Cambridge University Press
0521650801 - Theory of Solidification
Stephen H. Davis
Excerpt
More information

1

Introduction

The processes of freezing and melting were present at the beginning of the Earth and continue to affect the natural and industrial worlds. These processes created the Earth's crust and affect the dynamics of magmas and ice floes, which in turn affect the circulation of the oceans and the patterns of climate and weather. A huge majority of commercial solid materials were "born" as liquids and frozen into useful configurations. The systems in which solidification is important range in scale from nanometers to kilometers and couple with a vast spectrum of other physics.

The solidification of a liquid or the melting of a solid involves a complex-interplay of many physical effects. The solid–liquid interface is an active free boundary from which latent heat is liberated during phase transformation. This heat is conducted away from the interface through the solid and liquid, resulting in the presence of thermal boundary layers near the interface. Across the interface, the density changes, say, from ρ^ℓ to ρ^{s}. Thus, if $\rho^{\mathrm{s}} > \rho^\ell$, so that the material shrinks upon solidification, a flow is induced toward the interface from "infinity."

If the liquid is not pure but contains solute, preferential rejection or incorporation of solute occurs at the interface. For example, if a single solute is present and its solubility is smaller in the (crystalline) solid than it is in the liquid, the solute will be rejected at the interface. This rejected material will be diffused away from the interface through the solid, the liquid, or both, resulting in the presence of concentration boundary layers near the interface. The thermal and concentration boundary layer structures determine, in large part, whether morphological instabilities of the interface exist and what the ultimate microstructure of the solid becomes. Many a solidification problem of interest couples the preceding purely diffusive effects with effects of thermodynamic disequilibrium, crystalline anisotropy, and convection in the melt.

On the coarsest level of understanding, freezing is of concern only as a heat or mass transfer process. Thus, one cools a glass of bourbon by inserting ice cubes that extract heat by melting. Likewise, one places salt on icy roads in Evanston to facilitate melting because salt water has a lower melting temperature than pure water.

On a finer level of understanding, freezing can create solids whose microstructures are determined by the process parameters and the intrinsic instabilities of the solid–liquid front. Figure 1.1 shows a longitudinal section of a Zn–Al alloy casting. Notice the dendritic structures that extend inward from the cold boundary and a core region in which no microstructure is visible. At later times, spontaneous nucleation in the core can cause “snowflakes” to grow in the core. The coarseness or fineness of the microstructure helps determine whether mechanical and thermal reprocessing can be accomplished without the appearance of cracks.

Under certain conditions of freezing, the moving solidification front can be susceptible to traveling-wave instabilities, giving structural patterns that can be made visible; see Figure 1.2.

When a eutectic alloy is frozen, the solid can take the form of a lamellar structure, alternate plates of two alloys spatially periodic perpendicular to the freezing direction. Under certain conditions this mode of growth is stable, giving rise to the more complex modes of growth, an example of which is shown in Figure 1.3.

Under conditions of rapid solidification, the microstructure can take on metastable states and patterns inconsistent with equilibrium thermodynamics. Figure 1.4 shows a banded structure in an Al–Cu alloy consisting of alternate layers of structured and unstructured material spatially periodic in the freezing direction. The structured layers may contain cells, dendrites, or eutectic material, whereas the alternate layers seem to have no visible microstructure.

If the solidification process occurs in a gravitational field, the thermal and solutal gradients may induce buoyancy-driven convection, which is known to affect the interfacial patterns greatly and, hence, the solidification microstructures present in the solidified material. The coupling of fluid flow in the melt with phase transformation at the interface can result in changes of microstructure scale and pattern due to alterations of frontal instabilities and the creation of new ones.

When an alloy is frozen at moderate speeds and dendritic arrays are formed, interesting dynamics occur in the dendrite–liquid mixture – the mushy zone. Here, solutal convection can be localized, creating channels parallel to the freezing direction, as shown in Figure 1.5. The channels frozen into the solid are called freckles, and their presence can significantly weaken the structure of the solid.

