Simplified Computer Model for Predicting the Ablation of Teflon

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This paper describes a computer model of Teflon ablation. The model is constructed from simplified theories and utilizes an existing numerical analysis computer program. The model is used to predict both mass loss and temperature variations during and following aerothermic heating, either in ground-based facilities or in atmospheric flight. Full dense and partial dense Teflons are modeled. Predicted results are verified with available experimental data. The model is used to design a 30% dense heat shield for the base of a typical re-entry vehicle.

Nomenclature

A = area, m^2
B = mass transfer parameter, Eq. (20)
c_p = specific heat, $J/kg\,K$
H = enthalpy, MJ/kg
H_a = heat of ablation including sensible heat, MJ/kg
H_{eff} = $q_0/\dot{m}$, effective heat of ablation, MJ/kg
H_{dp} = lumped heat of depolymerization, MJ/kg
h_c = heat of combustion, MJ/kg
K = mass fraction of oxygen in air
k = thermal conductivity, $W/cm\,K$
M = molecular weight
$\dot{m}$ = mass loss rate, kg/m^2 sec
N = constant in Eq. (3)
p = pressure, atm
q = heating rate, kW/m^2
T = temperature, K
W = initial weight, kg
X_0 = initial thickness, m
α = constant in Eq. (3)
β = transpiration factor
θ = time, sec
ρ = density, kg/m^3
ψ = ratio of heat transfer with and without mass addition

Subscripts

$comb$ = combustion
cw = cold wall
e = boundary-layer edge
hw = hot wall
i = incident with blockage
L = laminar
o = stagnation point or initial
T = turbulent
v = vapor
1 = first order
2 = second order
∞ = freestream

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Introduction

MANY studies have been previously performed to understand the thermochemical behavior of Teflon when heated aerodynamically. A much greater emphasis has usually been placed upon the mass loss behavior of Teflon rather than upon the thermal protection capability of the material. Thus it is generally easy to estimate the amount of Teflon which will be ablated by a specified heating environment, but the prediction of the temperature history of the substrate being protected by the Teflon is a more difficult and uncertain task. However, to properly design an entry vehicle heat shield made of Teflon, the time-varying mass loss rate and the temperature variation in depth (including the substrate) with time must be calculable with sufficient accuracy.

Some of the earliest studies of Teflon behavior are represented by Refs. 1-5. Adams and Schmidt[1,2] both developed a general analytic relationship for the effective heat of ablation which included the effects of depolymerization, convective blockage, and combustion. Data obtained in electric arc-heated facilities[3-5] were compared with the analyses by Adams[1] and Sheridan et al.[3] Unfortunately, the effective heat of ablation is only an indicator of ablation rate for quasi-steady ablation.

Extensive measurements in arc-heated air, of not only quasi-steady Teflon ablation rates but also the maximum backface temperature rise are reported in Ref. 6. The backface temperature rise of both full dense and partial dense Teflon exposed to arc-heated nitrogen flows are reported in Ref. 7. Clark,[8] utilized measured ablation rates and temperatures to estimate 18 material and ablative properties of Teflon.

None of the studies previously mentioned provides the analytical tools required to predict both ablation rate and temperatures for a time-varying thermal environment. This paper describes a computer model of Teflon ablation, constructed from simplified theories, which can be used to predict the ablative performance of full dense and partial dense Teflon. The model, which is combined into an existing numerical analysis computer program, will provide (for specified heating conditions) the mass loss and temperature variations of Teflon mounted on arbitrarily specified substructures. The ablation is modeled in one dimension, whereas the substructure can be modeled in one, two, or three dimensions. The simplified theories used in constructing the computer model are summarized. The model utilizes the CINDA computer program,[9] and a brief description of the coding method is provided. Verification of the predictive method with experimental data is shown. To illustrate its application in design, the model is used to design a 30% dense Teflon shield for the base of a re-entry vehicle.

