Evaluation of Thermal and Kinetic Properties Suitable for High Heating Rate Computations

I. Auerbach,* D. A. Benson,† S. G. Beard,‡ and G. F. Wright Jr.§
Sandia National Laboratories, Albuquerque, New Mexico

Computer codes that model dimensional, weight, and energy changes in ablative or pyrolysis materials, such as ballistic missile re-entry vehicle heat shields or thermal insulators, generally have to use effective rather than measured property values for some of their input. A primary reason for the discrepancy in values is that the properties are a function of the heating rate and conditions in which they will be used. In this study, heat capacity, thermal conductivity, thermal diffusivity, and kinetic parameters from thermogravimetric analysis data were generated under heating rate conditions that can provide property data suitable for re-entry. Differences in values between steady-state or low heating rate data and high heating rate data are examined. The Charring Material Ablation Program was used to model heat-shield performance using high heating rate properties to show the improved correlation between computed and flight-test results.

Nomenclature

B_i = pre-exponential factor in the Arrhenius relationship
C_p = heat capacity
E_i = activation energy
K = thermal conductivity
R = universal gas constant
T = temperature
α = thermal diffusivity
θ = time
ρ = density
ρ_i = instantaneous density
ρ_{o_i} = initial density
ρ_{r_i} = char residual density
ψ_i = reaction order

Subscript
i = component = 1–3

Introduction

FLIGHT systems as well as other heat-sensitive systems that must be exposed to high temperatures, require special consideration in the choice of their insulation, since margins of weight and size are critical to the overall system performance. It is desirable, therefore, to minimize insulation requirements. Computer codes have been developed to estimate the thermal requirements and reduce the amount of confirmatory testing required to insure acceptable performance. Unfortunately, in some cases poor agreement with test data was obtained when the thermal property data derived from conventional steady-state measurement techniques were used in the calculations. To obtain satisfactory correlations between computed and observed test data, effective thermal conductivities, heat capacities, and so forth, had to be substituted as input.

Figure 1 (data from Ref. 1) is an example of the differences found in a carbon-phenolic composite that have motivated several investigators to address the discrepancy between measured and useful property values. Kratsch et al.[2] found it necessary to vary the residual char fraction to obtain useful thermal conductivities for a nylon-phenolic ablator. Shaw et al.[3] and Bueche et al.[1] studied the effects of uncertainties in property measurements on predicted performance. Brazel et al.[4] developed a technique for measuring the thermal conductivity of chars under transient rapid heating conditions. Baker et al.[5] developed a combined experimental and analytic technique for measuring the thermal conductivity of charring materials. These authors recognized the importance of heating rate on the evaluation of thermal properties, but did not fully develop a measurement technique that would yield values equivalent to the effective values without recourse to modification. For kinetic parameters, Melnick and Nolan[6] designed a thermogravimetric analyzer that could provide these parameters at high temperature-rise rates, which are proportional to heating rates. The large differences in the thermograms and parameter values, which they obtained from a nylon-phenolic composite at 10 and 100°C/min, underscored the importance of heating rates.

Improved empirical techniques are described in this paper that can provide thermal property values useful in computations. Thermal conductivity, diffusivity, heat capacity, and

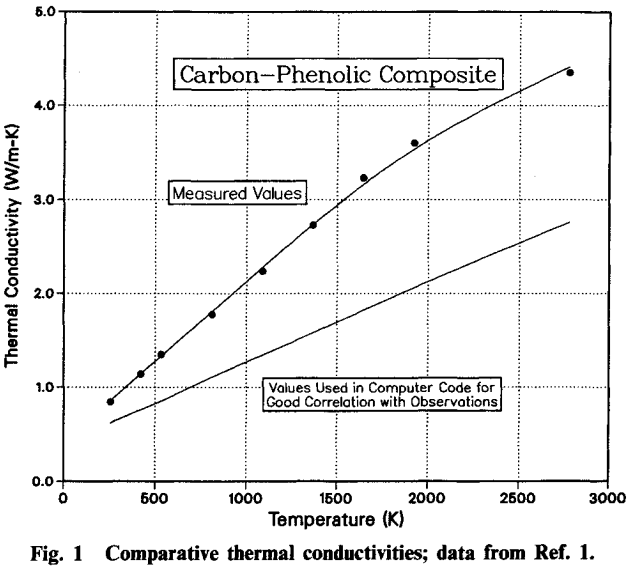

Fig. 1 Comparative thermal conductivities; data from Ref. 1.

