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ABLATION MODELS OF THERMAL PROTECTION MATERIALS

Two materials have shown promise as thermal insulation for future missile rocket motor cases. These materials, DC 93–104 and Aflas, ablate and/or pyrolyze at temperatures encountered during flight. Because these reactions use energy, they cool the insulation when they occur. To calculate the temperature of the insulation, thermal and chemical effects must be considered. This article describes thermal, pyrolysis, and ablation models created for the two materials and validates the models using experimental data.

INTRODUCTION

Faster speeds and longer flight times of future missiles require external thermal protection of rocket motor cases to prevent excessive propellent temperatures. Results from an investigation to determine the best material to meet missile constraints of weight, volume, handling, storage, thermal conductivity, ablation, processing, and cost indicate that DC 93-104 and Aflas are promising as external insulation materials for future rocket motor cases.[1] The DC 93-104 material is a silicone elastomeric ablative material manufactured by Dow Corning, and Aflas is a fluorine/carbon solid manufactured by Mosites Rubber Company. Both of these materials pyrolyze and/or ablate at temperatures and heat fluxes expected for rocket motor applications.

In addition to heat transfer by conduction, convection, and radiation, heat generation or absorption due to a chemical reaction of the material must be modeled. Figure 1 is a schematic of an ablating material. As the material is heated, the original virgin material pyrolyzes and yields a pyrolysis gas that percolates to the surface.[2] (Pyrolysis is a chemical reaction brought about by heat.) After pyrolysis, a porous residue, or char, is left. The surface of the char layer may then recede, a process known as ablation. This ablation model is one-dimensional. The different layers of material are split into nodes, and a finite-difference approach is used to calculate the temperature change through the depth of the system as modeled in Figure 1. Surface shear is not accounted for in this model.

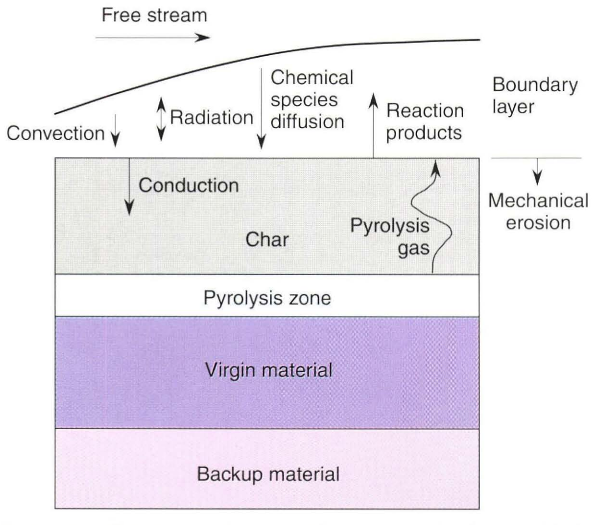


Figure 1. Schematic of heat and mass transfer for an ablating material.

CALCULATION OF SURFACE THERMOCHEMISTRY TABLES

The first requirement of an ablation model is the development of surface thermochemistry tables: temperature and enthalpy versus pressure, pyrolysis gas flow rate, and char rate for the surface gases. The surface thermochemistry tables consist partially of the temperature versus ablation rate. Figure 2 is a temperature versus ablation rate curve showing the three oxidation regimes of a surface. The normalized ablation rate β' is defined as $\dot{m}_c / h_m$, where $\dot{m}_c$ is the mass flow rate of char from the surface, and h_m is the mass transfer coefficient (similar to the convection heat transfer coefficient). The lower-temperature exponential region of the curve is the reac-

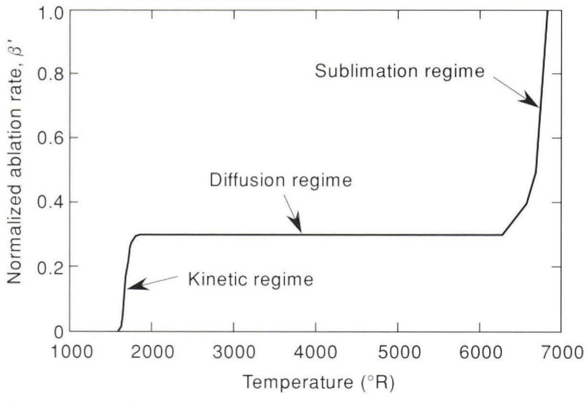


Figure 2. Normalized ablation rate (β') versus temperature calculated for Aflas.

tion-rate–controlled or kinetic regime, the flat region of the curve is the diffusion-controlled regime, and the higher-temperature exponential region of the curve is the sublimation regime. In the diffusion-controlled regime, the oxidation of the surface material is stoichiometric. In the kinetic regime, more oxygen reacts than in the stoichiometric part, whereas in the sublimation regime, less oxygen reacts.