Analysis

The thermal degradation of Teflon is often described as sublimation.[1,3] However, contrary to popular belief, the ablation of Teflon is a complex process. Indeed, the Teflon polymer does not sublime, but it melts and then vaporizes.[8-10] The polymer does not "unzip" to provide only the C_2F_4 monomer, but depolymerizes to a number of C_nF_m compounds.[10,12] The mole fractions of the various compounds produced by deploymerization in an inert environment can depend upon pressure, heating rate, etc. Depolymerization in an oxidizing or nitriding environment can provide many other $C_nO_kF_mN_\ell$ compounds, resulting from complex chemical reactions between the ablative products and high-energy boundary-layer species.[10,12] Furthermore, the thermal properties at high temperatures are not well defined.[8] Hence, a detailed mathematical model of Teflon ablation is impractical if not impossible,

The simplified theories which were used to construct the mathematical model (the computer code which was used) and the selection of material properties used in the model will now be described.

Simplified Theories

For the present mathematical model, the energy and mass transfer processes in the boundary layer in front of the ablating surface are handled in the following manner. It is first assumed that the convective heating environment is specified by the cold wall heating rate and the associated boundary-layer edge enthalpy. The standard hot wall correction is applied to obtain the hot wall heating rate:

$$q_{o,hw} - q_{o,cw}(H_e - H_{hw})/(H_e - H_{cw}) \tag{1}$$

The convective blockage can be expressed in terms of the linear relationship (for example, see Refs. 1 and 2):

$$\frac{q_i}{q_{o,hw}} = \psi = 1 - \beta \frac{\dot{m}(H_e - H_{hw})}{q_{o,hw}} \tag{2}$$

where the wall conditions are defined for the ablating wall temperature without the presence of ablative vapors. The term β_L is the laminar transpiration factor which is given by[1]

$$\beta_L = N(M_\infty / M_v)^\alpha \tag{3}$$

where $0.67 \leq N \leq 0.72$, and $0.25 \leq \alpha \leq 0.4$ Adams[1] further indicates that

$$\beta_T \approx (1/3)\beta_L \tag{4}$$

A second-order relationship for the convective blockage is[13]

$$\frac{q_i}{q_{o,hw}} = \psi = 1 - \beta_1 \frac{\dot{m}(H_e - H_{hw})}{q_{o,hw}} + \beta_2 \left\{ \frac{\dot{m}(H_e - H_{hw})}{q_{o,hw}} \right\}^2 \tag{5}$$

where, for this study, the values of the transpiration factors are chosen, for Teflon in air, to be

$$\beta_{1,L} = 0.72(M_v/M_\infty)^{0.4} = 0.72(29/100)^{0.4} = 0.44 \tag{6}$$

$$\beta_{2,L} = 0.13(M_v/M_\infty)^{0.8} = 0.048 \tag{7}$$

and by using Eq. (4)

$$\beta_{1,T} \approx 1/3\beta_{1,L} = 0.147 \tag{8}$$

$$\beta_{2,T} \approx 1/3\beta_{2,L} = 0.0161 \tag{9a}$$

or

$$\beta_{2,T} \approx 1/9\beta_{2,L} = 0.0053 \tag{9b}$$

This assumption presumes that the ablative vapor is all C_2F_4 monomer. These second-order relationships were used in the mathematical model. The $\beta_{2,T}$ term [Eqs. (9)], which is not well defined, is assumed to be between these two values.

As was indicated earlier, the ablative products can react chemically with the boundary-layer species. These reactions are generally exothermic, and, whereas the blockage reduces the heat transfer to the surface, the boundary-layer combustion increases the heat transfer to the surface. The heating from combustion is modeled by using the approximate results of Cohen et al.[14]

$$q_{\text{comb}} = \psi q_{o,hw} K h_c / (H_e - H_{hw}) \tag{10}$$

where it is assumed that the freestream mass fraction of oxygen, K, and the ablative species heat of combustion per unit mass of oxygen, h_c are known.

It is of interest to note that, for steady ablation (e.g., see Ref. 15),

$$q_i + q_{\text{comb}} = \dot{m} H_a \tag{11}$$

and Eqs. (5), (10), and (11) can be combined to yield a quadratic in q_i, independent of $\dot{m}$, as follows:

$$Aq_i^2 + Bq_i + q_{o,hw} = 0 \tag{12}$$

where

$$A = \frac{\beta_2}{q_{o,hw}} \left[1 + \frac{Kh_c}{(H_e - H_{hw})} \right]^2 \left[\frac{H_e - H_{hw}}{H_a} \right]^2 \tag{13}$$

and

$$B = \beta_1 (H_{hw} - H_e - Kh_c)/H_a - 1 \tag{14}$$

The use of Eq. (12) in the model is justified later.