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*Member, Technical Staff, Aerodynamics Department.
†Member, Technical Staff, Fluid and Thermal Sciences Department.
‡Member, Technical Staff, Aerodynamics Department. Member AIAA.
§Member, Technical Staff, Advanced Systems Development Department. Member AIAA.

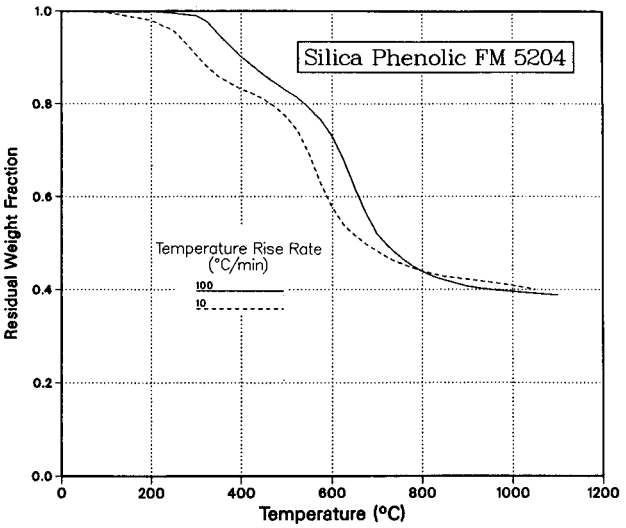

Fig. 2 Effect of temperature rise rates on the TGA curves; gas flow rate 55 ml/min.

thermogravimetric analysis (TGA) are considered. Measurement under high heating rates is the basic change in data acquisition from conventional techniques that permits direct application of measured property values. In this study, variations in heating rates during measurement were accomplished by varying the temperature rise rates. Heating rate is important for organic materials because large variations can provide appreciable differences in the thermal properties of materials that degrade at moderate temperatures.

An important advantage that is derived from the availability of appropriate thermal property values from the laboratory is that it is no longer necessary to derive effective values from flight or simulated test data for use as input in computer codes. The availability of these data can, therefore, result in appreciable savings of time, effort, and cost for flight or simulated tests. The improvement realized from the techniques described in this paper will be evident from comparisons made between computations from the charring material ablation (CMA) code using high heating rate values, those obtained from conventional heating rates, and test data.

The scope of this paper is limited. It covers the evaluation of the thermal properties and kinetic parameters of a virgin silica-phenolic composite, but not its char, nor does it cover other aspects of the ablation process. Other property values for these materials generally used in the CMA code were not changed. The primary motive for this study was to provide techniques for the direct evaluation of the preceding properties and parameters.

Charring Material Ablation Program

The Charring Material Ablation Program[7] is a code used to model dimensional, weight, and energy changes of insulators under high-temperature conditions. It is a one-dimensional code that is used for calculating the in-depth thermal response of a charring and/or ablating material. Decomposition reactions are based on a three-component model. Material properties such as thermal conductivity, specific heat, and emissivity are input as functions of temperature for the virgin resin composite and char. The model also requires the density, heat of formation of the resin, decomposition gas enthalpy, and kinetic parameters for the Arrhenius equation. The output provides temperatures, mass ablation rates, and blowing parameters for char and pyrolysis gas, total recession and recession rates of the surface, the char line, and pyrolysis line.

