Outline

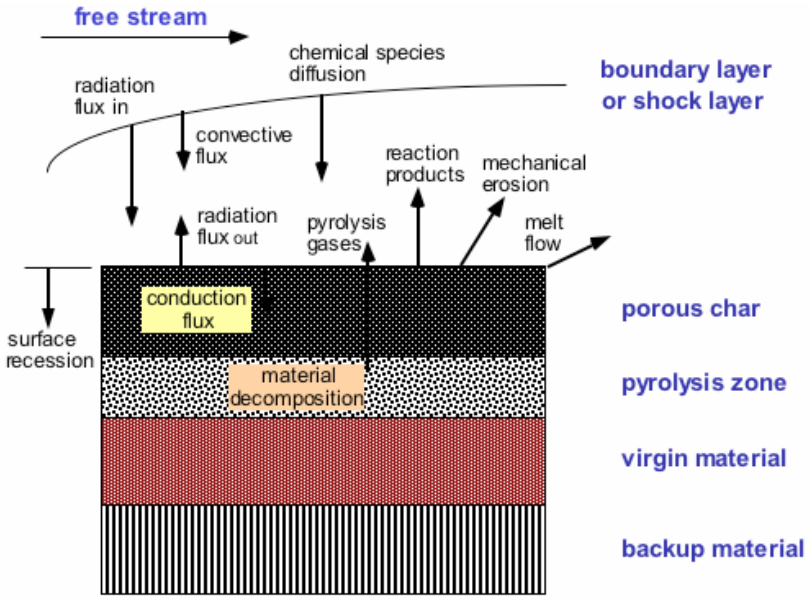
- Why this tutorial?
- Ablative TPS - early studies
- **Organic resin composites**
- Surface recession mechanisms/modeling
- High fidelity model development
- Testing approaches/requirements
- Future needs

Characteristics

- Organic resin (phenolic, silicone, epoxy, etc.)
  - Pyrolyzes when heated ⇒ gaseous products + carbon residue
  - Advantages:
    - In-depth (typically) endothermic chemical reactions
    - In-depth transpiration cooling
    - Carbonaceous surface char capable of high surface temperatures
- Reinforcement
  - Fibers (chopped, continuous)
  - Cloth (variety of weaves)
  - Honeycomb (organic, inorganic)
- Additives
  - Microballoons (organic, inorganic)

Density, ablation resistance, thermal & mechanical properties can be tailored to the application

The Problem


free stream
chemical species diffusion
boundary layer or shock layer
radiation flux in
convective flux
reaction products
mechanical erosion
radiation flux out
pyrolysis gases
melt flow
conduction flux
surface recession
material decomposition
porous char
pyrolysis zone
virgin material
backup material

Initial Modeling Approaches - 1

- Earliest model of in-depth thermal response for an organic resin composite was developed by Munson & Spindler[1] (Avco, 1962)

$$\rho c_p \frac{\partial T}{\partial \theta} = \frac{\partial}{\partial x}\left(k \frac{\partial T}{\partial x}\right) - c_{p_g} \dot{m} \frac{\partial T}{\partial x} + \dot{\rho} \Delta H \qquad (1)$$

where

$$\dot{m}(x,\theta) = \int_x^l \dot{\rho}(x,\theta) dx \qquad (2)$$

and

$$\dot{\rho}(x,\theta) = A\left(\rho(x,\theta) - \rho_c\right)^n \exp\left(-B/T(x,\theta)\right) \qquad (3)$$

Initial Modeling Approaches - 2

ρ	local, instantaneous value of material density
c_p	specific heat of the solid
T	local, instantaneous value of material temperature
x	depth from the original surface
θ	time
k	thermal conductivity of the solid
c_{p_g}	specific heat of the pyrolysis gases
$\dot{m}$	local mass flux of pyrolysis gases
$\dot{\rho}$	local, instantaneous rate of pyrolysis
ΔH	heat of pyrolysis
ρ_c	density of the residual char
A	pre-exponential coefficient
n	reaction order
B	Activation energy (E_a) / Gas constant (R)

Initial Modeling Approaches - 3

Notes:

1. Thermal properties a function of temperature and density
2. Pyrolysis represented by one Arrhenius reaction
3. Heat of pyrolysis assumed to be a constant
4. Specific heat of pyrolysis gases a function of temperature