Computer Code

The Chrysler Improved Numerical Differencing Analyzer[9] (CINDA) was used to perform the calcualtions. A third-generation, Sandia Laboratories version of the program was used on a CDC-6600 computer. The implict forward-back differencing numerical technique was used. During each computation interval, the heat flux to the surface defined by the solution of the quadratic Eq. (12) is determined prior to entering the network solution phase. The actual ablative calculations are performed with a one-dimensional subliming ablation subroutine available within the CINDA program. The data deck (i.e., the data and instruction cards) used for these calculations is available from the author upon request.

At this point, it is necessary to justify the use of the subliming ablation routine and the use of Eq. (12) in the calculations. As stated previously, Teflon does not sublime; however, the viscosity of the melt phase is usually so great that the melted Teflon does not flow but remains in situ to be vaporized. Thus, for convenience, the heat of melt and heat of vaporization are usually "lumped" together into a term which is equivalent to a heat of vaporization.[11] The situations where Teflon melt can be expected to flow are discussed in

Refs. 10 and 11. Usually, these conditions will not exist in a normal re-entry environment.

This one-dimensional sublimination routine provided within CINDA does not determine instantaneous mass loss rates. The ablator is divided into discrete nodes, and the fractional loss of a node is not indicated. Therefore, the mass loss rate, which is a result of the calculation, cannot be used prior to the network solution of a specific time interval. Therefore, Eq. (5) could not be used directly in the calculation of the imposed convective heating. For this reason, Eq. (12) was developed to provide the incident convective heating, q_i, independent of the $\dot{m}$. The net effect of this assumption is to slightly underestimate the incident heating. To minimize the effect of the quasi-steady assumption on the calculations, a small time interval of 0.0005 sec is used in the calculations.

Material Properties

Clark[8] provides an excellent summary of the material properties for full dense Teflon which are available from the literature. In addition, Clark used experimental data obtained in an arc-heater, and a mathematical model to predict material properties by the method of nonlinear estimation. Many of the parameters, as determined by different investigators, differ significantly. For example, the thermal conductivity at ambient temperature varies by a factor of 3.7.

From the array of data presented by Clark,[8] the properties of full dense Teflon were selected. Table 1 shows the thermal conductivity, specific heat, and density.

The depolymerization process is defined in terms of H_{dp}, the lumped depolymerization, vaporization, and melt energy, which is given by[16]

$$H_{dp} = 1.77 - 0.279 \times 10^{-3} T (MJ/kg) \tag{15}$$

The temperature T is the vaporization temperature which is determined from the wall pressure and the vapor pressure data in Ref. 11. The heat of combustion, which will depend upon the reactions occurring, has values between 14.6 and 23.7 MJ/kg. A value of 23.7 MJ/kg was selected for the present study.

The radiation from the ablating Teflon is a complicated process.[11,17] On the basis of reflectance measurement,[17] an effective emittance of 0.15 was assumed. The properties of partial dense Teflon are not defined. Since the partial dense material is still 100% polytetrofluoroethylene polymer, it was assumed that c_p, H_{dp}, and emittance are unchanged from the full dense value. The temperature variation of density seen in Table 1 for the full dense material was assumed to occur for the partial dense material; the variation is linearly related to the initial density. The thermal conductivity of the partial dense material was estimated with the mathematical model, the data in Ref. 7, and a parametric study to match calculated results with the data. The value determined is

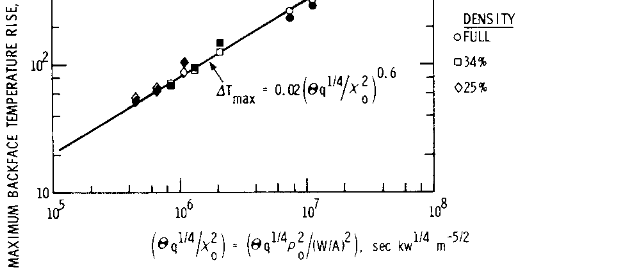

Fig. 1 Comaprison of data with model, for Teflon in nitrogen.