Cambridge University Press
0521650801 - Theory of Solidification
Stephen H. Davis
Excerpt
More information

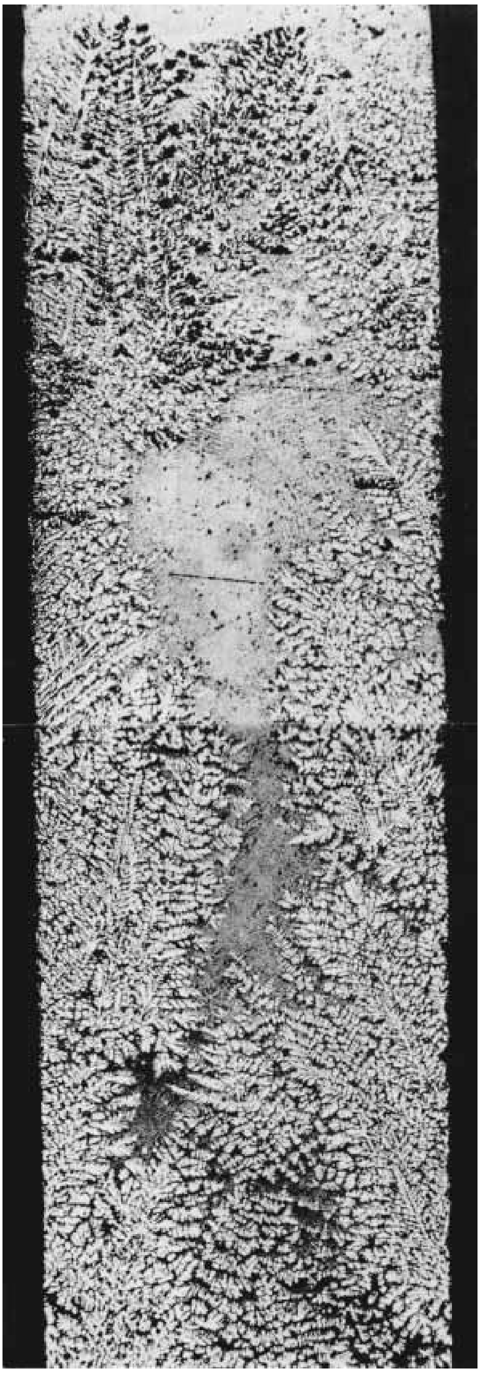

Figure 1.1. Longitudinal section of the quenched interface of the Zn–27%Al alloy. From Ayik et al. (1986).

Cambridge University Press
0521650801 - Theory of Solidification
Stephen H. Davis
Excerpt
More information

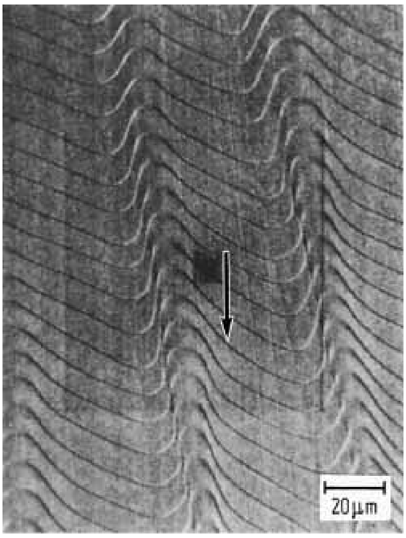

Figure 1.2. Etched longitudinal section of a Ga-doped Ge single crystal showing traveling waves on the interface. The *arrow* indicates the growth direction. From Singh, Witt, and Gatos (1974).

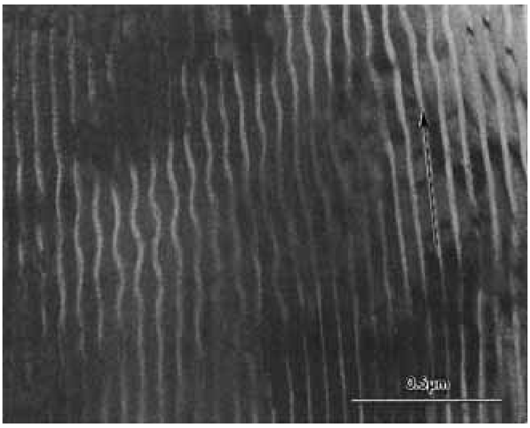

Figure 1.3. TEM micrographs of laser rapidly solidified Al–40 wt % Cu alloy oscillatory instabilities. $V = 0.03$ m/s. From Gill and Kurz (1993).

Given that the solid has crystalline structure, intrinsic symmetries in the material properties help define the continuum material. The surface energy and the kinetic coefficient on the interface as well as the bulk transport properties inherit the directional properties of the crystal, and thus anisotropies are often significant in determining the cellular or dendritic patterns that emerge. If the anisotropy is strong enough, the front can exhibit facets and corners.

