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Hypervelocity Heat Protection--A Review of Laboratory Experiments

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SUMMARY

Recent laboratory research concerned with boundary layer, surface, and internal ablation mechanisms is examined, particularly in relation to their coupling with the imposed heating environment. Emphasis is devoted to defining ablator response at heating conditions representative of those encountered by the atmospheric entry of manned NASA vehicles. Experimental results are presented for four ablative composites (Teflon, phenolic nylon, epoxy-novolac, and silicone elastomer), which differ significantly in chemical formulation and mode of degradation. The influence of both test stream variables and chemical composition on material behavior is demonstrated and discussed. Future areas of ablation research are delineated by calculations that illustrate the relative importance of the various heat accommodation mechanisms available to a charring ablator at entry speeds above 15 km/sec.

INTRODUCTION

The ablation process may be described in a broad sense as the sacrificial removal of material to protect structures subjected to high rates of heat transfer. Two approaches to the study of the ablation process have evolved from the past 10 years of extensive research: One is the use of analytical prediction techniques; that is, computer programs are used to furnish numerical solutions to complex coupled differential equations that describe the process [1-6]. The second approach is to conduct experiments both in the laboratory [7-10] and, to a lesser degree, in flight [11-13], to characterize empirically the individual ablation mechanisms and their coupling with the external environment. Because of the complexity of the problem, which involves a host of disciplines (chemistry, physics, thermodynamics, solid and fluid mechanics), neither approach is sufficient by itself but rather a combination of the experimental and analytical results is necessary to understand fully the physics of ablation and thereby develop a rational basis for tailoring new materials for the variety of high-temperature environments encountered in space. The specific applications and associated problems are varied and include, for example, rocket nozzles with the attendant high rates of surface shear, stagnation regions of re-entry vehicles that are exposed to both convective and radiative heating, and manned lifting vehicles with afterbodies that experience low levels of convective heating for extremely long periods of time.

This survey highlights recent experimental developments that have enhanced the understanding of ablation mechanisms obtained at conditions representative of the environments associated with the entry into the earth's atmosphere of manned vehicles. In order to provide a logical framework for the discussion, the physical model and associated mathematical formulation of the ablation problem are briefly reviewed. Some typical entry heating conditions are presented and compared with the simulation capability of arc-jet wind tunnels. Ablation experiments dealing with boundary layer, surface, and internal phenomena are described, and the influence of both the chemical formulation of the material and the environmental parameters is delineated. Finally, calculations are provided for the response of a heat shield for a manned return from Mars to illustrate those areas of heat shield technology considered important to future research.

DESCRIPTION OF ABLATION

Physical Description

The physical ablation process of a composite material, which involves the simultaneous transfer of mass, momentum, and energy, is illustrated schematically in Fig. 1. The virgin polymer is initially degraded by the action of the imposed heating to yield a carbonaceous char layer through which the gaseous degradation products are percolated—driven by the pressure gradient established by the kinetic decomposition occurring in





Fig. 1. Physical representation of ablation process for a charring composite.

depth. The idealized system may then be characterized by three distinct zones: a char, a degradation layer, and the virgin material, each with distinct thermophysical and mechanical properties. The primary function of the ablator is to limit the flow of heat through these zones and thereby restrict the associated temperature rise of the primary load-bearing structure of the vehicle. In order to evaluate the response of an ablator numerically, we must first formulate the equations that mathematically describe the behavior of the idealized physical system proposed above.

Mathematical Description

Definition of Symbols

- B normalized ablation rate, $m_g \Delta H/q$
- cp specific heat
- D base diameter
- H enthalpy
- k thermal conductivity
- M molecular weight
- m mass loss rate

р	pressure
Q	heat load, ∫ qdθ
q	heat transfer rate
R	effective nose radius
Т	temperature
х	space coordinate
x	time rate of change of position
V	velocity
W	weight
Δ	difference
θ	time
ρ	density
BLK	blockage
CHEM	chemical
с	convective
С	char
D	decomposition
E	entry
eq	equilibrium
f	frozen
g	gas
max	maximum
r	radiation
rr	reradiation
S	surface
t	total
v	virgin