Table 1 Properties of full dense Teflon

	Temperature (K)			
	296	600	601	889
k_o (W/cm K)	0.336	0.540	0.429	0.373
C_p (J/kgK)	711	1213	1477	1536
ρ (kg/m^3)	2193	2172	1739	1085

$$k = \{(0.45\ \rho/\rho_o) + 0.55\} k_o \tag{16}$$

where ρ and ρ_0 are the density of partial and full dense Teflon, respectively, and k_o is the thermal conductivity of full dense Teflon.

Results

Nitrogen Data

The results for Teflon which were presented in Ref. 7 are detailed in Table 2 and are compared with the analytical results. These tests are for Teflon models exposed to arc-heated, supersonic nitrogen flows. The rear face of the model was shielded from the flow, insulated from the sting support, and instrumented with a thermocouple. For the nine cases, the calculated values are within 20% of the measured values. In Ref. 7, a correlation of backface temperature rise with the parameters θ, q_o, and X_o was developed.

The data shown in Table 2 are compared with the calculated results, in terms of this correlation, in Fig. 1. Generally, the comparison between the measured and calculated data are good. These data are those which were used to select the conductivity relation given by Eq. (16).

Argon Data

Clark[8] presented temperature-history data for a thin sample of Teflon exposed in an arc-heated argon flow for 1.4 sec. These results for depths of 0.25, 0.50, and 0.75 mm are compared with the calculations in Fig. 2. Again, the experiment and the calculations compare well, within 10%.

Air Data

Extensive test results in air were obtained[6] in a large number of facilities during the NASA round-robin program. A great deal of scatter was exhibited within the data. Correlations with mass loss rates and enthalpies yielded standard deviations as large as 30 to 46%. The ablative test models were very thick and were generally not protected from side heating and partial base heating. Conduction from the steel base plate and sting support into the rear of the model

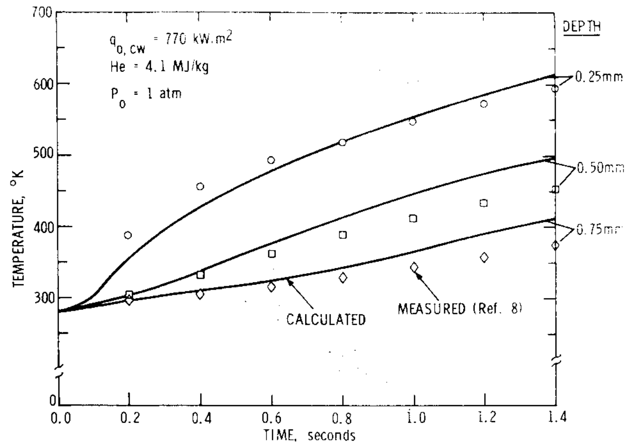

Fig. 2 Comparison of measured and calculated temperature histories in arch-heated argon, full dense Teflon.

Table 3 Comparison of experimental and calculated data for teflon ablation in air[a]

Model number	Test facility	q_o, cw (kW/m^2)	p_o (atm)	H_e (MJ/kg)	Θ (sec)	ΔT (°K)		ΔX (mm)	
						Measured	Calculated	Measured	Calculated
T99	Ames	1500	0.086	7.9	28.6	56	34	4.0	4.7
T103	Ames	1250	0.082	7.2	30.1	51	38	3.5	4.1
T21	Giannini	930	0.057	7.1	30.0	33	41	2.5	3.2
T18	Avco	840	0.025	10.7	30.0	72	48	4.8	1.9
T14	Avco	930	0.025	11.6	30.0	56	48	2.6	1.9
T72	Martin	1100±200	0.027	11.6	30.0	78	48	2.1	2.8
T74	Martin	1100±200	0.027	11.6	30.0	111	48	2.1	2.8
T76	Martin	1100±200	0.027	11.6	30.0	137	48	2.3	2.8
T62	GE	3630	0.063	31.5	30.0	81	38	6.2	4.1
T23	Giannini	3360	0.048	35.0	30.0	97	38	3.7	3.6

[a] The experimental data were obtained at the facilities indicated in conjunction with the NASA round-robin test study[6] conducted by the Stanford Research Institute.