Thermogravimetric Analysis

Thermogravimetric analysis involves measuring changes in the weight of a substance as it is heated to elevated temperatures. It can be used to establish threshold thermal stabilities, identify intermediate reaction products, the sequence of reactions and, ultimately, the kinetics of the degradation reactions, as well as the values of the kinetic parameters.

The degradation rate relationship used in the CMA code, Eq. (1), requires values for the kinetic parameters B, E, and ψ. These are obtained from TGA data.

$$-\frac{d\rho_i}{d\theta} = B_1 \exp(-E_i/RT)\,\rho_{o_i}\left[\frac{\rho_i - \rho_{r_i}}{\rho_{o_i}}\right]^{\psi} \qquad (1)$$

Although the degradation of organic materials involves a series of consecutive and competitive reactions, CMA limits the modeling of the degradation process to three consecutive and competitive steps. Three steps are generally sufficient. Evaluation of the preceding parameters, as well as the fraction of the total mass loss in each step, was accomplished with the kinetic parameter evaluation code, a least-squares solution program.

The effect of temperature rise rate on TGA and subsequent CMA output was studied with the FM-5204 silica-phenolic heat-shield material (U.S. Polymeric Corp.). An example of the temperature rise rate effect on TGA for this material is seen in Fig. 2, where it is evident that the phenolic resin in the composite experiences equivalent weight losses at different temperatures because of the difference in temperature rise rates of 10 and 100°C/min. The degradation occurred in an airflow environment of 55 ml/min. The conventional TGA instrumental conditions are a temperature rise rate of 5–10°C/min. Although the maximum temperature rise rate on the DuPont 951 Thermogravimetric Analyzer is 100°C/min, which is greatly below that experienced during re-entry, it will be shown that using this TGA data acquisition setting greatly improved the correlation between computed and test data.

Silica-Phenolic Composite

Heat Capacity

The effective heat capacities of polymeric or resin-type materials evaluated at high heating rates have lower values than those obtained at low heating rates, and the differences between these values increase at higher temperatures. This apparent anomaly arises from the occurrence of relatively slow time-dependent processes during pyrolysis and mass diffusion, which are minimized by high heating rates. These processes include 1) the diffusion and vaporization of water and other byproducts formed during resin formation, 2) additional resin formation, i.e., curing, and 3) subsequent production and vaporization of decomposition products, which occur at higher temperatures. The degradation and mobility of polymer segments also may contribute to energy absorption.

The preceding processes are best illustrated with the phenolic resin, which, in combination with silica or carbon fibers, is commonly used as a heat-shield material for re-entry vehicles. This resin is a polymer product of phenol and formaldehyde. Water is a byproduct. Heat capacity measurements would involve energy absorption not only of the resin but moisture, unreacted phenol, catalysts, and other residual materials. Energy would also be absorbed by diffusion of these mobile materials. Volatilization of these materials at the surface will consume even greater amounts of energy. Residual phenol may continue to polymerize; however, this is an exothermic reaction. On the other hand, decomposition is initiated at about 200°C, is endothermic, and would be more prominent. The moisture and organic byproducts from the decomposition will also undergo energy-absorbing diffusion and vaporization. Phenolic resins soften at higher temperatures and are subject to possible viscous effects that may absorb energy. All of these processes are time-dependent and would, therefore, influence heat absorption minimally during the approximately 30-s high-heating-rate re-entry period. On the other hand,