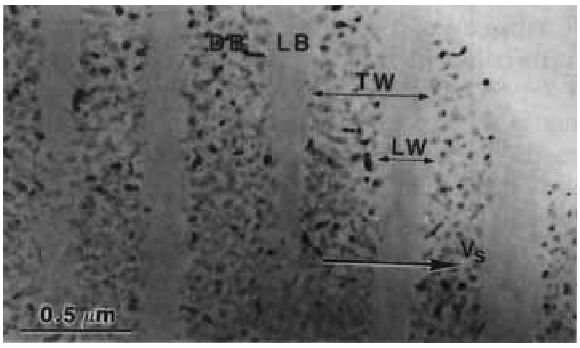

Figure 1.4. Enlarged view of the banded structure in Al–Cu 17 wt %. The dark bands have a dendritic structure, whereas the light bands are microsegregation free. DB = dark band, LB = light band, TW = total bandwidth, LW = light bandwidth, and V_s = growth rate. From Zimmermann et al. (1991).

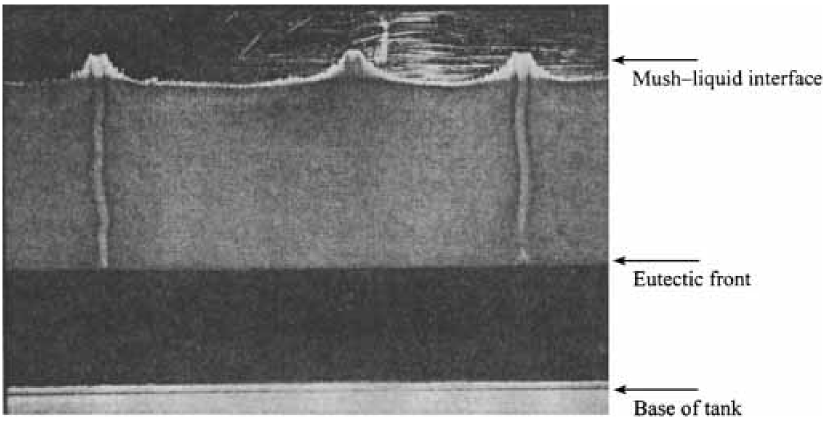

Figure 1.5. A photograph of mushy layer chimneys during an experiment with an ammonium chloride solution. In this system, pure ammonium chloride crystals are formed when the solution is cooled below its freezing temperature, leaving behind a diluted solution with a density lower than that of the bulk fluid. In the present case, the mushy layer is growing away from a fixed cold base that is at a temperature below the eutectic point, and thus both the solid–mush and mush–liquid interfaces are advancing at a decreasing rate. At the time the photograph was taken the distance between the base of the tank and the eutectic front was about 3 cm. Notice that the chimney walls and the mush–liquid interface are flat to a good first approximation. From Schulze and Worster (1998).

Finally, single crystals can be grown having, one would hope, uniform properties as long as the growth rate is very small. However, even in such cases the structure can be interrupted by defects or striations. In Figure 1.6, thermal fluctuations have created solute variations in the form of concentric rings, making the crystal inhomogeneous. If the crystal were rotated to remove azimuthal

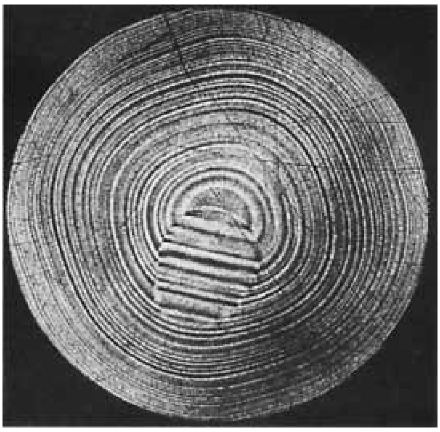

Figure 1.6. Transverse section of a $Ba_2NaNb_5O_{15}$ crystal whose rotational striations form concentric closed loops. The striations are caused by temperature fluctuations in the melt. From Hurle (1993).

thermal variations, rotational striations could occur having the form of spirals emanating from the center of rotation.

The challenge to the scientist is to understand the sources of such inhomogeneities, quantify the phenomena at work, and learn to control the processes so as to create desired microstructures in situ on demand. Significant progress has been made in these directions, though the end point is not at hand. Clearly, this is a huge field, and inevitably an author must make subjective choices of what material to include. The view taken here is that one should delve into a "core" of the field. A grasp of the physics is developed by using examples of increasing complexity intended to create a deep physical insight applicable to more complex problems.

References

Ayik, O., Ghoreshy, M., Sahoo, M., and Smith, R. W. (1986). Solidification and foundry studies of Zn/Al alloys, *J. Crystal Growth* **79**, 594–603.

Gill, S. C., and Kurz, W. (1993). Rapidly solidified Al–Cu alloys – I. Experimental determination of the microstructure selection map, *Acta Metall. Mater*. **41**, 3563–3573.

