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7. APPENDIX

We define a new dimensionless, similarity coordinate η as:

$$\eta = y(|u_w - u_\infty|)Re/x)^{0.5}, \quad (21)$$

and a transformed stream function $F(\eta)$ given by:

$$(u_w - u)/(u_w - u_\infty) = F'(\eta). \quad (22)$$

This gives the stream function:

$$\psi(x, y) = \pm(x|u_w - u_\infty|/Re)^{0.5}F(\eta) + u_w y. \quad (23)$$

The upper (positive) sign in the previous as well as the following equations refers to the case $u_\infty > u_w$ and the lower (negative) sign for $u_w > u_\infty$.

If $u_\infty > u_w$, then: $\bar{u}_r = \bar{u}_\infty$, $u_\infty = 1$, $0 < u_w < 1$.

If $u_w > u_\infty$, then: $\bar{u}_r = \bar{u}_w$, $u_w = 1$, $0 < u_\infty < 1$.

It is to be noted that equations (21)–(23) reduce to the similarity transformation of Blasius [1] when $u_w = 0$. The boundary-layer equations may be reduced to:

$$\eta(u_w/|u_\infty - u_w|)F'' \pm FF'' + 2F''' = 0, \quad (24a,b)$$

with the boundary conditions:

$$F'(0) = 0, \quad F'(\eta_\delta) = 1, \quad F(0) = 0. \quad (25)$$

Thus the boundary-layer problem has been reduced to two different ordinary differential equations 24(a,b) to be solved with the boundary conditions (25) as those of Blasius.

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A Stefan problem for exothermic non-catalytic reactions

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NOMENCLATURE

C	concentration
C_p	heat capacity
E	activation energy
H	enthalpy
k	rate constant
L	latent heat
(ΔQ)	heat of reaction
R	gas constant
R_S	rate of reaction
T	temperature
T_*	reference temperature
t	time
z	distance.

Greek symbols

ε	porosity
λ	thermal conductivity
ρ	density.

Subscripts

A, S	solids.

1. INTRODUCTION

HEAT conduction problems involving chemical reaction and phase change are encountered in many areas of interest [1]. Solid–solid exothermic reactions accompanied by melting phenomena are important in pyrotechnics and synthesis of refractory materials. These problems are usually solved by numerical methods [2]. The present communication aims at solving a phase change problem associated with exothermic condensed-phase reacting systems in which the reaction temperature can be sufficiently higher than the melting point of the solid reactant. Thus, there exists a sharply defined phase interface whose rate of movement depends on the rate of heat release, rate of heat conduction and the latent heat of phase change. The problem closely resembles the classical Stefan problem, the difference being the added complication of a non-linear source term.

The enthalpy method is used to solve the system of equations. It has the advantage of not requiring the explicit tracking of the phase change interface. Also, there is no need to consider the solid and liquid regions separately [1, 2].

2. THE PHYSICAL PROBLEM

A heterogeneous reaction occurring between a solid S and solid A is considered:

$$A(s) + S(s) \rightarrow P(s). \quad (1)$$

The reaction rate may be represented by the following equation

$$-R_S = kC_S. \quad (2)$$

The temperature dependence of the reaction rate constant is of Arrhenius type.

The heterogeneous system consisting of solid particles may be treated as though it were homogeneous and a hypothetical continuum is considered.

All system physical properties are constant.

The problems associated with mass diffusion of the solid phase and the phase equilibrium are not considered.

With these assumptions the governing mass balance and

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energy balance can be expressed as

$$[C_{pA}\rho_{A0}\varepsilon + C_{pS}\rho_{S0}(1-\varepsilon)]\frac{\partial T}{\partial t} = \lambda\frac{\partial^2 T}{\partial z^2} + k(-\Delta Q)C_S \quad (3)$$

$$(1-\varepsilon)\frac{\partial C_S}{\partial t} = -kC_S. \quad (4)$$

The boundary conditions are

$$t = 0, \quad z > 0, \quad T = T_i, \quad C_S = C_{Si} \quad (5)$$

$$t > 0, \quad z = 0, \quad T = T_0; \quad z \to \infty, \quad T = T_i. \quad (6)$$

Denoting

$$C_{pA}\rho_{A0}\varepsilon + (1-\varepsilon)C_{pS}\rho_{S0} = \overline{\rho C_p}, \quad k = k' \exp(-E/RT)$$

$$t^* = \frac{\overline{\rho C_p} RT_*^2 \exp(E/RT_*)}{Ek'(-\Delta Q)C_{Si}}, \quad \tau = t/t^*, \quad \beta = \frac{RT_*}{E}$$

$$u = z\sqrt{\overline{\rho C_p}/\lambda t^*}, \quad \gamma_S = \frac{(\overline{\rho C_p})RT_*^2}{C_{Si}E(-\Delta Q)}$$

$$\theta = \frac{E}{RT_*^2}(T - T_*), \quad \eta_S = \frac{C_S}{C_{Si}}$$

$$\bar{H} = \frac{H}{(\overline{\rho C_p})}\frac{E}{RT_*^2}, \quad \bar{L} = \frac{(1-\varepsilon)\rho_S L}{(\overline{\rho C_p})}\frac{E}{RT_*^2}.$$

We can render the equations (3)–(6) dimensionless:

$$\frac{\partial \bar{H}}{\partial \tau} = \frac{\partial^2 \theta}{\partial u^2} + \eta_S \exp[\theta/(1+\beta\theta)] \quad (7)$$

$$(1-\varepsilon)\frac{\partial \eta_S}{\partial \tau} = -\gamma_S \eta_S \exp[\theta/(1+\beta\theta)]. \quad (8)$$