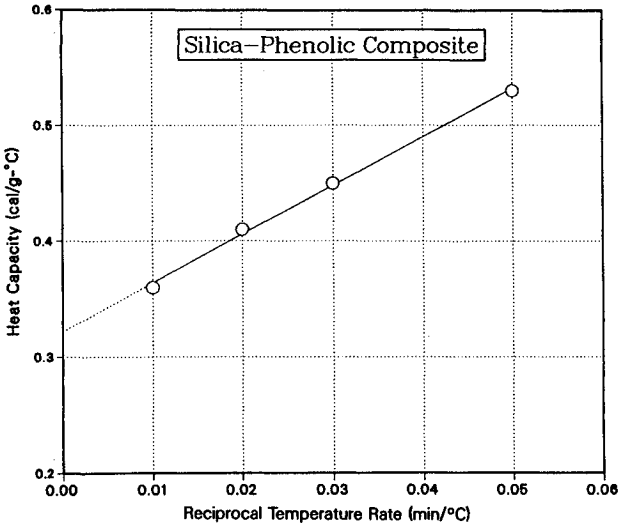

Fig. 3 Evaluation of the heat capacity at very high heating rates.

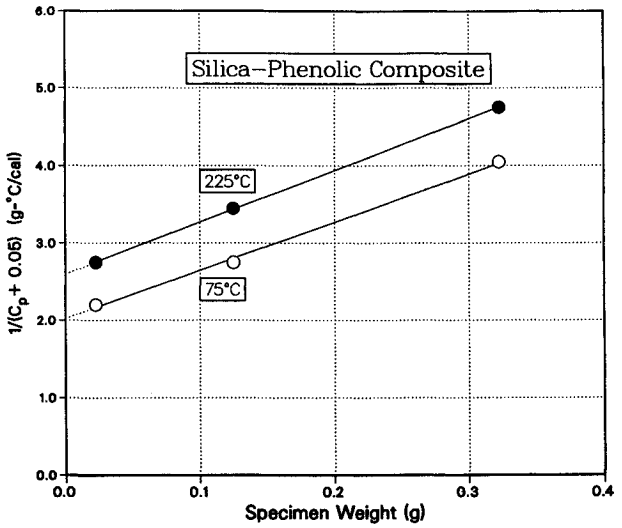

Fig. 4 Correction of heat capacity for nonthermal equilibration due to weight and high heating rates.

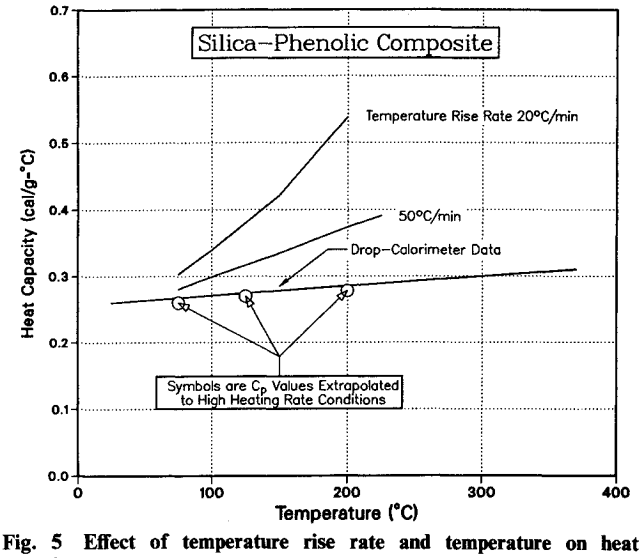

Fig. 5 Effect of temperature rise rate and temperature on heat capacity.

conventional heat capacity measurements over a 200°C temperature span may take up to 40 min. Therefore, the preceding processes will influence the heat capacity values, especially at the higher temperatures.

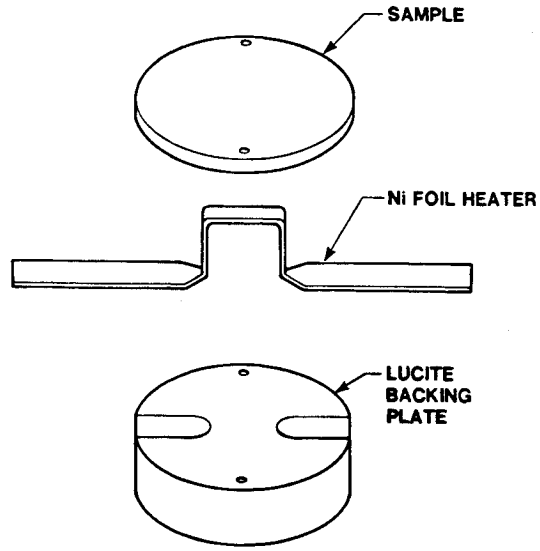

Fig. 6 Sample geometry.