Hurle, D. T. J. (1993). *Crystal Pulling from the Melt*, Springer-Verlag, Berlin.

Schulze, T. P., and Worster, M. G. (1998). A numerical investigation of steady convection in mushylayers during directional solidification of binary alloys, *J. Fluid Mech*. **356**, 199–220.

Singh, R., Witt, A. F., and Gatos, H. C. (1974). Oscillatory interface instability during Czochralski growth of a heavily doped germanium, *J. Electrochem. Soc*. **121**, 380–385.

Zimmermann, M., Carrard, M., Gremaud, M., and Kurz, W. (1991). Characterization of a banded structure in rapidly solidified Al–Cu alloys, *Mater. Sci. Eng.* **A134**, 1279–1282.

2

Pure substances

2.1 Planar Interfaces

2.1.1 Mathematical Model

Consider a system in thermal equilibrium so that the temperature T is uniform. Part of the system is liquid and part is solid. For the two phases to coexist, the solid–liquid interfaces must be *planar*, and the temperature must be T_{m}, the *melting temperature*; T_{m} may depend on pressure and is here taken to be constant.

The amount of heat required to change a unit *mass* of solid into liquid at $T = T_{\mathrm{m}}$ is the *latent heat* L; if ρ^{s} is the density of the solid, then the latent heat per unit volume is $L_{\mathcal{V}}$, $L_{\mathcal{V}} = \rho^{\mathrm{s}} L$. The amount of heat required to raise, without change of phase, the temperature of a unit mass of solid or liquid by 1°C is the specific heat c_p.

Consider now a system in which temperature gradients are present so that there are heat fluxes. The bulk heat balance in either phase alone can be obtained by considering a material volume $\mathcal{V}(t)$, as shown in Figure 2.1, and is given by

$$\frac{d}{dt}\int_{\mathcal{V}(t)} \rho c_p T\, dV = -\int_{\partial\mathcal{V}(t)} \mathbf{q}\cdot\mathbf{n}\, dS, \tag{2.1}$$

where ρ is the density, $\mathbf{q}$ is the heat flux, and $\mathbf{n}$ is the unit outward–normal vector to $\mathcal{V}$ on its (closed) boundary $\partial\mathcal{V}$.

The transport theorem for any smooth field F passing through $\mathcal{V}$ states that

$$\frac{d}{dt}\int_{\mathcal{V}(t)} F\, dV = \int_{\mathcal{V}(t)} \left[\frac{\partial F}{\partial t} + \nabla\cdot(F\mathbf{v})\right] dV, \tag{2.2}$$

where $\mathbf{v}$ is the velocity field of the material (see, e.g., Serrin 1959).

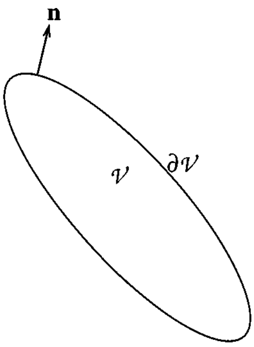

Figure 2.1. A control volume $\mathcal{V}$ entirely with a bulk phase; $\partial\mathcal{V}$ is its boundary and $\mathbf{n}$ is the unit outward normal.

If Gauss's theorem and identity (2.2) are used on relation (2.1), then

$$\int_{\mathcal{V}(t)} \left\{ \frac{\partial}{\partial t}(\rho c_p T) + \nabla \cdot (\rho c_p T \mathbf{v}) \right\} dV = - \int_{\mathcal{V}(t)} \nabla \cdot \mathbf{q} dV,$$

and since $\mathcal{V}$ is arbitrary and the integrands are supposed smooth, the point form of the bulk mass balance is obtained as

$$\frac{d}{dt}(\rho c_p T) + \rho c_p T \nabla \cdot \mathbf{v} = -\nabla \cdot \mathbf{q}, \tag{2.3}$$

where the material derivative is given by

$$\frac{d}{dt} = \frac{\partial}{\partial t} + \mathbf{v} \cdot \nabla. \tag{2.4}$$

To complete the specification of the heat balance, a constitutive law is required that relates $\mathbf{q}$ to the temperature field. It is assumed here that the Fourier law of heat conduction holds, that is

$$\mathbf{q} = -k_{\mathrm{T}} \nabla T, \tag{2.5}$$

where k_{T} is the thermal conductivity of the phase. Thus, the final form of the bulk heat balance is given by

$$\frac{d}{dt}(\rho c_p T) + \rho c_p T \nabla \cdot \mathbf{v} = \nabla \cdot k_{\mathrm{T}} \nabla T. \tag{2.6}$$