The Aerotherm chemical equilibrium (ACE) software program[3] calculates the thermodynamic state (temperature and pressure) of the surface gases in equilibrium for the diffusion and sublimation regimes. The temperature and enthalpy are calculated as a function of pressure, the dimensionless pyrolysis gas flow rate β'_g ($\beta'_g = \dot{m}_g / h_m$, where $\dot{m}_g$ is the pyrolysis gas flow rate), and the dimensionless ablation rate β'. In the ACE program, the mass transfer coefficient is assumed to be equal to the convection heat transfer coefficient. Thus, the ACE program calculates the thermodynamic state as a function of pressure, pyrolysis gas flow rate, char rate, and heat transfer rate. Inputs to the ACE program are the composition of the gas flowing over the surface, the composition of the pyrolysis gas, the composition of the char, and the specific heat versus temperature for each species (e.g., CO, H_2O, and CO_2) expected to be created at the surface during the pyrolysis and ablation of the material. The ACE program uses the law of conservation of mass, the boundary-layer energy equation, and boundary-layer species conservation to calculate temperature and enthalpy as a function of pressure, pyrolysis gas flow rate, char rate, and heat transfer rate, given specific heat values and compositions of surface gases.

For the kinetic regime, the Naval Ordnance Test Station (NOTS) software program[4] calculates enthalpy under equilibrium conditions when given temperature, pressure, and the normalized ablation rate. The normalized ablation rate is determined from the assumed kinetics, chosen by considering the endpoint of the diffusion-controlled regime given by the ACE program, the material ablation temperature, and the fact that the curve should be exponential.

DC 93-104 ABLATION MODEL

For the ablation model of DC 93-104, the gas flowing over the surface was air composed of 78% nitrogen and 22% oxygen by mass. The pyrolysis gas composition was calculated from the elemental analysis of the virgin material, along with the measured weight loss in converting from the virgin material to the char. The pyrolysis gas was assumed to consist of only carbon and hydrogen.[5] Its elemental composition was found to be 32% hydrogen and 68% carbon by mass, and its molecular composition was evaluated by the ACE program. The char composition was calculated by subtracting the composition of the pyrolysis gas from that of the virgin material. The char composition was 0.22% hydrogen, 21.40% carbon, 35.71% oxygen, and 42.67% silicon by mass. Twenty species were selected to be created during the ablation of the material.[5]

Table 1. Specific heat and thermal conductivity values of virgin and char DC 93-104 at various temperatures.

Temperature (°R)	Specific heat [Btu/(lb·°R)]	Thermal conductivity [10^{-5} Btu/(ft·s·°R)]
	Virgin DC 93-104	
560	0.300	7.4
760	0.330	6.3
960	0.350	5.1
	Char DC 93-104	
660	0.275	14.8
960	0.275	15.7
1210	0.304	16.9
1460	0.333	17.8
1710	0.347	18.5
1960	0.360	19.1
2460	0.373	20.2
2960	0.383	20.3
3460	0.392	20.3

The char properties were measured on a char sample similar to that created on a rocket motor in flight. Table 1 shows specific heat and thermal conductivity values of virgin and char DC 93-104 at various temperatures. (Data are from Ref. 5 and from a letter with attachments from G. W. Driggers, Southern Research Institute, to L. B. Weckesser, JHU/APL, 20 Sep 1979.) The heats of formation of the virgin DC 93-104, char, and pyrolysis gas were necessary for the model and were found to be –5000, –4000, and –978 Btu/(lb·°R), respectively. The DC 93-104 material was modeled as having a three-component decomposition because different components of the material began to ablate at different temperatures. The resin filler of DC 93-104 consisted of two of the components, one that began to ablate at about 850°R, and another that began to ablate at about 1300°R. The third component was reinforcing material, and it began to ablate at about 1850°R. The resin components were assumed to be 50% of the volume of the material, and the reinforcing material was the other 50%. The weights of the two resin components were 4.56 and 25.38 lb per total cubic feet of resin, and the density of the reinforcing material was 152.27 lb/ft^3. Thus, the density of virgin DC 93-104 was calculated as follows: $0.5(4.56 + 25.38) + 0.5(152.27) = 91$ lb/ft^3. The density change with time as the material charred was assumed to be described by the empirical Arrhenius rate equation:

$$d\rho / dt = \rho_i \left[\left(\rho_r - \rho_i \right) / \rho_i \right]^{\psi} \beta \, e^{-E/RT} ,$$

where ρ_i is the initial density in pounds per cubic feet, ρ_r is the residual density in pounds per cubic feet, ψ is the decomposition reaction order, β is the pre-exponential factor, the quotient E/R (in degrees Rankine) is the activation energy divided by the universal gas constant for the surface gases, and T is the temperature in degrees Rankine. The initial density was that of the virgin material, 91 lb/ft^3. The residual density was that of the char, 72 lb/ft^3. The density change with time was measured for a high heating rate, which would be expected for the rocket motor in flight. The values of E/R, ψ, and β were then calculated[5] using the density data. The char was assumed to consist of only reinforcing material. The values of E/R, ψ, and β for the first resin material were 26,160°R, 3.95, and 8.815×10^9, respectively; for the second resin material, 16,770°R, 1.32, and 6.426×10^2, respectively; and for the reinforcing material, 52,640°R, 2.00, and 5.532×10^{11}, respectively.

DC 93-104 TEST DESCRIPTION

The thermal model discussed previously was validated by experiment. Figure 3 shows a schematic of the Atlantic Research Corporation test setup. A silica phenolic shroud surrounded the steel casing and insulation, creating an annulus through which the gases flowed. Hot gases were created using a liquid-fueled combustor. Excess oxygen was added to the combusted air/fuel mixture so that it would contain the same percentage of oxygen as air. Since there was only 1.5 in. between the DC 93-104 material and the shroud, the material could see only the shroud for nearly all of the 96-in. length of the annulus. The shroud was at about the same temperature as the DC 93-104, so essentially no radiation heat transfer occurred between the DC 93-104 and its environment. Thermocouples were located on the steel motor casing at five positions along the axis of the annulus; four thermocouples were located at each axial position—at 0°, 90°, 180°, and 270° from the top of the case—for a total of twenty thermocouples. Each quarter of the casing had a different insulation thickness. Four thermocouples measuring the temperature of the gas in the annulus were located at the inlet, and two were located at the outlet. The temperatures of the gases at various positions along the annulus were determined by interpolating the inlet and outlet temperatures linearly. The mass flow rate was also measured during the test. Measured mass flow rates ($\dot{m}$) and temperatures were used to calculate the temperature-based heat transfer coefficient (h) using the equations for heat transfer through an annulus.[6] Two locations on the test article were modeled for comparison: 3.0 in. aft of the inlet, and 18.5 in. aft of the inlet.

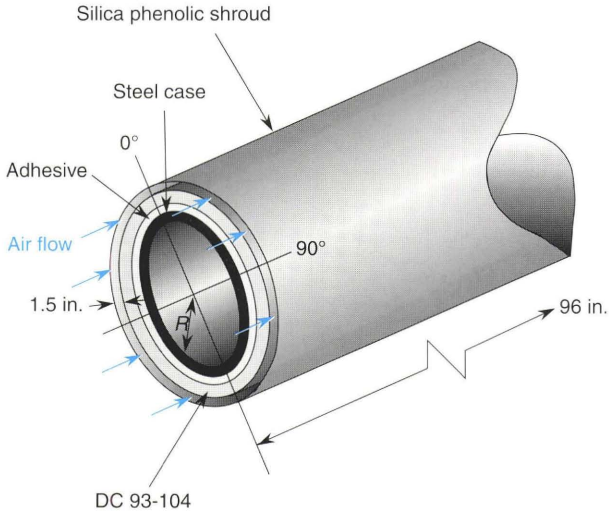


Figure 3. Schematic of Atlantic Research Corporation test article to measure ablation of DC 93-104. $R = 13.4$ in.