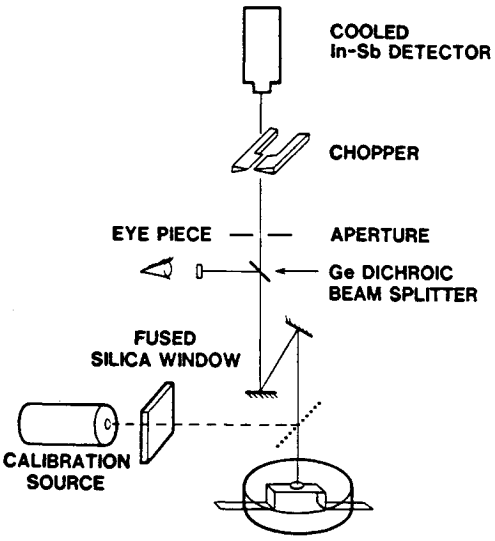

Fig. 7 Infrared temperature measurement system.

Heat capacities of the composite at very high heating rates were evaluated with the DuPont 910 differential scanning calorimeter, which measures heat input as a function of temperature increase. A sapphire standard was used to calibrate the instrument. The rate at which the temperature is raised can be set at 5–100°C/min. It was found that the heat capacity was linear with the reciprocal of the rate at which the temperature increases. Thus, a plot of this type, Fig. 3, extrapolated to a reciprocal temperature rate value of zero, provided a heat capacity at very high heating rates. Note that the "effective" heat capacity decreases with increasing temperature rise rate.

Temperature equilibration within the measured specimen is important and may not take place at the high heating rates if the specimen is large. To correct for this source of error, linear plots for the empirical relationship of $1/(C_p + 0.05)$ vs specimen weight were extrapolated to zero weight. Figure 4 shows representative plots for heat capacities at two temperatures.

Heat capacity values obtained by this technique compared favorably with values obtained from the older drop-type calorimeter (Fig. 5). The correlation of values with this latter but less accurate and more involved technique stems from the fact that samples are heated slowly and maintained at temperature for about 30 min and then are rapidly quenched in a

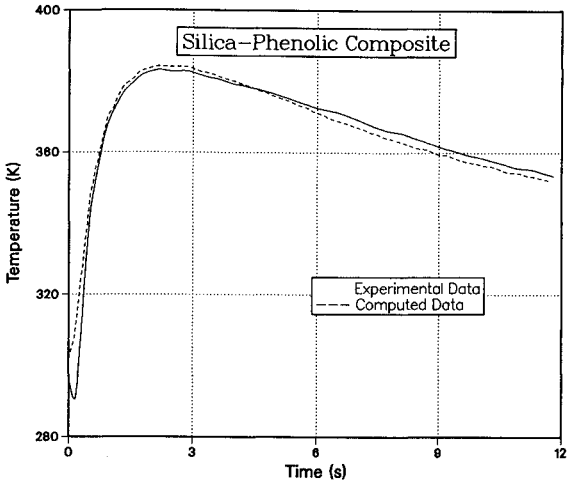

Fig. 8 Comparison between numerical values obtained from the SINDA code and experimental values.