The Governing Equations. The governing equations for a typical charring ablator have been treated extensively in the literature [1-6]. If we consider a typical control volume and invoke the conservation of energy we have the one-dimensional partial-differential equation for the temperature as a function of both position and time, which may be expressed in a body fixed coordinate system as follows:

$$\rho c_{p} \frac{\partial T}{\partial \theta} = \frac{\partial}{\partial x} \left(k \frac{\partial T}{\partial x} \right) + \dot{m}_{g} \frac{\partial H_{g}}{\partial x} + \frac{\partial \rho_{s}}{\partial \theta} H_{D}$$
(1)

The various terms in the equation account, respectively, for the time rate of change of stored energy, conduction, flow of chemical energy, and the time

rate of change of decomposition energy which may be either a sink or source term, depending upon the overall nature of the decomposition reaction. Since the coefficients of this equation are all temperature dependent, the resulting equation is nonlinear. There are three boundary conditions that must be satisfied. The first two account for the conservation of energy:

$$\dot{q}_{r} + \dot{q}_{c} - \left\{ \dot{q}_{rr} + \dot{q}_{BLK} - \dot{q}_{CHEM} \right\} = \left\{ k_{c} \frac{\partial T}{\partial x} \right\}_{s}$$
(2)

and the instantaneous position of the receding surface:

$$x_{s}(o) - x_{s}(\theta) = \int_{o}^{\theta} \dot{x}_{s}(\theta) d\theta$$
(3)

The third condition specifies the nature of the rear surface of the material, i.e., for an insulated surface

$$\left\{ k_{\rm V} \frac{\partial T}{\partial x} \right\} = 0 \tag{4}$$

The coupling of the ablative response with the imposed heating environment is illustrated by Eq. (2)-the surface energy balance. Initially the ionized species of the high-temperature shock layer, which envelops the entry vehicle, generates radiative (q_r) and convective (q_c) heating, which is balanced solely by the energy conducted into the interior of the material $[k_{C}(\partial T/\partial x)]_{s}$. However, as the severity of the environment is increased, the ablator experiences a corresponding increase in temperature, and degradation is initiated in the manner described above with other time-dependent mechanisms becoming active in blocking the heat from the surface. These mechanisms are the reradiation from the high-temperature surface (qrr), blockage of the convective heating by the action of the transpired vapors (\dot{q}_{RIK}) , and energy accommodated or generated by chemical reactions occurring at the surface such as combustion and/or sublimation of the char (q_{CHFM}). The reradiation term, which follows the Stefan-Boltzmann law, is proportional to the fourth power of temperature, and therefore this boundary condition is also nonlinear. Furthermore, the blockage and chemical terms are interrelated with the internal response of the ablator through their respective dependence upon the rate at which ablation gases are injected through the char into the boundary layer. This system of equations does not have an analytic solution, and recourse must be made

to iterative numerical integration techniques employing finite difference methods. The complexity of the mathematics has stimulated the experimental approach to the problem wherein the various mechanisms described above may be isolated and quantitatively evaluated on a macroscopic scale. The ultimate goal of most experimental programs is to provide means for independently determining the influence of such environmental parameters as pressure, enthalpy, and heating rate as well as model scale on these mechanisms. In addition, the results can be used to check the assumptions underlying the formulation of the mathematical model and verify the adequacy of computer solutions for particular ranges of the variables.

HEATING

In order to judge the overall applicability and value of the experiments in terms of various space missions, this section of the paper first briefly describes the heating environment to be encountered by manned vehicles entering the earth's atmosphere and then considers how well these conditions are simulated in the laboratory by the use of arc-heated wind tunnels.

Earth Entry

Heating during atmospheric entry depends on the trajectory, which is a function of the vehicle configuration and weight as well as its initial entry angle and speed.

Figure 2 shows the predicted aerothermodynamic environment for the stagnation region of an Apollo-type configuration, which was calculated by the analytical techniques described in Ref. [14]. The range in entry speeds was chosen to encompass entry from Earth orbit to Mars missions. The trajectories were chosen so that peak heating occurred at an altitude of 61 km for all missions. The lower curve represents the dependence of convective heating rate on entry speed. The upper curve includes the contribution from the radiation of species in the shock layer. Note that the predominant mode of heat transfer shifts from convective to radiative as the entry speed is increased. The thermodynamic state of the gas in the boundary layer as characterized by the stagnation point pressure and temperature is indicated along the abscissa. The pressure levels are moderate when compared with those experienced by unmanned entry vehicles for which there is no fixed upper limit for the deceleration rate.