Table 2 Test conditions and results, data from Ref. 7 compared with analytical results

	Condition 1	Condition 2	Condition 3
Test gas	N2	N2	N2
Total stream enthalpy (*MJ/kg*)	4.4	8.1	13.9
Stagnation point pressure (atm)	0.010	0.011	0.012
Heating rage (kW/m^2)	170	340	570
Model exposure time (sec)	100	50	30
Total heating (*KJ*/m^2)	17,000	17,000	17,000
Full dense Teflon:			
ΔT measured (K)	432	317	254
ΔT calculated (K)	417	298	225
34% dense Teflon:			
ΔT measured (K)	122	90	72
ΔT calculated (K)	147	94	70
25% dense Teflon:			
ΔT measured (K)	88	67	54
ΔT calculated (K)	103	64	52

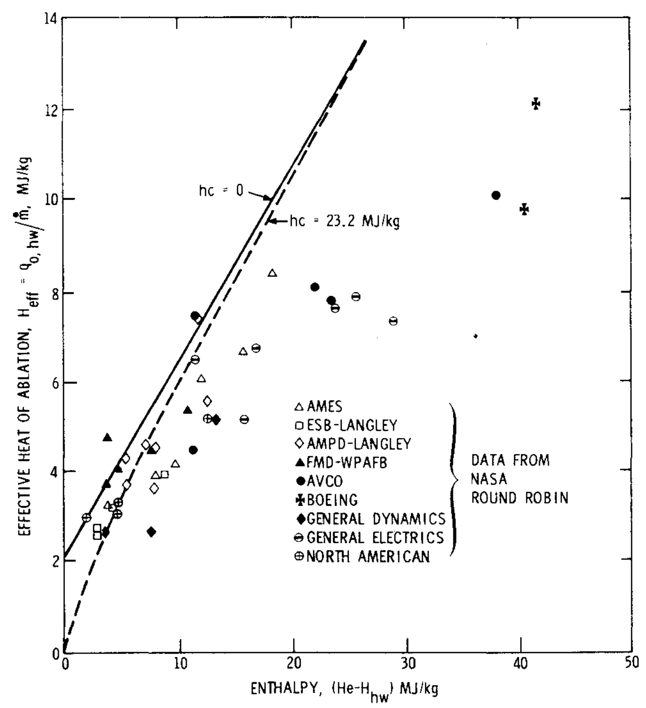

Fig. 3 Effective heat of ablation for Teflon, comparison of linear theory with experimental data.

was probably significant, especially during the heat soak following termination of heating.

Despite the limitations of the round-robin data, calculated results are compared with these experimental results in Table 3. These are just a few of the data obtained during the test program.[6] The data shown in Table 3 are separated into three groups having similar exposure conditions. In each group, data obtained in two separate facilities are compared. Generally, the agreement between the data and the experiment is not as close as it was with the nitrogen and argon data. However, a great deal of scatter in the experimental data is also exhibited within the sets. For example, with T18, T14, T72, and T76, the expsoure conditions were similar, but the measured values of ΔT and ΔX varied by a factor of two. The calculated ΔT values are generally lower than the measured values. This is probably explained by the heat added by conduction from the base after the exposure period. The calculated recession values, ΔX, bracket the measured values within 30%.

The statements made previously concerning the comparison between the calculated and measured responses in air for the three sets of data shown in Table 3 also hold true for the other comparisons made with the NASA round-robin[6] test data.

Effective Heat of Ablation

The effective heat of ablation is a measure of the mass loss response of a material to the aerothermal environment. If the linear convective blockage relationship, Eq. (2), is used with Eqs. (10) and (11), the following is obtained for the effective heat of ablation of Teflon:

$$H_{eff} = \frac{q_{o,hw}}{\dot{m}} = \frac{H_a}{1+Kh_c/(H_e-H_{hw})} + \beta(H_e-H_{hw}) \quad (17)$$

