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Alloy Solidification with Convection in the Melt

Abstract

Most models of alloy solidification are severely limited by the assumption of constant density, thus excluding all convective effects. We present a thermodynamically consistent model for binary alloy solidification that incorporates energy, species and momentum conservation, constitutional supercooling, as well as temperature, concentration, and pressure dependence of thermophysical parameters. The crucial aspect is the development of an Equation of State capturing the thermochemistry of the phases. A numerical algorithm will also be outlined.

1 Introduction

We outline the main features of a macroscopic model for solidification of a binary alloy with convective and diffusive heat and mass transfer.

Given a binary melt $A_{1-x}B_x$ and initial and boundary conditions, the goal is to describe macroscopically the evolution of the phases as the melt undergoes solidification, by modeling the heat and mass transfer in the melt and solid.

The basic physical assumptions underlying the model are:

- rather slow cooling (not quenched), so that *local* thermodynamic equilibrium prevails (the lever rule applies to the phase diagram of the A-B binary);
- thermophysical properties may depend on temperature, composition, and pressure;
- negligible nucleation difficulties (freezing starts at the liquidus);
- negligible surface tension effects.

The mathematical model of the solidification process is an extension of Alexiades [1], [2] to include convective effects, further generalizing the well-known “enthalpy formulation” ([3]).

The main features of the model include:

- coupled heat and mass transfer (conduction, diffusion and convection), with possible cross effects (Soret, Dufour);
- solidification with constitutional supercooling;
- thermochemistry of the phases incorporated via an actual Equation of State;
- macroscopic description in terms of local variables: C = mass fraction of component B, u = internal energy, T = temperature, P = pressure, \vec{v} = velocity, Λ = liquid fraction;
- conservation laws valid everywhere in weak (integral) sense; phases are dis-

tinguished only by values of the liquid fraction ($\Lambda = 1$ in melt, $\Lambda = 0$ in solid, $0 \leq \Lambda \leq 1$ in two-phase, constitutionally supercooled, regions);

- front “capturing” (not tracking).

2 Conservation Laws

Let C_i = mass fraction of component $i = A, B$, $\rho_i = \rho C_i$ = partial density of i , $\rho = \rho_A + \rho_B$ = total density, u = internal energy (per gram), \vec{v} = velocity, P = pressure, \vec{J}_i = mass flux of species i , \vec{Q} = energy flux, τ = stress tensor of fluid.

The conservation laws for species, energy, and momentum may be expressed as follows, understood in a weak (distributional) sense, throughout the material:

$$\partial_t(\rho_A) + \nabla \cdot (\rho_A \vec{v} + \vec{J}_A) = 0, \quad \partial_t(\rho_B) + \nabla \cdot (\rho_B \vec{v} + \vec{J}_B) = 0, \quad (1)$$

$$\partial_t(\rho u) + \nabla \cdot (\rho u \vec{v} + \vec{Q}) = -P \nabla \cdot \vec{v}, \quad (2)$$

$$\partial_t(\rho \vec{v}) + \nabla \cdot (\rho \vec{v} \vec{v} - \tau) = -\nabla P + \rho \vec{g}, \quad (3)$$

$$\partial_t(\rho) + \nabla \cdot (\rho \vec{v}) = 0. \quad (4)$$

The fluxes are specified by the constitutive relations:

Fick’s Law, including pressure-diffusion and thermal-diffusion (Soret) effects:

$$\vec{J}_i = -\rho (D \nabla C_i + \delta_i^P \nabla P + \delta_i^T \nabla T), \quad i = A, B, \quad \text{with } \tilde{J}_A + \tilde{J}_B = 0, \quad (5)$$

where D = interdiffusion coefficient, and δ^P , δ^T are the pressure-diffusion and Soret coefficients, T = temperature.

Fourier’s Law for conduction, with interdiffusion, and Dufour effect:

$$\vec{Q} = -k \nabla T + \bar{h}_A \vec{J}_A + \bar{h}_B \vec{J}_B + Q^D, \quad (6)$$

with k = thermal conductivity (tensor), $\bar{h}_i :=$ partial (specific) enthalpy of i , and Q^D = Dufour energy flux (diffusion-thermo effect).

Note that the Soret and Dufour cross effects are usually negligible, but the other flux terms are principal couplings and cannot be neglected a priori.

Finally, an Equation of State (see below), relating the energy to the fields C_i , T , P , is needed to close the system of equations.

The thermophysical parameters depend on the local state, characterized by the triplet (C_i, T, P) , and this dependence is generally different in different phases, with possible jump discontinuities across interfaces. Thus the system is highly nonlinear.