Fig. 2. Aerothermodynamic environment encountered by a manned spacecraft during entry into the earth's atmosphere.

Laboratory Simulation

The most common technique for providing the high-temperature continuous-flow system required for the simulation of the ablation aspects of hypervelocity flight is indicated schematically in the upper portion of Fig. 3. The test gas, which is heated by means of an electric discharge, expands through a supersonic nozzle and then impinges on a stationary sting-supported model. The scaling equation for convective heating indicates the way in which enthalpy, pressure, and model size may be adjusted to achieve the desired level of heating. For example, deficiencies in enthalpy simulation may be compensated for by reducing the model scale or increasing the pressure level of the experiment. Symbols indicate heating and pressure attainable for an effective nose radius of 5.5 cm in NASA and the industry arc-jet test facilities, which participated in phase 2 of the NASA-Stanford Research Institute Round Robin ablation program. The



Fig. 3. Laboratory simulation of convective heating environment.

NASA-SRI program [15, 16], a contract effort monitored at the Ames Research Center, was undertaken to evaluate ablative materials in this class of test facilities by comparing stream diagnostic and ablation measurements obtained with instruments supplied by SRI. Ablation measurements typical of those obtained during the course of this study are presented and discussed in the next section of the paper.

As previously noted, the radiative heat transfer comprises a substantial fraction of the total heating at high entry speeds. In contrast to the convective heating rate, the radiative rate scales with the nose radius, and therefore simultaneous simulation of both the convective and radiative rates of heating, is not possible unless the full-sized vehicle is tested at the appropriate values of enthalpy and pressure. To overcome this difficulty of testing procedure, radiation may be supplied from an external source focused on the test specimen by means of mirrors and controlled independently of the convective heating environment. Heating currently attainable by means of external sources is of the order of 1 kW/cm². Details of existing and proposed facilities at the Ames Research Center that utilize this principle have been described by Gowen et al. [17].

Even though arc-heated flows do not simulate all aspects of the entry environment, particularly the peak radiative heating rates, they provide a useful research tool for the study of ablator response from a phenomenological standpoint; i.e., it is possible to isolate and quantitatively evaluate the various heat-shielding mechanisms and to define their dependence upon the environmental parameters: stream chemical composition, enthalpy, and pressure. Such experiments, when combined with information from flight tests and analysis, provide a basis for interpreting the physics of ablation and thereby help in the design of new polymers for specific applications.

ABLATION EXPERIMENTS

Some of the experimental programs that have been directed toward providing a detailed understanding of the ablation process are now considered. The studies chosen for discussion have been confined primarily to the work currently under way at and under the direction of the Ames Research Center. The main objectives and significant findings are emphasized and no attempt is made to go into all of the details which are readily available in the cited references. The four polymeric composites selected for evaluation in these studies indicate current state-of-the-art formulations and range in complexity from Teflon, a linear polymer that degrades to yield only gaseous ablation products, to a silicone elastomer that, upon heating, yields a layer of primarily inorganic debris through which decomposition gases percolate. The nominal elemental composition, mode of degradation, char yield, and structure for the various polymers to be discussed are contained in Table 1. The experiments related to boundary layer mechanisms are discussed first, followed by a discussion of studies pertaining to surface and internal phenomena.

Boundary Layer

The study of the multicomponent high-temperature boundary layers on ablating surfaces has been the subject of extensive analytical work, which, to date, is unmatched in intensity by experimental research. One of the first programs to successfully identify boundary layer species near the surface of a relatively simple ablator (Teflon) was recently completed by Pope and Parker [18]. Their results were used in conjunction with stoichiometric considerations to reconstruct the possible reactions that led to the formation of the observed species in their ground state. Figure 4 illustrates the basic experimental approach and contains a tabulation of the results in terms of mole fraction for the various test environments. A

Organic content mass fraction of carbon of char, 0.50 0.10 0.95 L yield^a, pc/pv Char 0.43 0.48 0.90 0 Decomposition degradation Mode of Vaporization residue and in depth to percolating --yield char gases virgin material, ρ_v (specific gravity) Density of 0.569 0.569 0.537 2.16 C₁H_{2.9}O₁Si_{0.6}Fe_{0.2}Al_{0.1} composition elemental Relative C4H4.5O1.8Si0.4 C₁₃H₁₈O₂N₁ C_2F_4 Material elastomer 2. Phenolic novolac 4. Silicone 1. Teflon nylon 3. Epoxy

Table 1. Description of Ablative Composites

^a Average of measurements obtained with arc-jet chars formed over a range of heating conditions [15].



