

CHAPTER 6

KINETICS OF TRANSFORMATION

Horie and Duvall²⁰ treated wave propagation in a phase-transforming material by assuming that:

1. Phases do not separate mechanically; i.e., particle velocity is common to both phases.
2. Pressure and temperature are common to both phases.
3. Interfacial energy is a small fraction of the total energy.
4. Mass transfer is irreversible and df/dt is a known function of the state variables.

These assumptions can be incorporated in the flow equations to provide a theoretical basis for calculating evolution of a shock wave in the transforming material, including the effects of transformation kinetics. Their principal result can be expressed in the form:

$$\frac{d\bar{P}}{dt} = a_{11} \frac{d\rho}{dt} + a_{12} \frac{df}{dt}, \quad (6.1)$$

$$\frac{dT}{dt} = a_{21} \frac{d\rho}{dt} + a_{22} \frac{df}{dt}, \quad (6.2)$$

$$\frac{df}{dt} = \Psi(G_{21}, f), \quad (6.3)$$

where a_{11} is frozen sound speed at mass fraction f ; the other a_{ij} are functions of V, T, P, f . They assumed for calculational purposes a simple relaxation function for $\Psi(G_{21}, f)$:

$$\psi = (f^{eq} - f) / \tau_1, \quad (6.4)$$

where τ_1 is a relaxation time.

Andrews^{27,29} modified ψ to a form more obviously related to the Gibbs function:

$$\frac{df}{dt} = \psi = \frac{-JG_{21}}{|A|\tau_2}, \quad 0 \leq f^{eq} \leq 1, \quad (6.5)$$

where J is the Jacobian, $J = \partial(V,E)/\partial(P,T)_f = -C_{Pf}VK_{Sf}$, and $|A|$ is the matrix of coefficients of differential equations describing the mixed phase region. (See Appendix D.)

Relaxation time, τ , is not uniquely defined and must be associated with a specific model for f^{eq} . Horie and Duvall²⁰ assumed f^{eq} to be defined by states on the equilibrium PVT surface in the mixed phase region at the same volume and temperature as the considered state. Figure 6.1 shows a cross section of the PVT surface at constant T and two possible transient states of the transforming mixture, A and B. State A projects to a volume V_A on the isotherm, giving

$$-f^{eq} = \frac{V_1^T - V_A}{V_2^T - V_1} \quad (6.6)$$

which is a function of pressure and temperature. State B is a more completely transformed state at the same temperature. For this case $V_B < V_2^T$ and $f^{eq} = 1$.

Andrews assumed f^{eq} to be defined by states on the equilibrium PVE surface for the same volume and energy as the