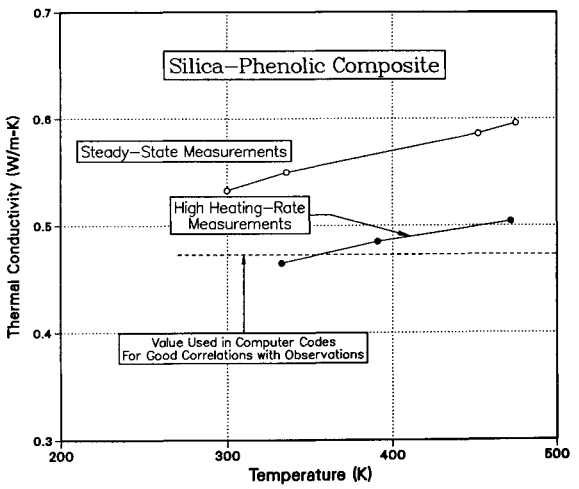

Fig. 9 Comparative thermal conductivities of the virgin material.

Table 1 Comparative thermal diffusivity values obtained under high-heating-rate and steady-state or low-heating-rate conditions

	Thermal diffusivity, cm^2/s		
		Steady-state conditions	
Material	High-heating-rate conditions	Laser flash technique	Calculated from Eq. (2)
Silica phenolic FM-5204	0.0026	0.0034	0.0029–0.0014 (30–210°C)
Carbon phenolic FM-5055G	0.0050	0.0055	0.0070–0.0054 (30–200°C)

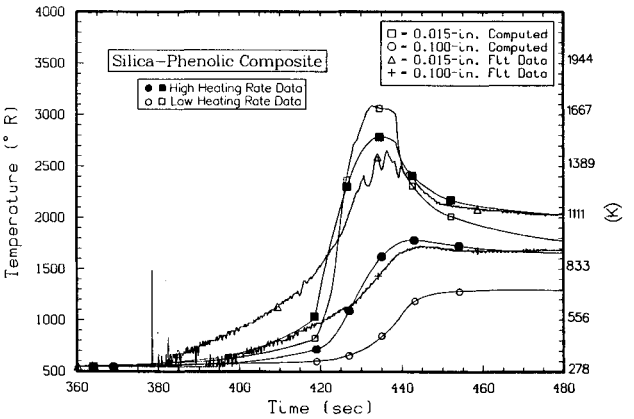

Fig. 10 Station 35. Comparisons between computed and flight-test data; thermal properties and kinetic parameters derived from high- and low-heating-rate data.

suitable liquid. The irreversible processes that normally absorb energy during heating have been largely eliminated and are not transferred to the quench medium.

Thermal Conductivity

Thermal conductivities were evaluated from the following relationship:

$$K = \alpha \cdot C_p \cdot \rho \qquad (2)$$

Thermal diffusivities were also determined under high-heating-rate conditions. Since the instrumentation and evaluation techniques are unique, they will be described briefly. The sample-heater setup is shown in Fig. 6. An electrical pulse of about 10^5 W is applied to the nickel foil heater over a 0.1-ms period to the undersurface of the sample. The surface temperature response is recorded with the infrared sensitive instrumentation shown in Fig. 7. Diffusivities are evaluated from a thermal model of the test using the SINDA heat-transfer code.[8] Figure 8 shows a comparison between the measured sample surface temperatures as a function of time and those computed with the SINDA model. Although the upper surface temperature range is only about 100°C, the lower surface varied over a range in excess of 200°C. These results indicate a surface temperature rise rate of about 200 K/s. The thermal diffusivity parameter evaluated by matching this model to the surface temperature measurements is then used in other analyses.

The thermal diffusivity values obtained under this high-heating rate condition are compared in Table 1 with two other methods using steady-state heating rates. Silica-phenolic FM-5204 and carbon-phenolic FM-5055G were the test materials. The data sources were the high heating-rate technique previously described, a laser flash technique in which specimens were maintained at a steady-state temperature, and the third source involved values calculated from Eq. (2) using conductivity and heat-capacity data measured under steady-state temperature or low heating-rate conditions. The steady-state thermal conductivities were measured using a comparator technique with a silica standard.