Fig. 4. Mass spectrometric identification of boundary layer products with Teflon ablation.

comparison of the data obtained in a vacuum oven at moderate levels of heating with the data obtained in an arc-jet with a test gas of argon shows that the primary effect of an increase in heating rate is thermal degradation of the polymer to the more active fragments (CF₄, C₂F, C₃F₆, C₄F₈). As the chemical composition of the test stream is altered from the inert argon to include nitrogen and oxygen, we can observe a corresponding increase in both the number and complexity of measured species. Since the heating rate was maintained at a constant level for all of the arc-jet test cases, we may conclude that the increase in observable species is directly attributable to chemical reactions between the ablative gas and its environment. A detailed analysis of the nitrogen results, described in Ref. [18], led to the conclusion that high-temperature radicals were present in the boundary layer, but these species were relaxed to their respective ground states during the analysis of the sample. Therefore, current efforts are under way to modify the existing equipment to provide a real time analysis of the products. In addition, high-resolution optical measurements of emission and absorption spectra are planned to provide an independent in situ measure of the species population in the stagnation region of the model.

The influence of the observed boundary layer chemical reactions on the heat transfer rate experienced by the surface of a Teflon ablator will now be considered. The effectiveness of ablation in reducing the convective



Fig. 5. Stagnation region heating with Teflon ablation.

heat transfer is illustrated in Fig. 5. First, the results obtained in nitrogen streams [19] indicate a strong dependence of the heating rate ratio on the total enthalpy level of the stream. As the severity of the test environment is increased, the normalized ablation rate, B, is accordingly increased, with the result that the fraction of imposed heating that is blocked also increases until an asymptotic value of 0.8 is reached. This finding is in contrast to the illustrated results for forced transpiration tests wherein the rate of mass flow into the boundary layer is a free parameter that is independently controlled. The equations describing the coupled ablation situation have been formulated and programmed for computer evaluation by a colleague, Mr. M. Alan Covington. The experimental results, represented by the dotted line, exhibit good agreement with his preliminary calculations.

The influence of the exothermic oxidation reactions observed in the air boundary layer on the net heat transfer to the surface is indicated by the difference between the data obtained in nitrogen and those obtained in air [16, 20]. The effect is most pronounced at low-stream total enthalpy where the exothermic heat of reaction is comparable in magnitude to the enthalpy of the stream. We can see that as the enthalpy is increased, the effect of oxidative reactions is diminished until at the highest enthalpy there is no distinguishable difference due to stream chemical composition. The highest value of B was obtained by Pope and co-workers [18, 19] in the Ames Constricted Arc Facility by testing at a stream enthalpy level that duplicates the value expected for a Mars return mission. A charring composite—low-density phenolic nylon—was also tested at this condition and the result of the test, as modified to include the effect of reradiation in the numerator of the ordinate, is indicated in Fig. 5 by the cross. The dramatic difference in the convective heat blockage behavior of the two materials is attributable to the favorable radiative characteristics of the carbonaceous char layer which forms when the phenolic nylon composite degrades. In contrast to the Teflon, which ablates at a relatively low surface temperature, the charring material blocks a substantial fraction of the incident heating by reradiation. Accordingly, for the charring material less mass is ablated into the boundary layer. The magnitude of the difference in ablation rate can be obtained directly by comparing the values of the parameter B for the two materials.

Surface

The dependence of surface temperature on the imposed convective heating rate for two distinct types of polymeric composites is illustrated in Fig. 6. The data, obtained in phase 2 of the previously described NASA-SRI Round Robin ablation program [15], illustrate the compensating



Fig. 6. Surface temperature as a function of imposed heating.

coupling of the surface temperature with the environment. That is, as the imposed heating is increased, the surface temperature is correspondingly increased to maintain a constant value of the ratio of convective to reradiated heating. The difference in the response of the two materials is partly attributable to differences in their measured surface emittance [21] and chemical structures of the char. At the highest heating rate the surface temperature does not continue to increase without a limit. The sublimation temperature represents an upper limit to which the surface may be driven. On the basis of both the recent calculations of Dolton et al. [22] and the magnitude of the surface recession, the tailing off of the data at high heating rates is probably not due to the onset of sublimation, but rather to higher ablation rates encountered at these conditions. The corresponding blockage of convective heating becomes more pronounced. If the data were plotted as a function of net convective heating, the data obtained at high heating rate would shift to the left and agree substantially with the line that correlates the data obtained at conditions where the rates of heating and ablation are low. The salient feature of these results is that reradiation from the char surface is found to depend on the chemical formula of the polymer and also to constitute a predominant mode of heat rejection that is not available to the low-temperature melting and vaporizing class of ablators.