DC 93-104 TEST RESULTS

Figure 4 compares the measured and calculated temperature histories of the outer diameter of the steel case at three positions chosen for their different insulation thicknesses. Where the insulation was 0.115 in. thick, the model overpredicted the measured temperature of the steel case at the end of the test by about 40°R, or 20% of the measured temperature rise. Where the insulation was 0.075 in. thick, the recorded thermocouple measurements increased to about 2500°R (not shown) after 60 s, indicating that the thermocouples possibly lost contact with the case. At a test time of 60 s, the model underpredicted the temperature by about 25°R, or 15% of the measured temperature rise. Where the insulation was 0.048 in. thick, the model overpredicted the temperature by about 70°R, or 20% of the measured temperature rise, at a test time of 60 s. Because the thermocouple measurements rose quickly to a sharp peak and then rapidly dropped off for the insulation thickness of 0.048 in., the measured temperature was suspected to be inaccurate after a test time of about 65 s.

AFLAS ABLATION MODEL

Aflas is an ablative, rubberlike material that ablates at 1300°R without pyrolyzing or producing a layer of char. Aflas is composed of 50.4% carbon, 45.8% fluorine, 3.1% hydrogen, and 0.7% nitrogen by mass. These percentages were used in the ACE and NOTS programs to create surface thermochemistry tables.

The ACE program calculates temperature and enthalpy versus ablation rate for the diffusion-controlled (stoichiometric) and sublimation regimes for a given pressure, as discussed earlier. For Aflas, the char composition used in the ACE program was the same as the composition of the virgin material because no char forms; nothing was input

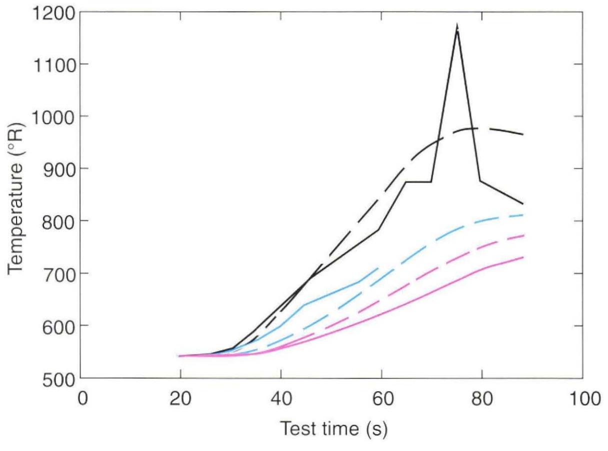


Figure 4. Measured (solid curves) and calculated (dashed curves) outer temperatures of the steel case for DC 93-104 ablation test. Black curves: insulation thickness of 0.048 in., test article located 18.5 in. aft of the inlet and 270° from the top of the case; blue curves: insulation thickness of 0.075 in., test article located 3.0 in. aft of the inlet and 180° from the top of the case; red curves: insulation thickness of 0.115 in., test article located 18.5 in. aft of the inlet and 0° from the top of the case.

for the pyrolysis gas composition because the material does not pyrolyze. After these compositions were entered into the ACE program, equations for specific heat versus temperature were input for each species expected to be created during the ablation of the material.[7]

For the kinetic regime, the NOTS program was used to calculate enthalpy when given temperature, pressure, and the normalized ablation rate under equilibrium assumptions. Figure 2 shows the normalized ablation rate versus temperature for Aflas. For the kinetic regime, the points were chosen by considering the endpoint of the diffusion-controlled regime given by the ACE program, the material ablation temperature of 1600°R, and the fact that the curve should be exponential. The chosen points were then input to NOTS to calculate enthalpy.

Next, the specific heat and thermal conductivity values of the Aflas at various tempertures were needed. These values are given in Table 2. Atlantic Research Corporation conducted a full characterization of Aflas. The density of Aflas is 99.5 lb/ft^3, as measured by a pycnometer at 530°R. The specific heat of Aflas was measured with a differential scanning calorimeter at a heating rate of 18°R/min in nitrogen from 582°R to 1077°R. The thermal conductivity (k) of Aflas was determined from the measured values for thermal diffusivity (κ), specific heat (C_p), and density (ρ) using the relationship $k = \kappa\rho C_p$.

Since Aflas ablates without producing a layer of char, the Arrhenius equation for the change in density of the material as it chars does not apply here.

AFLAS TEST RESULTS

The Aflas model was validated by an experiment similar to that described previously for DC 93-104. Figure 5 compares the measured and calculated temperature histories of the outer diameter of the steel case at three positions chosen for their different insulation thicknesses. Where the insulation was 0.15 in. thick, the model underpredicted the measured temperature of the steel case at a test time of 35 s by about 21°R, or 28% of the measured temperature rise. After 35 s, the recorded thermocouple measurements became quite large, about 1960°R (not shown), indicating thermocouple problems. Where the insulation was 0.09 in. thick, the model overpredicted the temperature by about 38°R, or 12% of the measured temperature rise, at the end of the test. Where the insulation was 0.06 in. thick, the model underpredicted the temperature by about 26°R, or 8% of the measured temperature rise, at the time of the last thermocouple reading at 35 s.