In addition, the system is undergoing a phase transition, as dictated by the phase diagram of the A-B binary, the simplest cases of which, and under fixed pressure, are shown in Figure 1. The liquidus and solidus curves seen in the Figure are constant-pressure level curves of surfaces in 3-dimensional (C, T, P) space. The phase diagram describes the phase of each (C, T, P) state at thermodynamic equilibrium, and the possible coexistence of phases. States lying between the solidus and liquidus are "constitutionally supercooled", thermodynamically metastable, and are actually mixtures of solid and liquid, referred to as "mushy". The phase diagram encapsulates the thermochemistry of the binary system, and both are encoded into the Equation of State, of the form:

$$h = \begin{cases} h^L & \text{in liquid} \\ h^M & \text{in mushy} \\ h^S & \text{in solid.} \end{cases} \quad (7)$$

presented in the next section. Here h is the enthalpy, from which the internal energy can be found via

$$u = h - P/\rho. \quad (8)$$

Remark on Fickian diffusion:

There are, of course, many details glossed over in the brief description above. In particular, one must be careful with the definition of the Fickian diffusion term " $-D \nabla C$ " in 2-phase (mushy) regions.

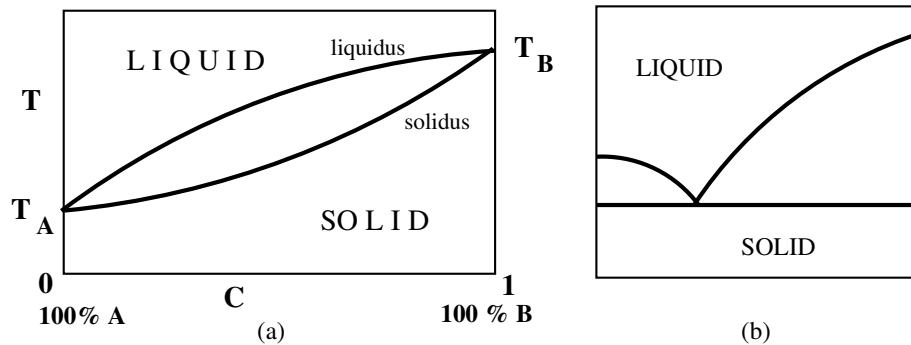


Figure 1

Simple phase diagrams: (a) A and B soluble in all proportions; (b) eutectic

To make it precise, define the fields $(C := C_B)$:

$$C^L = \begin{cases} C & \text{in liquid} \\ \text{Liquidus composition} & \text{in mushy} \\ 0 & \text{in solid.} \end{cases}$$

$$C^S = \begin{cases} 0 & \text{in liquid} \\ \text{Solidus composition} & \text{in mushy} \\ C & \text{in solid.} \end{cases}$$

and

$$\Lambda = (C - C^L)/(C^S - C^L) = \text{liquid fraction by weight.}$$

Then

$$\text{diffusion flux} = \Lambda(-D^L \nabla C^L) + [1 - \Lambda](-D^S \nabla C^S)$$

with D^L and D^S the interdiffusion coefficients in liquid and solid, respectively.

Thus, diffusion is driven by gradients of the Liquidus and Solidus concentrations and **not** by gradients of the mean concentration C , which is

$$C = \Lambda C^L + [1 - \Lambda] C^S.$$

In isothermal mushy regions, C^L and C^S will be uniform, so their gradients will be zero, and therefore there will be no Fickian diffusion in such regions, even if C is not uniform (due to different Λ 's).

3 Equation of State

The state is determined by (C, T, P) and the phase diagram. Let $T = T^L(C, P)$, $T = T^S(C, P)$ be the liquidus and solidus temperatures at composition C , pressure P , and let $C = C^L(T, P)$, $C = C^S(T, P)$ be the liquidus and solidus compositions at temperature T , pressure P . Choose a *reference state* (C_0, T_0, P_0) , say solid at $(C = 0, T = T_A, P = P_{atm})$, and integrate along appropriate C , T , and P paths the basic Gibbs relation:

$$\begin{aligned} du(C, T, P) &= (u_C)dC + (u_T)dT + (u_P)dP \\ &= [\bar{u}_B - \bar{u}_A]dC + [c_p - \alpha_T P/\rho]dT - [\alpha_T T/\rho - \alpha_P P/\rho]dP, \end{aligned} \quad (9)$$

with \bar{u}_i the partial u 's, c_p the specific heat, α_T the thermal expansion coefficient, α_P the compressibility ($= 0$ here), of the appropriate phase. The enthalpy, $h = u + P/\rho$, in each phase can be written as follows:

Liquid: $T \geq T^L(C, P)$:

$$h^L(C, T, P) = H^L(C, P) + \int_{T^L(C, P)}^T c_p^L(C, \tau, P) d\tau \quad (10)$$

with $H^L(C, P)$ = enthalpy of liquidus at the point $(C, T^L(C, P^L), P)$ given by

$$\begin{aligned} H^L(C, P) &= h_0 + \Delta h_0^{fus} + \frac{P - P_0}{\rho_0} [1 - T_0 \alpha_T^L] \\ &+ \int_{C_0}^C \bar{h}^L(\xi, T^L(C, P), P) d\xi \\ &+ \int_{T_0}^{T^L(C, P)} c_p^L(C_0, \tau, P) d\tau \end{aligned} \quad (11)$$

h_0 being the enthalpy of formation and Δh_0^{fus} the heat of fusion at the reference state.