The surface ablation characteristics of polymeric composites are now examined. The identification and characterization of surface removal mechanisms is important since the solution of the internal conduction problem as described by Eq. (1) and the prediction of the associated heat shield weight depends critically on a knowledge of the surface position. The ratio of char removal rate for low-density phenolic nylon to the boundary layer oxygen diffusion rate is presented in Fig. 7 as a function of the measured surface temperature. Scatter in the data could be attributable to a number of factors; measurements of char density [15], shrinkage [23], nonchemical removal of the char, and boundary layer consumption of the oxygen by reaction with the pyrolysis gases [23]. However, there is no discernible trend of the data with temperature level. Furthermore, the statistical average of the data agrees very favorably with the theoretical prediction, which has been based on complete consumption of the available oxygen at the char surface to yield carbon monoxide. These findings suggest very strongly that the overall rate-limiting step in the process of chemical surface removal of the char is the rate at which oxygen diffuses through the boundary layer. Vojvodich and Pope [7] and Lundell et al. [24] also obtained data that support this conclusion.



Fig. 7. Surface removal of phenolic nylon.

Let us now turn our attention to an ablator which has substantially different virgin material and char composition. The surface recession rate measurements for an epoxy-novolac resin containing 25% by weight of reinforcing glass fibers is presented in Fig. 8. The results were obtained in three separate sets of tests. The NASA-SRI Round Robin [15] data and the measurements of Schaefer and co-workers [25, 26] pertain to the stagnation region of blunted models having the nose radius shown in the figure, exposed to laminar flow conditions. The results of Gaudette et al. [27] were obtained with a flat plate configuration exposed to turbulent flow conditions. If the diffusion of oxygen were the rate-limiting step for this material, then under turbulent boundary layer heating conditionswherein mixing and diffusion are enhanced-we would expect considerably more erosion than under laminar conditions at comparable surface temperatures and pressure. It is seen, however, that all three sets of data are correlated reasonably well by the Arrhenius type of inverse temperature dependence represented by the solid line and which may be described by the equation, $\dot{x}_{s} = 513e^{-9,210/T_{s}}$.

It has been suggested that the reaction rate-limited nature of the surface recession for this particular polymer may well be associated with the large fraction of silica in the char layer. Indeed, measurements of the chemical composition of the char layer formed by the degradation of this polymer have been conducted at Aerotherm Corporation [26], and in some cases



Fig. 8. Surface recession rate of epoxy novolac.

as much as 25% by weight of the char was found to be in the form of silica. The complications introduced by the presence of silica-carbon reactions have been studied in detail [28-31]. The findings of these studies with regard to the kinetic behavior of silica-bearing polymers corroborate similar evidence obtained in the arc-jet results as presented in Fig. 8. This is an example of how additives play a strong role in influencing the ablative behavior of composites.

It must be emphasized that extreme precaution must be exercised when attempting to extend the use of these or similar data to predict the ablative behavior of a polymeric system at conditions far removed from those at which the tests were conducted. For instance, the majority of the data shown in Fig. 8 were obtained at surface pressures below 1 atm. When this value is exceeded, for this material, a combination of thermomechanical and sublimation mechanisms has been observed to enhance the rate of surface removal considerably above the values obtained by extrapolation of the line that has been fit to the data [26].