Table 2. Specific heat and thermal conductivity values of Aflas at various temperatures.

Temperature (°R)	Specific heat [Btu/(lb·°R)]	Thermal conductivity [10^{-5} Btu/(ft·s·°R)]
360	0.268	3.9
511	0.268	3.9
582	0.268	3.7
672	0.283	3.3
762	0.295	2.7
852	0.296	1.9
942	0.303	1.5
1032	0.298	1.3
1122	0.298	1.2
1212	0.298	1.1
1502	0.298	1.1

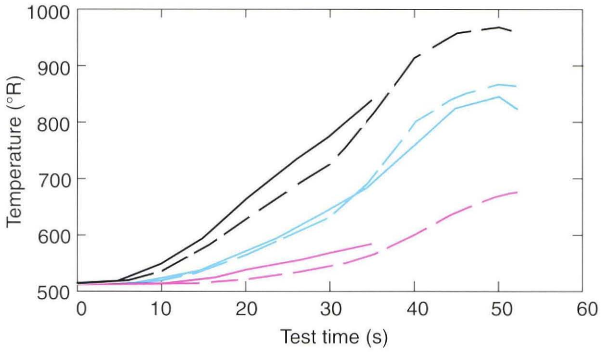


Figure 5. Measured (solid curves) and calculated (dashed curves) outer temperatures of the steel case for Aflas ablation test. All data are for a test article located 3.0 in. aft of the inlet. Black curves: insulation thickness of 0.06 in., test article located 90° from the top of the case; blue curves: insulation thickness of 0.09 in., test article located 0° from the top of the case; red curves: insulation thickness of 0.15 in., test article located 180° from the top of the case.

CONCLUSIONS

Suitable ablation models for DC 93-104 and Aflas were created using the charring materials ablation code. The models were verified by comparing predictions with test results at three locations on each of the two test articles, each with different insulation thicknesses. Predicted and measured temperatures varied by about ±20%. This degree of accuracy is adequate for helping to choose which ablating insulation material should be used for a rocket motor.

Much better ablation models would result if the materials were better characterized by experiment. The surface thermochemistry tables should be verified by thermal gravimetric analysis.

REFERENCES

[1] Newman, R. W., Resch, C. L., Williams, G. S., and Dykstra, J. E., "AFLAS: An External Insulation for Rocket Motors," in *Proc. 1990 JANNAF Propulsion Meeting*, Anaheim, Calif. (Oct 1990).

[2] Aerotherm Corporation, *Aerotherm Charring Material Thermal Response and Ablation (CMA) Program, Version 3*, Aerotherm Report UM-70-14, Mountain View, Calif. (1970).

[3] Aerotherm Corporation, *User's Manual, Aerotherm Chemical Equilibrium Computer Program (ACE 81)*, Aerotherm Report UM-81-11/ATD, Mountain View, Calif. (1981).

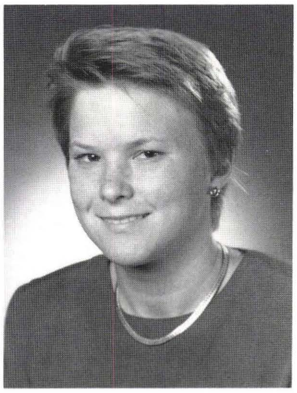
[4] Perini, L. L., *Thermochemical Equilibrium Computer Code for a Personal Computer*, JHU/APL AEO-86-28, Laurel, Md. (11 Mar 1986).

[5] Weckesser, L. B., and Perini, L. L., "Thermal Modeling of Combustor Insulation—DC 93-104," in *Proc. 1980 JANNAF Propulsion Meeting*, Monterey, Calif. (Mar 1980).

[6] Holman, J. P., *Heat Transfer*, McGraw-Hill, New York, pp. 228–229 (1981).

[7] Resch, C. L., *Thermal Analysis of Aflas as External Insulation for the SM-2 Blk IV Rocket Motor Casing*, JHU/APL AM-90-E024, Laurel, Md. (12 Feb 1990).

THE AUTHOR



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