Of the two steady-state techniques, the laser flash method is more reliable. It confirmed a constant diffusivity value (30–200°C), which was assumed in the high-heating-rate model used in the current study. The constant value is also consistent with constant values for fused silica and the essentially constant values for silica-phenolic found in the TPRC Data Series.[9] The laser flash values are, however, higher than those from the current study. The values calculated from Eq. (2) are considered inaccurate because they are higher and/or they cover a moderate to broad range.

Figure 9 shows plots comparing thermal conductivities as a function of temperature for conductivities determined from high heating rates and steady-state techniques. Included is the effective conductivity value, which in the past has provided good correlation between computed and flight data.

Comparative Computed and Flight Temperature Data

Figures 10–13 demonstrate the improvement that can be realized from a silica-phenolic heat shield with values obtained under high-heating-rate conditions. Flight data (jagged lines) are compared with computed values obtained under high-heating-rate conditions (solid circles and squares) and low-heating-rate conditions (open circles and squares). The comparative results are for locations on a conic section of a

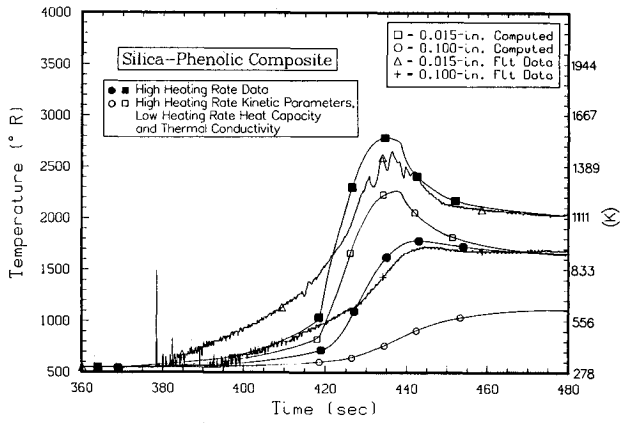

Fig. 11 Station 35. Comparisons between computed and flight-test data; thermal properties and kinetic parameters derived from high- and low-heating-rate data.

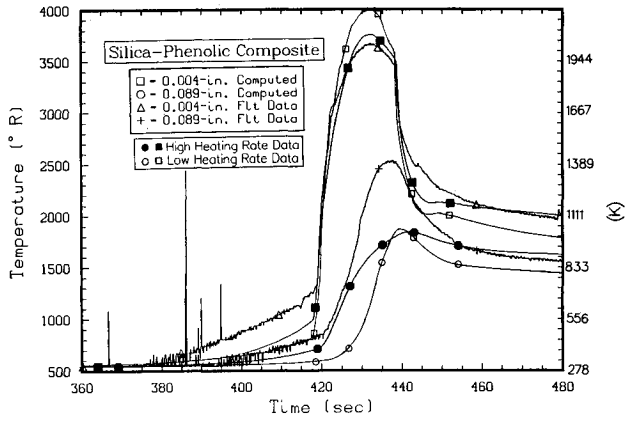

Fig. 12 Station 77. Comparisons between computed and flight-test data; thermal properties and kinetic parameters derived from high- and low-heating-rate data.

re-entry vehicle at 88.9, 195.6, and 251.5 cm (35, 77, and 99 in.) axial stations.

Two thermocouple locations are considered, one near the surface, 0.0102 or 0.0381 cm (0.004 or 0.015 in.) and another in depth, 0.226 or 0.254 cm (0.089 or 0.100 in.). The thermocouples were isothermally installed in a silica-phenolic plug and then bonded to the heat shield.

The flight test of a maneuverable re-entry vehicle subjected to Intermediate Range Ballistic Missile (IRBM) re-entry conditions provided the source of flight data. Re-entry velocities of ~12,500 ft/s provided a maximum turbulent heating rate of approximately 135 Btu/ft^2-s on the conic section. Flight-test data had indicated that boundary-layer transition from laminar to turbulent flow had occurred at 418 s in Figs. 10–12 and 438 s in Fig. 13. Reference 10 provides additional temperature vs time plots and photodiode sensor information regarding transition for this flight.