Internal Factors

One of the most effective modes of heat blockage available to the charring class of ablators is the process of thermal cracking of the initial gaseous products of degradation as they pass through the high-temperature char layer. The magnitude of the increase in energy content of the gases depends upon a number of factors, including the elemental composition of the polymer and its char, the thermochemical state of the vapors, and the temperature and pressure at the surface of the char. The variation of the pyrolysis gas enthalpy with temperature for the composition products of a phenolic nylon ablator is illustrated in Fig. 9. The two limiting situations with regard to the chemical state of the gases-equilibrium and frozen compositionare shown. The upper curves illustrate the influence of pressure for complete thermochemical equilibrium. The initial products of degradation (CH4, CO, and CO₂) have exothermic heats of formation and the enthalpy of the mixture at low temperatures is negative. At higher temperatures the unpublished calculations performed by Goldstein of Applied Space Products show that the principal equilibrium constituents are endothermic and include atomic and molecular hydrogen and acetylene, which account for the substantial reduction in the average molecular weight and associated increase in energy content. The lower curve is the lower limit on the enthalpy of the pyrolysis gases. The curve was calculated assuming that the residence time of the gases is much less than the reaction time, with the result that chemical composition remains frozen at its degradation temperature composition. A comparison of the limiting cases shows that a sizable reduction may occur in the enthalpy if the gases are, in fact, frozen. This is especially true at higher temperatures.

A number of exploratory studies have been initiated to investigate the chemical state of the pyrolysis gas. One technique is a thermodynamic approach in which an energy balance is performed on the char layer of a model that has been exposed to radiative heating. This technique simplifies the analysis considerably by eliminating the complicating influences of a boundary layer, as can be seen by considering Eq. (2). The measurements of char growth, surface temperature, and mass loss by Lundell et al. [10] were used to deduce the values of gas enthalpy indicated on the figure. The results, which agree closely with the frozen prediction, are susceptible to a high degree of uncertainty since the method involves taking the small difference of two numbers (imposed and reradiated energy) that are comparable in magnitude.

A second technique—that of mass spectrometric identification of the ablation vapors—is a more direct method. Liston of SRI has performed such measurements as part of a NASA-funded contract effort [32]. He found that at 2200°K and 0.001 atm, the average molecular weight of the pyrolysis vapors is 15.5. This value is bracketed by the predicted





Fig. 9. Influence of gas chemistry on enthalpy of pyrolysis products.

values of 11.6 and 19.4, which are indicated in Fig. 9 and which correspond to the equilibrium and frozen assumptions, respectively. However, this technique is plagued by the same experimental difficulties encountered by Pope and Parker [18]. Namely, the gases analyzed are in their ground states, and some of the higher molecular weight species were observed to condense on the piping of the apparatus. The estimated molecular weight is therefore biased in a low direction.

The kinetics of possible pyrolysis gas compositions have been analyzed extensively by Pike et al. [33]. They also conducted some gas chromatograph experiments with hydrocarbons flowing through chars formed in an arc-jet, and the results of both the analysis and experiment tend to substantiate the conclusion that the residence times of the typical pyrolysis vapors are very small when compared with the reaction times.

If, indeed, the vapors are chemically frozen, a possible solution might be the addition of a small concentration of highly active catalyst during the material formulation which would promote the desired reactions. The relative importance of the observed departure of the gases from equilibrium



Fig. 10. Influence of material density on insulation effectiveness of ablators.

on heat-shielding requirements for the environments expected for advanced missions are considered in a subsequent section of the paper.

Up to this point we have been concerned with the heat and mass transfer aspects of ablation studies as treated from a mechanistic standpoint. However, the ultimate function of an ablative heat shield is to limit the temperature rise of the primary load-bearing structure to a tolerable level. The insulation effectiveness of some typical ablative polymers and a demonstration of how these materials may be tailored to improve their thermal efficiency is now considered.

Figure 10 illustrates how the density of virgin material influences backface temperature rise measurements. The tests were performed by Pope in the Ames Planetary Entry Ablation Facility at three convective heating rates. The test times were adjusted to give a total heat load of 1703 J/cm^2 , which is representative of the environment expected for entry into the tenuous atmosphere of Mars. The density of the three composites was reduced by foaming, keeping the basic chemical composition fixed. To provide a common basis for comparison, a fixed weight per unit area was obtained for all test samples by adjusting the total thickness of the material ahead of the sensing thermocouple. The effect of material virgin density on the maximum observed temperature rise is shown to be characterized reasonably well by the linear correlation represented by the solid line. We note that although the results obtained with Teflon are relatively insensitive to the level of heating, the charring materials are found to be more effective at the higher rates of heating. This trend of insulation effectiveness with heating rate agrees well with work of Vojvodich and Winkler [34] and the recent tests of Strauss [35].