This is the form of the equation generally used; it is compared with the data from Ref. 6 in Fig. 3. In these calculations, a value of 2.2 MJ/kg is used for H_a, and values of 0.0 and 23.2 MJ/kg are used for h_c. The figure illustrates three important points. First, gas-phase combustion effects are significant only at the low values of enthalpy. Second, the wide scatter in the data is readily apparent. For these data, the enthalpy was calculated from the measured heating rate. Hiester and Clark[6] show that, if facility reported enthalpies are used, the scatter is much greater. Third, the data significantly deviate from the linear theory at high values of enthalpy. This deviation is caused by two factors: 1) the linear relationship is not valid for high enthalpies, and 2) the catalytic effects on heat transfer have not been considered. Catalytic effects on ablative performance cannot be considered without more detailed measurements than are available in Ref. 8. This problem has been considered in depth by Marvin and Pope.[13]

The effect of nonlinear blockage curves on H_{eff} will now be considered. Combining Eqs. (5), (10), and (11) and solving the resulting quadratic for H_{eff}, yields

$$H_{eff} = [\frac{H_a}{(H_e - H_{hw} + Kh_c)} + \beta_1 + \{[\frac{H_a}{(H_e - H_{hw} + Kh_c)} + \beta_1]^2 - \beta_2\}^{1/2}]\frac{(H_e - H_{hw})}{2} \tag{18}$$

A different result for convective blockage with Teflon is given by Vojvodich and Pope.[15] The relationship, which was developed empirically, is given by

$$\psi = q_i/q_o = 0.85\ e^{-4/3B} + 0.15 \tag{19}$$

where

$$V = \dot{m}(H_e - H_{hw})/q_{o,hw} \tag{20}$$

A blockage curve similar to that of Eq. (19) (also obtained empirically) was later presented by Luikov et al.[18] Equations (10), (11), and (19) were solved iteratively to obtain the H_{eff} variation with enthalpy.

All the preceding results are compared (Fig. 4) with the linear theory, the experimental data, and the results from the present computer model. The second-order relationship, Eq. (18), does not significantly change the results from the linear relationship, Eq. (17). The exponential/asymptotic relationship, Eq. (19), provides a much closer approximation of the data; whereas, the results from the computer model lie between the second-order and exponential results. Therefore, if the experimental data are correct, then at high enthalpies the results from the computer model could be optimistic and could provide a higher effective heat of ablation than can actually be obtained.

A correlation of the data in air, similar to the correlation shown in Fig. 1 for nitrogen, is not possible with the data available. The parameter $(\theta q^{1/4}/X_o)$ was varied by about 45% for the air data[6] rather than the two orders of magnitude for the nitrogen tests.[7] However, because of combustion heating, the air data provided higher ΔT's than did the nitrogen data.

Sample Entry Calculations

The computer model was used to analyze the thermal performance of a 30% dense Teflon heatshield located on the base of an entry vehicle. A typical thermal environment for a specific location on the base is shown in Fig. 5. The heatshield analyzed was 2.5-mm-thick, and the substructure was 6.4-mm-thick-aluminum.

The calculated response of the heatshield is shown in Fig. 6 for the two different values of the turbulent transpiration factor, $\beta_{2,T}$ (Eqs. (9)). Once the heat transfer becomes turbulent and the recovery enthalpy drops so that the combustion heating becomes significant, the material is rapidly ablated and the aluminum temperature increases significantly just prior to impact. The effect of the uncertainty in $\beta_{2,T}$ is clearly demonstrated: about a 50K difference in temperature is provided at impact.

The heatshield performance was calculated for different initial thicknesses. Results of these calculations are shown in Fig. 7. From these data, the heatshield thickness is tailored to provide the maximum desired aluminum temperature.

The CINDA computer code was used to construct a two-dimensional model of the base plate which includes radial variations in the heatshield thickness, and applied heat load and heating by conduction from the vehicle forebody. This model was operated successfully, and the results were used to design the base heatshield for the re-entry vehicle.