Figure 10 shows the poor correlation of flight and computed data obtained with low-heating-rate data (open symbols) and the improved correlation with the high-heating-rate data (solid symbols). Figure 11 shows the effect of substituting high-heating-rate kinetic parameter values, but maintaining low-heating-rate thermal properties. The lower computed temperatures show that less heat-shield pyrolysis and charring occurred, which is consistent with the TGA data in Fig. 2. When, in addition, high-heating-rate thermal properties, i.e., lower heat capacities and thermal conductivities were used (solid symbols), the improved correlations were obtained. Thus, the lower exothermic pyrolysis rate reduces the peak surface temperature and the lower thermal conductivity raises the near surface and surface temperatures during the maneu-

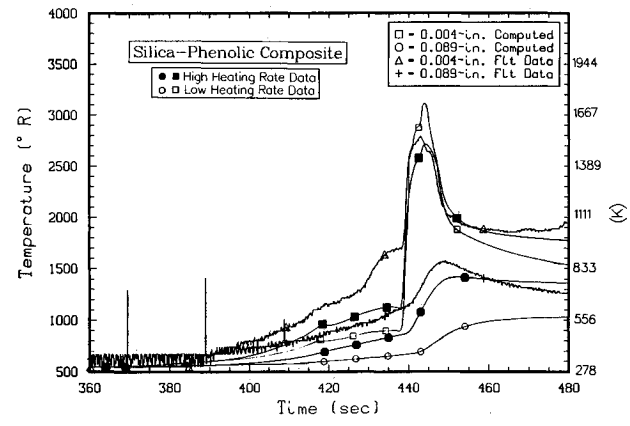

Fig. 13 Station 99. Comparisons between computed and flight-test data; thermal properties and kinetic parameters derived from high- and low-heating-rate data.

vering phase once the surface is charred. Figures 12 and 13 show similar sets of data for the 77- and 99-in. stations. For all stations, the high-heating-rate data provided better correlations with flight data than the effective values previously used in the CMA code.

One area of major disagreement between flight and computed data is during the early time period following re-entry. In the analysis procedure used, the last continuum aerodynamic heating rate calculation is made at ~240 kft. The heating rate is thus extrapolated linearly to zero at the selected re-entry altitude, usually 300 kft. This procedure underpredicts the actual heating in this altitude range and gives rise to the temperature discrepancy shown in the figures. Experience has shown that the underprediction of this low-level, early-time heating has no significant effect on the final thermal performance of heat-shields used in the design of high ballistic coefficient re-entry vehicles.

The opportunity to measure the thermal properties of the char under high-heating-rate conditions was not available in this study. Figure 1 suggests, however, that additional improvement in the correlations, especially for in-depth values, might be possible. An effective value derived from other sources was used in the current CMA code.

Conclusions

Improvement in the capability of the Charring Material Ablation Program code to predict ablation performance can be obtained when thermal properties and Arrhenius kinetic parameters are evaluated ideally under the high-heating-rate and environmental conditions suitable for their application.

In this study, heat capacities of a silica-phenolic composite (FM-5204) were evaluated from measurements at progressively increasing heating rates and extrapolations of these values to very high rates. High-heating-rate thermal diffusivities (~200°C/s) were evaluated from specimens subjected to short-period, high-temperature pulses. Thermal conductivities were calculated from these heat capacity and diffusivity data as well as densities. The measured values agreed favorably with effective values currently in use. Kinetic parameter values were evaluated from TGA data generated at 100°C/min. These data were used as input in the CMA code, which predicted temperatures that correlated well with flight data from a maneuvering re-entry vehicle. The correlations were better than those obtained from effective values derived from flight data.

This study shows that appropriate property and parameter values can be obtained at the laboratory level. They can reduce the necessity to rely on effective values from flight or simulated test data and can lead to appreciable savings in time, effort, and cost.

Acknowledgments

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