The observed trend of material insulation effectiveness with density provides a design guide for ablative materials exposed to environments for which the shear and pressure levels are moderate and the primary function of the ablative material is insulation as opposed to mechanical strength. This approach has been adopted by Dr. J. A. Parker and his colleagues at Ames, who have developed an extremely low-density polyurethane foam (s.g. = 0.03) which has been characterized both in the laboratory and on a recent test flight of the Apollo vehicle [36]. This particular program is only one example of the way in which ground-based experiments can provide direction in the formulation of material composites for specific applications.

ABLATION CALCULATIONS

This section of the paper deals with the analytical approach to the ablation problem. First, a typical finite difference solution of the coupled mathematical equations (1)-(4) is described and compared with experiment. Second, results obtained using such a program to predict the response of a heat shield during return from a Mars mission are reviewed.

Comparison of Experiment and Theory

As noted earlier in the paper, the successful analysis of the ablation process depends critically upon the completeness of the mathematical formulation which must rigorously account for all the significant mechanisms. Furthermore, the various thermophysical properties must be known as a function of temperature. Since the problem involves many parameters, a computer program is a useful method for evaluating the relative importance of the various terms in the heat conduction equation. Studies of this type are useful for selecting the properties and mechanisms that require the most exact definition.



Fig. 11. Comparison of arc-jet experiment with machine computation.

In the past decade many finite difference techniques of various degrees of sophistication have been developed for machine computation of ablation response. The computing program, developed by Matting and Chapman, described in detail in Ref. [4], has been modified to account for charring materials and is considered to be representative of the more advanced of these finite difference techniques. The predictions provided by this program are compared in Fig. 11 with arc-jet measurements for an epoxynovolac material. There is very good agreement between the measured variation of surface temperature, surface ablation, and char thickness with time and the corresponding calculations. Despite the agreement between experiment and theory for the surface response, the measured temperature rise at a depth of 1.01 cm was found to be 94°K, as compared with the predicted value of 31°K. This difference, which might be attributed to uncertainties in either the char conductivity or the degradation kinetics, highlights the overall complexity of the problem; prediction of one quantity does not verify the completeness of a program. Furthermore, program qualification should be conducted over as wide a range of

environmental conditions as possible to ensure that all phenomena have been properly treated in the analysis. Unfortunately, as discussed earlier, conditions currently attainable in laboratory facilities do not reproduce all aspects of the entry heating environment expected for advanced missions. In spite of this lack of complete laboratory simulation, computer programs, which have been characterized by comparison with experiments conducted at relatively mild conditions, provide a useful and relatively inexpensive means for predicting the response of ablative materials. Furthermore, programs are useful for parametrically investigating the influence of both environmental and ablator performance uncertainties on the heat-shielding requirements for such advanced missions as return from Mars. The next section describes some of the results obtained in a study of this type recently carried out by Lockheed Missiles and Space Company under a NASA contract.

Heat-Shielding Requirements for Mars Return Mission

The contract, described in Ref. [14], was initiated at the Ames Research Center and had a number of basic goals. The effect of altering the heating environment, i.e., changing the entry capsule geometry from a relatively blunt vehicle where radiative heating predominated to a slender configuration where convective heating predominated, was to be investigated. In addition, a number of material property values were perturbed in the analysis to reflect current uncertainty limits, and the influence of these uncertainties on heat-shielfing requirements were to be studied parametrically as a function of entry speed to delineate areas of future research. Figures 12, 13, and 14 are considered representative of the study findings and deal respectively with heat accommodation mechanisms, surface ablation, and total heat shield weight for a blunt Apollo configuration as protected with a nylon phenolic ablator.

Figure 12 illustrates the way in which the total applied heating rate and the corresponding energy accommodation mechanisms vary with time for entry at a speed of 15.2 km/sec. The calculations pertain to the geometric center line of the body at which conditions represent the average experienced by the vehicle forebody. At the peak heating condition it is noted that the convective blockage, which would be the only defensive mechanism available to a Teflon ablation, reduces the heating by only a small amount. The relatively small effect of the blockage mechanism is directly attributable to the environment, which is primarily radiative heating at this time in the trajectory. The increase efficiency afforded by



Fig. 12. Surface energy balance terms for Mars return mission.