Surface Boundary Condition:

$$\phi\,\dot{q}_{hw} - \sigma\varepsilon T_w^4 = -k\left(\frac{\partial T}{\partial x}\right)_w + \rho\dot{s}\left(f_1\Delta H_{v_1} + f_2\Delta H_{v_2}\right) \qquad (4)$$

where ϕ is a transpiration correction on convective heating expressed as:

$$\phi = \exp\left(-f\left(1+\alpha f\right)\right) \qquad (5)$$

and

$$f = \left(\eta_s\rho_w\dot{s} + \eta_g\dot{m}\right)^{h_s}\!\Big/\dot{q}_{cw} \qquad (6)$$

Initial Modeling Approaches - 4

- Surface recession could be modeled by one of three options:
  - Constant temperature ablation
    - $T_A, \eta, \Delta H_v$ from empirical correlation of Q* data
  - Non-carbonaceous material ablation
    - $$\dot{s} = \beta_1 T_w + \beta_2 (T_w)^{\beta_3} \exp(-\beta_4 / T_w)$$
      where the coefficients are derived from empirical correlation of arc jet recession data
  - Carbonaceous material ablation
    - Set of equations considering carbon oxidation (reaction rate-limited and diffusion limited) and sublimation

More Advanced Modeling - 1

- A more rigorous, chemical modeling approach was introduced by Kratsch, Hearne & McChesney[2] (Lockheed, 1963)
  - Modeled the composite as a mixture of organic resin and reinforcement (organic or inorganic), i.e.,

$$\rho_s = \Gamma \rho_{resin}(T,\theta) + (1-\Gamma)\rho_{reinf}(T,\theta) \qquad (7)$$

where Γ is the resin volume fraction.

  - Goldstein[3] identified that pyrolysis of phenolic resin is well-represented as two reactions and, therefore, the pyrolysis rate of the composite can be written as:

$$\frac{d\rho_s}{d\theta} = \Gamma\left[\frac{d\rho_1}{d\theta} + \frac{d\rho_2}{d\theta}\right] + (1-\Gamma)\frac{d\rho_{reinf}}{d\theta} \qquad (8)$$

where

$$\frac{d\rho}{d\theta} = -k_f \rho_0 \left(\frac{\rho - \rho_r}{\rho_0}\right)^n \qquad (9)$$

and

$$k_f = k_0 \exp(-E/RT) \qquad (10)$$

More Advanced Modeling - 2

- The in-depth energy equation is similar to Eq. (1) but recognizes that some parameters involve complex chemical processes and should be expressed in more general terms, i.e.,

$$\frac{\partial(\rho_s H_s)}{\partial\theta} = \frac{\partial}{\partial y}\left[k\frac{\partial T}{\partial y} + \dot{m}_g H_g\right] + \frac{\partial\rho_s}{\partial\theta}\Delta H_d \qquad (11)$$

where

$$\dot{m}_g = \int_y^l \frac{d\rho_s}{d\theta} dy \qquad (12)$$

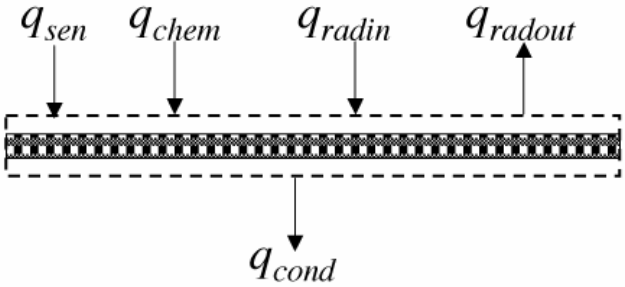
and y is measured from the moving (receding) surface.

More Advanced Modeling - 3

ρ_s	Local, instantaneous value of material density
ρ_0	Initial density of constituents in reaction *i*
ρ_r	Residual density of constituents in reaction *i*
ρ_{reinf}	Density of the (organic or inorganic) reinforcement
ρ_{resin}	Density of the organic resin
Γ	Resin volume fraction
H_g	Enthalpy of the pyrolysis gases
H_s	Enthalpy of the solid
ΔH_d	Heat of decomposition (pyrolysis)
$\dot{m}_g$	Local mass flux of pyrolysis gases
y	Depth from the moving surface

More Advanced Modeling - 4

- Kratsch, Hearne & McChesney adopted a transfer-coefficient approach (developed by Lees[4]) for approximating the heat transfer to an ablating surface from a chemically-reacting boundary layer



$$\underbrace{\rho_e u_e C_H \left(H_r - h_{e_w}\right)}_{q_{sen}} + \underbrace{\rho_e u_e C_M \left[\left(Z_{i_e}^* - Z_{i_w}^*\right) h_i^{T_w} - B' h_w\right] + \dot{m}_c h_c + \dot{m}_g h_g}_{q_{chem}}$$

$$+ \underbrace{\alpha_w q_{rad}}_{q_{radin}} - \underbrace{F \sigma \varepsilon T_w^4}_{q_{radout}} - q_{cond} = 0 \qquad (13)$$