The corresponding initial and boundary conditions are

$$\tau = 0, \quad u > 0: \quad \theta = \theta_i, \quad \eta_S = \eta_{Si} \quad (9)$$

$$\tau > 0, \quad u = 0: \quad \theta = \theta_0; \quad u \to \infty, \quad \theta = \theta_i. \quad (10)$$

Considering temperature as a function of enthalpy:

$$\theta = F[\bar{H}] \quad (11)$$

with

$$F[\bar{H}] = \bar{H}, \quad \bar{H} < \theta_m$$
$$F[\bar{H}] = \theta_m, \quad \theta_m < \bar{H} < \theta_m + \bar{L} \quad (12)$$
$$F[\bar{H}] = \bar{H} - \bar{L}, \quad \bar{H} > \theta_m + \bar{L}$$

where θ_m is the dimensionless melting temperature and $\bar{L}$ is the dimensionless latent heat.

The governing equations can now be iteratively solved adopting the procedure of Voller and Cross [3]. Due to the presence of steep gradients in space and time, we have chosen the high-order implicit finite-difference Størmer–Numerov scheme to solve the system of equations [8].

3. RESULTS AND DISCUSSION

The results of the numerical calculations are shown in Figs. 1–4. Figure 1 depicts the temperature profiles for a set of parameters without melting and Fig. 2, the corresponding profiles with melting for the same set of parameters. It can be seen from the figures that the movement of the reaction front is considerably retarded with melting. Also, the maximum reaction temperature at any instant is lower than the corresponding no melting case. This happens due to the coupling of phase change phenomenon with exothermic heat release and conduction processes.

The theoretical and experimental works of Merzhanov and co-workers [4–7] have demonstrated the existence and occurrence of oscillating fronts in exothermic non-catalytic reaction systems. Figure 3 represents one such oscillating front which is periodic in nature. Figure 4 shows the corresponding profiles with melting. It is of interest to note that with melting,

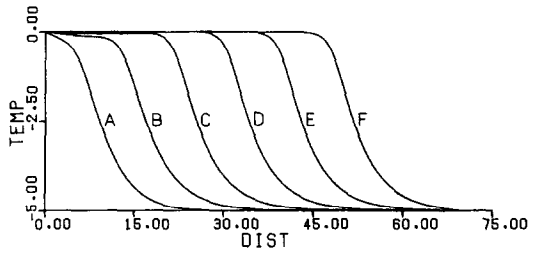

FIG. 1. Space–time distribution of temperature without melting ($\beta = 0.1$, $\gamma_S = 0.2$, $\theta_0 = 0.0$, $\theta_i = -5.0$; τ: A—40.5, B—81.0, C—121.5, D—162, E—202, F—242).

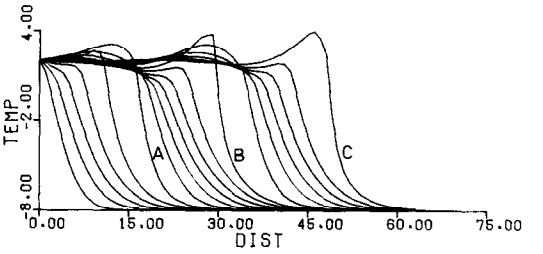

FIG. 3. Space–time distribution of temperature without melting ($\beta = 0.03$, $\gamma_S = 0.1$, $\theta_0 = 2.0$, $\theta_i = -8.0$; τ: A—60.5, B—119.5, C—180.5).

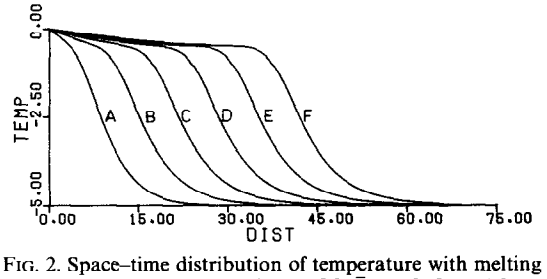

FIG. 2. Space–time distribution of temperature with melting ($\beta = 0.1$, $\gamma_s = 0.2$, $\theta_0 = 0.0$, $\theta_i = -5.0$, $\bar{L} = 1.0$, $\theta_m = 1.0$; τ: A—40.5, B—81.0, C—121.5, D—162, E—202, F—242).

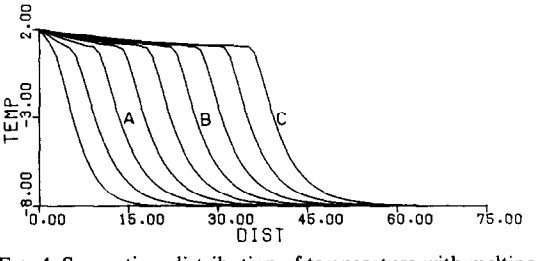

FIG. 4. Space–time distribution of temperature with melting ($\beta = 0.03$, $\gamma_s = 0.1$, $\theta_0 = 2.0$, $\theta_i = -8.0$, $\bar{L} = 1.0$, $\theta_m = 1.0$; τ: A—60.5, B—119.5, C—180.5).

the oscillations have ceased and constant pattern profiles have emerged. This is due to the fact that phase change acts as a heat sink and absorbs a portion of heat generated in the form of latent heat.

4. CONCLUSIONS

The above results clearly indicate that for a solid component having a low melting point, the coupling of phase change phenomenon with reaction can alter both the qualitative and quantitative nature of the system. In the case of constant pattern profiles the velocity of the reaction front is considerably reduced with melting. More significantly, oscillations of the reaction fronts can be totally extinguished with the change of phase. Work in systems comprising more than one dimension is in progress.

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