1</sup> and is consistent with the fact that the oxidation of carbon is exothermic: a slower rate of reaction tends to reduce surface temperature because heat is being generated at a slower rate.

A particularly intriguing aspect of the temperature data in Fig. 1b is that they pass through a maximum with increasing chlorine concentration. Since these temperature data are believed to be accurate to within approximately 50°K, this maximum cannot be easily ascribed to experimental error. Yet, no alternative

Received December 1, 1971.

Index category: Material Ablation.

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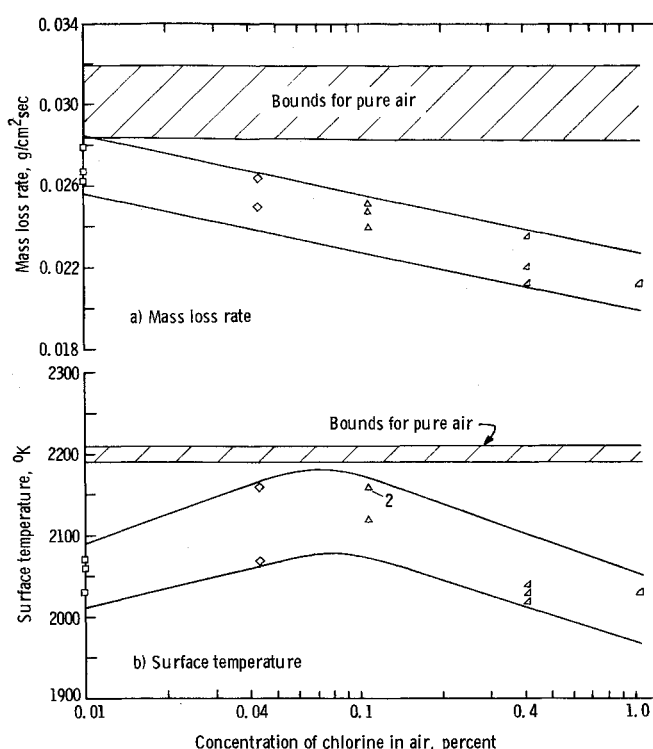


Fig. 1 Effects of chlorine addition on ablation performance.

explanation for this peculiar behavior is offered here. To put this apparent anomaly into perspective, however, attention is drawn to the similarly peculiar behavior of carbon in exhibiting a maximum in its oxidation rate curve as a function of temperature (see, for instance, Ref. 10), a common explanation for which is that there are two types of active reaction sites on the surface.<sup>10</sup> It is not altogether unreasonable that the present phenomenon might be somehow related.

In agreement with the previously mentioned results of other investigators, the surfaces of the graphite specimens oxidized in the presence of chlorine differ in appearance from those oxidized in pure air. They tend to be blacker, less reflective, and are thoroughly dotted with minute pits, which are likely due to selective oxidation of the surface. This latter phenomenon is probably related to the increase in BET area noted by Pallmer.<sup>6</sup> These differences in surface appearance are negligible at the lower chlorine concentrations but become quite noticeable at the higher concentrations.

In addition to the chlorine concentration itself, the extent to which chlorine inhibits carbon oxidation may depend on other factors such as temperature, pressure, and specific type of carbon. For example, whereas in the present study a reduction in mass loss rate of one-third was measured at a chlorine concentration of 1%, Ref. 2 experienced a reduction of as great as 79% at the same chlorine concentration, but at different reaction conditions. Moreover, because chlorine will be less strongly bound to the surface the higher the temperature, it is expected that the extent of inhibition will tend to decrease as the surface temperature increases. Hence, to establish the full potential for chlorine as an inhibitor for aerospace applications, its effect on ablation should be determined in a wide variety of dynamic environments.

#### Potential Applications

The methods by which the inhibiting effect of chlorine can be applied in practical situations to reduce the ablation rate of graphite or of charring ablators are several. In those situations in which forced transpiration cooling is being employed, the obvious method of application would be to add small amounts of chlorine to the injected gas. Another method of application, particular for use with graphite, would be to impregnate the pore structure of the graphite with a polymer which releases chlorine

upon pyrolysis. For charring ablators, a related method would be to build chlorine or chlorine-containing groups into the polymer structure itself, which chlorine would then be released as the polymer chars. One rather fascinating method which could be used with many charring ablators takes advantage of the fact that hollow spheres of phenolic resin or glass are often added to the polymer as structural, low-density fillers. These spheres could be filled with chlorine during their fabrication, and, as the spheres ablated or melted, this chlorine would be released to inhibit char oxidation.

#### Conclusions

It has been shown that small amounts of chlorine gas, when present in a high-temperature, supersonic air environment, can inhibit the ablation rate of graphite and depress its surface temperature below that obtained in pure air. The extent of inhibition and temperature depression depends on chlorine concentration. In the present study at a chlorine concentration of only 1%, mass loss rate was reduced by almost one-third of that in pure air. Several methods have been suggested by which this inhibiting effect of chlorine can be applied in practical situations to reduce the ablation rate of graphite or of charring ablators.

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## Feedback Control of Flutter Instability in a Continuous Elastic System

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THIS Note reports progress made since presentation of Ref. 1 at the 11th Structures, Structural Dynamics and Materials Conference in April 1970. In that paper, Moon and Dowell derived the equations for a cantilevered beam with follower force controlled by a separated sensor feedback force. A sketch

Received December 7, 1971. The author is indebted to his advisors E. H. Dowell and F. C. Moon for their continuing support and guidance.

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