More Advanced Modeling - 5

B'	dimensionless mass loss rate $\dot{m}/\rho_e u_e C_M = \left(\dot{m}_g + \dot{m}_c\right)/\rho_e u_e C_M$
B'_g	dimensionless pyrolysis gas gas rate $\dot{m}_g/\rho_e u_e C_M$
C_H	Stanton number corrected for transpiration
C_{H_0}	Stanton number not corrected for transpiration
C_M	Mass transfer Stanton number
F	View factor
H_r	Recovery enthalpy
h_c	Enthalpy of the surface char
h_g	Enthalpy of the pyrolysis gases at surface temperature and pressure
$\dot{m}_c$	Char mass flux injected into the boundary layer due to surface gasification
$\dot{m}_g$	Pyrolysis gas mass flux injected into the boundary layer
T_w	Surface temperature
Z_i^*	Diffusion driving force

More Advanced Modeling - 6

For high speed chemically-reacting boundary layers. Lees showed that the energy equation (for equal diffusion coefficients, unity Lewis and Prandtl numbers) can be written as:

$$\rho u \frac{\partial H}{\partial x} + \rho v \frac{\partial H}{\partial y} = \frac{\partial}{\partial y}\left(\mu \frac{\partial H}{\partial y} \right) \tag{14}$$

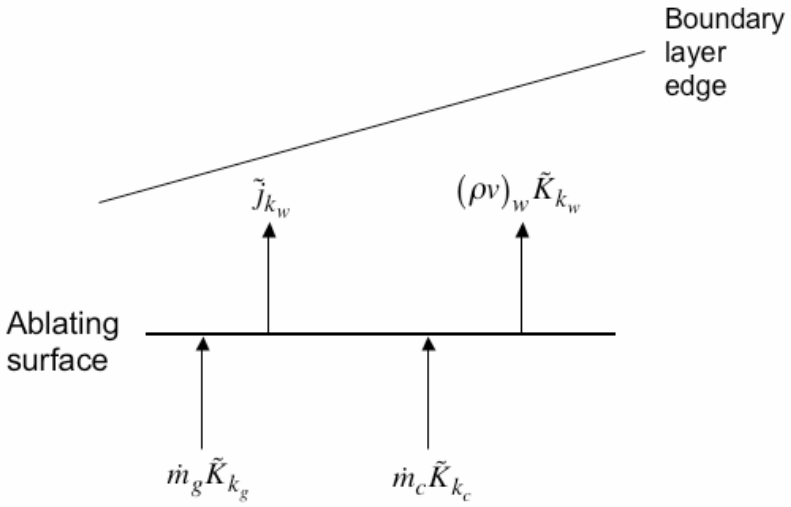
where H is the total enthalpy (sensible + chemical + kinetic), and solutions can be expressed in terms of a dimensionless heat transfer coefficient, C_H, where

$$\dot{q} = \rho_e u_e C_H \left(H_e - H_w \right) \tag{15}$$

The boundary layer species conservation equation (for equal diffusion coefficients) can be written as:

$$\rho u \frac{\partial \tilde{K}_k}{\partial x} + \rho v \frac{\partial \tilde{K}_k}{\partial y} = \frac{\partial}{\partial y}\left(\rho D \frac{\partial \tilde{K}_k}{\partial y} \right) \tag{16}$$

More Advanced Modeling - 7



Conservation of chemical elements (see above sketch) requires:

$$\tilde{j}_{k_w} + (\rho v)_w \tilde{K}_{k_w} = \dot{m}_g \tilde{K}_{k_g} + \dot{m}_c \tilde{K}_{k_c} \qquad (17)$$

And, summing over all elements k (in absence of condensed phase removal)

$$(\rho v)_w = \dot{m}_g + \dot{m}_c \qquad (18)$$

More Advanced Modeling - 8

By analogy to Eq. (14), the solution to Eq. (16) can be correlated in terms of a dimensionless mass transfer coefficient, C_M, where

$$-\tilde{j}_{k_w} = \rho_e u_e C_M \left(\tilde{K}_{k_e} - \tilde{K}_{k_w}\right) \tag{19}$$

$\tilde{j}_k$	Total diffusional mass flux of element k independent of molecular configuration
$\tilde{K}_k$	Total mass fraction of element k independent of molecular configuration