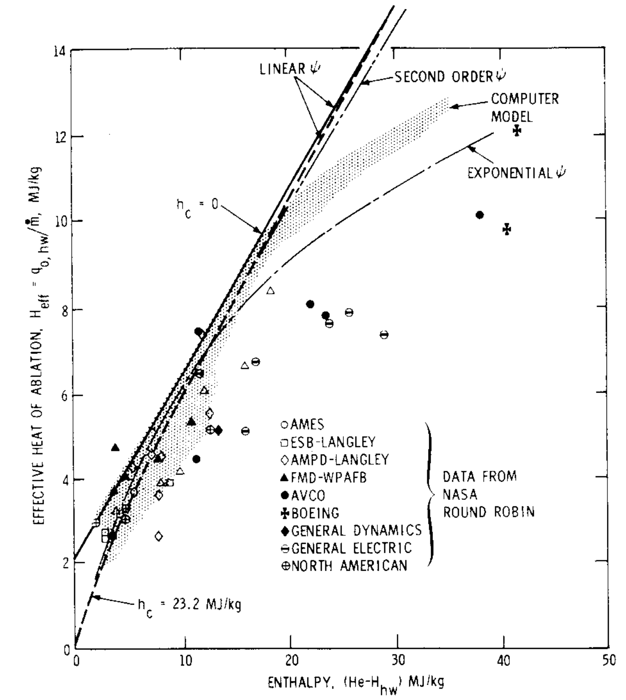

Fig. 4 Effective Heat of ablation of Teflon comparison of data and theories.

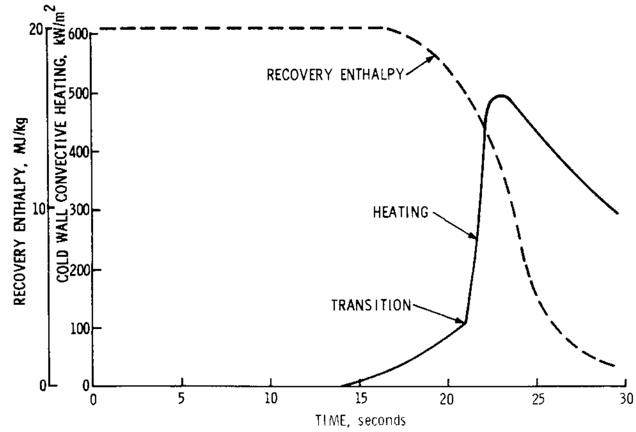

Fig. 5 Typical thermal environment on the base plate of an entry vehicle.

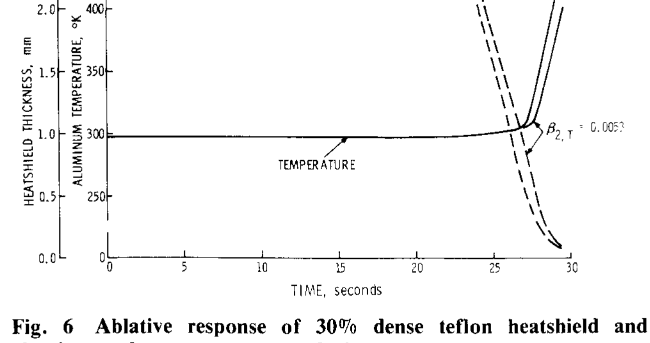

Fig. 6 Ablative response of 30% dense teflon heatshield and aluminum substrate temperature during re-entry.

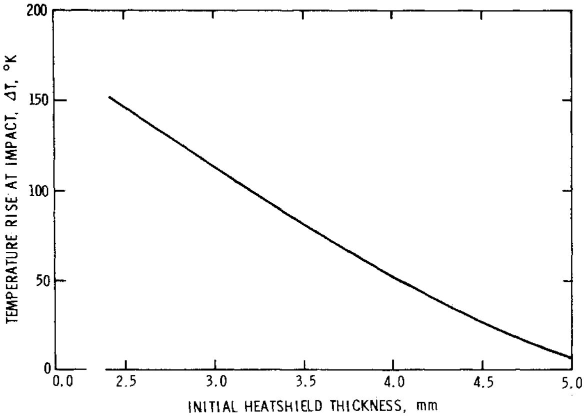

Fig. 7 Maximum temperature rise of the aluminum substrate.

Summary

Simplified theories have been used to analytically model the boundary layer and depolymerization process for a Teflon heatshield exposed to an aerothermic environment. The analytic modeling, which is for full dense or partial dense Teflon, has been coupled with the CINDA numerical analysis computer program to facilitate the detailed calculation of material response and the resulting ablator and substrate temperature histories. The calculational methods have been adequately verified by comparing the analytical results with experimental data obtained in electric arc-heated facilities. The computer model has been used to design a base heatshield for a re-entry vehicle. Typical results of these calculations have been presented.

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