Solid: $T \leq T^S(C, P)$:

$$h^S(C, T, P) = H^S(C, P) - \int_T^{T^S(C, P)} c_p^S(C, \tau, P) d\tau \quad (12)$$

with $H^S(C, P)$ = enthalpy of solidus at the point $(C, T^S(C, P^S), P)$ given by

$$\begin{aligned} H^S(C, P) &= h_0 + \frac{P - P_0}{\rho_0} [1 - T_0 \alpha_T^S] \\ &+ \int_{C_0}^C \bar{h}^S(\xi, T^S(C, P), P) d\xi \\ &+ \int_{T_0}^{T^S(C, P)} c_p^S(C, \tau, P) d\tau \end{aligned} \quad (13)$$

Mushy: $T^S(C, P) \leq T \leq T^L(C, P)$:

$$h^M(C, T, P) = \Lambda h^L(C^L(T, P), T, P) + [1 - \Lambda] h^S(C^S(T, P), T, P) \quad (14)$$

with $\Lambda(C, T, P)$ the liquid fraction from the ‘‘lever rule’’:

$$\Lambda(C, T, P) = \frac{C - C^L(T, P)}{C^S(T, P) - C^L(T, P)}. \quad (15)$$

Relations (10),(12),(14) define the Equation of State (7), namely the enthalpy h as function of the triplet (C, T, P) . Thus, knowing (C, T, P) we can determine the phase and the enthalpy (hence also the energy u). However, the conservation laws update the quantities C , h , P , ρ , but *not* the temperature T , which has to be found from the Equation of State. The particular way we have expressed the EoS enables us to use the enthalpy as the phase indicator, and then determine the temperature. This can be accomplished as follows.

4 Enthaply as phase indicator

Given C, h, P , we compute the quantities $H^L(C, P)$ and $H^S(C, P)$ from (11) and (13), and we compare h with them.

If $h \geq H^L(C, P)$ then the phase is **liquid**: set $\Lambda(C, T, P) = 0$ and find T ($\geq T^L(C, P)$) by solving:

$$\int_{T^L(C, P)}^T c_p^L(C, \tau, P) d\tau = h - H^L(C, P) \geq 0;$$

If $h \leq H^S(C, P)$ then **solid**: set $\Lambda(C, T, P) = 1$ and find T ($\leq T^S(C, P)$) by solving:

$$- \int_T^{T^S(C, P)} c_p^S(C, \tau, P) d\tau = h - H^S(C, P) \leq 0;$$

If $H^S(C, P) \leq h \leq H^L(C, P)$ then **mushy**: set $\Lambda = \frac{h - H^S(C, P)}{H^L(C, P) - H^S(C, P)}$ and find T by solving:

$$\Lambda h^L(C^L(T, P), T, P) + [1 - \Lambda] h^S(C^S(T, P), T, P) = h.$$

5 Outline of updating scheme

An algorithm for updating the values of $C, T, P, \Lambda, \rho, \vec{v}, u, h$ from a time t to time $t + \Delta t$ would go as follows:

Step 1. The balance laws update the quantities $\rho_A, \rho_B, (\rho u), (\rho \vec{v}), P$ (for each control volume) to new time.

Step 2. From these we deduce:

$$\begin{aligned} \rho &= \rho_A + \rho_B, & C_A &= \frac{\rho_A}{\rho}, & C_B &= \frac{\rho_B}{\rho}, \\ u &= \frac{(\rho u)}{\rho}, & h &= u + P/\rho. \end{aligned}$$

Step 3. Determine the new phase of each control volume from the Equation of State and find T and (weight) liquid fraction Λ , as described in Section 4.

Step 4. The consistency of the updated values may be checked as follows: Find the volume fraction of liquid:

$$\beta = \frac{\Lambda/\rho^L}{\Lambda/\rho^L + [1 - \Lambda]/\rho^S}$$

and the “fluid” (non-void) fraction (of each control volume):

$$f = \frac{(\rho u)}{\beta \rho^L u^L(T, P, C^L) + [1 - \beta] \rho^S u^S(T, P, C^S)};$$

check the consistency of the value of density:

$$\rho^* := f [\beta \rho^L + (1 - \beta) \rho^S] + (1 - f) \rho^{gas} = \rho ?$$

This may be used as criterion for convergence of an iterative numerical scheme.

References

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