additional ablation mechanisms available to the charring ablator is readily apparent when we consider the amount of energy accommodated by reradiation, sublimation, and enthalpy increase of the pyrolysis gases. The magnitude of the latter mechanism was calculated assuming the ablation vapors to be in complete thermochemical equilibrium. The numbers in parentheses represent the fraction of the total heat accommodated during the high heating rate portion of the trajectory by each mechanism and were obtained by integrating with respect to time. The most important mechanisms are reradiation, convective blockage, and enthalpy increase of the pyrolysis gases which accommodate 41, 27, and 24%, respectively, of the heating applied during this phase of the entry. The overall efficiency of the ablator can be measured in terms of the fraction of the imposed heating available for decomposing the virgin material, which in the present case was found to be only 3%. It is of interest to consider how the surface ablation and temperature vary with time at this station of the vehicle.

The ablative response is indicated in Fig. 13. The coupling of the ablator with the external flow is demonstrated by the similarity of the



Fig. 13. Surface temperature and ablation history during entry.

surface temperature history to the imposed heating history illustrated in Fig. 12—both exhibit a sinusoidal dependence upon time. It can also be seen that a large rate of surface ablation is experienced by the heat shield during the early, high heating rate portion of the entry where the surface temperature is driven into the sublimation regime.[†] At the lower heating rates, which occur at the later stages of entry, the surface recession occurs at a substantially lower rate described by the diffusion-limited combustion process discussed earlier. Furthermore, the char thickness is found to attain a constant value, indicating that a quasi-steady ablation condition has been established. Additional material must be provided for insulation of the substructure. The amount required for this purpose was found to be 1.1 cm for this vehicle station.

In order to estimate the total heat shield weight, calculations similar to those described in Figs. 12 and 13 must be conducted at a sufficient number of body stations to allow an accurate integration of the required

[†]Conditions of pressure and temperature for which the sublimation rate exceeds the surface oxidation rate and for which carbon atoms and molecules are present in the gas phase [22].



Fig. 14. Influence of pyrolysis gas chemistry on heat-shielding requirements.

thickness with distance along the body. The variation of heat shield weight, as obtained in this manner, with entry speed is presented in Fig. 14 for the two extremes of the chemical state of the pyrolysis gases. The effect of this chemical state on heat-shielding requirements is found to have a pronounced dependence on entry speed. This observed effect may be explained qualitatively as follows: At the lower entry speeds the surface heating rates are low and the assocaited surface temperature increases as the heating rate increases (see Fig. 6). Therefore, a decrease in the efficiency of the energy absorption by the gases is countered by a higher rate of surface reradiation. However, as the surface temperature is driven into the sublimation regime, the heating accommodated by reradiation approaches a limiting value, and any reduction in the efficiency of the pyrolysis gas absorption mechanism results in a corresponding increase in both the rate of surface ablation and char thickness. The net effect of the nonequilibrium is to incur a penalty in heat shield weight. At the upper end of the speed range there is an increase of approximately a factor of 2 in heat shield weight. This indicates the importance of accurately defining the chemical state of the ablation vapors since, as Syvertson [37] has demonstrated, each additional kilogram carried throughout a manned planetary mission can represent between

300 and 1000 kg on the launch pad. Therefore, on the basis of the numbers presented in Fig. 14, the uncertainty in heat shield requirements may represent a total of 500 metric tons.

CONCLUDING REMARKS

In review, then, a description has been presented of: (a) the equations which illustrate the coupling between the imposed heating environment and ablation phenomena, (b) the manner in which some of these phenomena are quantitatively evaluated in the laboratory, and (c) the reliability of available analytical techniques for predicting the details of the ablation process. Future areas of research have also been indicated by presenting some illustrative calculations that demonstrate the relative importance of the various ablation mechanisms for atmospheric entry of manned vehicles at elevated entry speeds associated with a Mars return mission. Among the tasks that currently appear to need the highest priority is the development of sophisticated in situ techniques for measuring the high-temperature thermophysical properties of degrading ablative materials in real time with particular emphasis on the accurate determination of ablator sublimation characteristics. Detailed studies of the chemistry of ablation products are also need to furnish the answers to an important question: Can the primary products of degradation be brought to thermochemical equilibrium with the char layer, as they percolate toward the surface, by the addition of efficient catalytic agents? Research directed toward the solution of this and associated chemical problems will be useful in generating information that will provide a starting point for the development of new materials which can be tailored to cope efficiently with the extreme thermal environments to be encountered during the atmospheric entry of future vehicle systems.

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