In the absence of bulk flow, $\mathbf{v} = \mathbf{0}$, and for ρ, c_p, k_{T} constant, Eq. (2.6) reduces to the standard heat-conduction equation

$$\frac{\partial T}{\partial t} = \kappa \nabla^2 T, \tag{2.7}$$

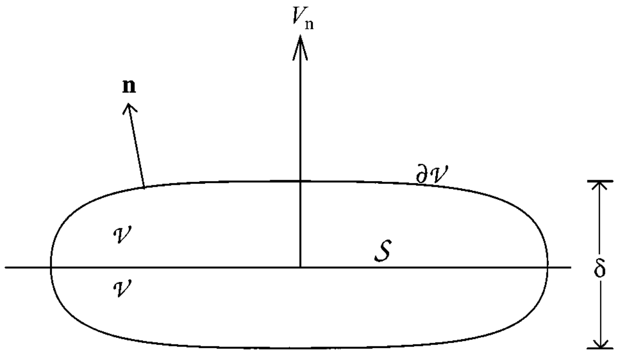

Figure 2.2. A control voume $\mathcal{V}$ spanning the interface $\mathcal{S}$ that moves at speed V_n normal to itself: $\partial\mathcal{V}$ is the boundary of $\mathcal{V}$ and $\mathbf{n}$ is the unit outward normal.

where

$$\kappa = k_T/\rho c_p$$

is the thermal diffusivity of the phase.

On a moving (planar) interface, there is a heat balance. Consider a (two-dimensional) volume of height δ spanning the interface, as shown in Figure 2.2. If V_n is the speed of the interface (normal to itself), then in a time δt and for $\delta \to 0$,

$$\rho^s L V_n \delta t = (\mathbf{q}_\ell - \mathbf{q}_s) \cdot \mathbf{n}\delta t$$

because the (smooth) heat accumulation vanishes as $\delta \to 0$. Thus, if Fourier heat conduction is applied, Eq. (2.5), the interfacial heat balance is

$$\rho^s L V_n = (k_T^s \nabla T^s - k_T^\ell \nabla T^\ell) \cdot \mathbf{n}. \tag{2.8}$$

One sees that the net heat entering the interface, the right-hand side, determines the speed V_n of the front.

In addition, the temperature is continuous across the interface and is known to be the equilibrium melting temperature T_m,

$$T^s = T^\ell = T_m. \tag{2.9}$$

2.1.2 One-Dimensional Freezing from a Cold Boundary

Consider a plane boundary at $z = 0$, which is adjacent to a liquid at initial temperature $T = T_m$, as shown in Figure 2.3. At $t = 0$, the boundary is impulsively

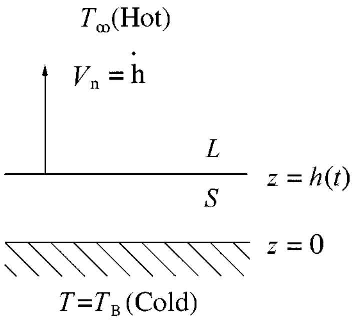

Figure 2.3. Planar solidification from a cold boundary at $z = 0$ with temperature T_B into a warmer melt at temperature T_∞. The interface between solid and liquid is at $z = h(t)$.

cooled to a temperature T_B, such that the undercooling ΔT is

$$\Delta T = T_m - T_B > 0, \tag{2.10}$$

creating a solid–liquid interface at $z = h(t)$ and it will be supposed that $\rho^s = \rho^\ell$.

Because for $t < 0$, $T = T_m$, the temperature in the liquid will not fall below T_m, hence, the temperature in the liquid is constant for all time,

$$T^\ell = T_m \qquad z > h(t). \tag{2.11a}$$

In the solid there is heat conduction

$$T_t^s = \kappa^s T_{zz}^s \qquad 0 < z < h(t). \tag{2.11b}$$

For $t > 0$

$$T^s = T_B \qquad z = 0 \tag{2.11c}$$

$$T^\ell = T^s = T_m \qquad z = h(t) \tag{2.11d}$$

$$\rho^s L\dot{a} = k_T^s T_z^s \qquad z = h(t). \tag{2.11e}$$

For $t = 0$,

$$T^s = T_m, \quad h = 0. \tag{2.11f}$$

Note that the heat flux in the liquid is zero because the temperature there is constant.

There are no natural time and space scales here, and therefore a similarity solution can be sought. Let the new independent variable be η,

$$\eta = \frac{z}{2\sqrt{\kappa^s t}}, \tag{2.12a}$$