Substituting Eq. (19) into Eq. (17), yields

$$\rho_e u_e C_M \left(\tilde{K}_{k_w} - \tilde{K}_{k_e}\right) + (\rho v)_w \tilde{K}_{k_w} = \dot{m}_g \tilde{K}_{k_g} + \dot{m}_c \tilde{K}_{k_c} \tag{20}$$

Define dimensionless pyrolysis and char mass loss rates as

$$B'_g = \frac{\dot{m}_g}{\rho_e u_e C_M}, \quad B'_c = \frac{\dot{m}_c}{\rho_e u_e C_M} \quad \text{and } B' = \frac{(\rho v)_w}{\rho_e u_e C_M} \tag{21}$$

More Advanced Modeling - 9

Substituting Eq. (21) into Eq. (20) and solving for the total mass fraction of element k at the wall (equal diffusion coefficients, Pr=Le=1.0, and no condensed phase removal) yields:

$$\tilde{K}_{k_w} = \frac{B'_g \tilde{K}_{k_g} + B'_c \tilde{K}_{k_c} + \tilde{K}_{k_e}}{1 + B'} \tag{22}$$

Given the relative amounts of chemical elements specified by Eq. (22), the chemical and thermodynamic state of the gases adjacent to the ablating surface may be calculated from equilibrium relations.

For Le=Pr=1.0, equal diffusion coefficients, and no condensed phase removal, similarity arguments require that $C_M = C_H$

More Advanced Modeling - 9

- Kendall, Rindal and Bartlett[5] (Aerotherm, 1967) extended the work of Kratsch, Hearne & McChesney under contract to NASA JSC
  - One-dimensional thermal/ablation response of the charring ablator *fully coupled* to the non-similar, chemically reacting boundary layer (CABLE)
  - Bifurcation approximation for diffusion coefficients extended the formulation to cases of unequal diffusion coefficients and Pr≠Le≠1.0
  - Corrected energy equation (11) to account for energy associated with surface recession

$$\rho c_p \left.\frac{\partial T}{\partial \theta}\right)_x = \frac{1}{A}\frac{\partial}{\partial x}\left(kA\frac{\partial T}{\partial x}\right)_\theta + \left(h_g - \bar{h}\right)\left.\frac{\partial \rho}{\partial \theta}\right)_y \left.\frac{\dot{m}_g}{A}\frac{\partial h_g}{\partial x}\right)_\theta + \dot{s}\rho c_p \left.\frac{\partial T}{\partial x}\right)_\theta \qquad (23)$$

- Under USAF sponsorship, separated CABLE into three standalone codes that became industry standards
  - BLIMP: Non-similar chemically-reacting boundary layer code
  - CMA: one-dimensional charring ablation code
  - ACE: chemical equilibrium code (treated open systems, i.e., produces thermochemical equilibrium solutions of B' for any chemical system (with limited capability to treat reaction-rate limited chemistry)

More Advanced Modeling - 10

- NASA Ames extended/improved the Aerotherm ablation codes
  - Chen[6] rewrote CMA to be fully implicit in the subsurface solution (FIAT)
    - Improved stability
  - Milos[7] extended ACE to consider multiple surface species in developing surface thermochemical solutions (MAT)
    - Eliminated constraint in ACE for modeling many composites

Other Important Studies/Models

- Char coking
  - Post-flight studies of Apollo heatshield (unmanned flight tests) demonstrated density reversal in char requiring significant deviation from classical charring ablator models
  - Moyer (Aerotherm, 1970) developed modification to CMA that successfully modeled this phenomenon (CMAC)
  - Observed in other materials where thick chars are developed
- Char spallation
  - Several studies over 25+ years that attempted simplified models for a complex phenomenon
  - Most valuable work done under the Solid Propulsion Integrity Program (SPIP) sponsored by NASA MSFC in early 90s
    - Calculated internal gas pressure in char; required measurements of char porosity and permeability
    - Required solution of the (transient) pyrolysis gas momentum equation

Other Important Studies/Models (concluded)

- Pyrolysis gas state and composition
  - Early studies at Louisiana State University[8,9] (1970) looked at the flow of pyrolysis gases within the char to determine:
    - Changes in chemical composition through a char with an imposed (known) temperature gradient
    - Regions (temperature) where the gas composition could be modeled as frozen, equilibrium, or non-equilibrium mixture
  - Friedman (USAF, WPAFB) assembled TGA/Mass spec apparatus (1970s) and studied gaseous products of pyrolysis for several resin systems
  - Unaware of anyone who has modeled pyrolysis gas chemistry in an ablative composite coupled to material thermal/ablation response

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