

Chapter 1

Fundamental Aspects

1.1 General and Local Equilibrium in Alloy Systems

The original semisolid forming process, developed at MIT in 1972, involved stirring an alloy during solidification to produce a slurry of spheroidal primary particles in a liquid matrix, which was then injected directly into a die to produce a solid component. This was termed “rheocasting.” Subsequently, it was found more convenient to solidify the slurry completely during the continuous casting of an electromagnetically stirred strand, which was then cut into slugs for partial remelting back into semisolid billets on demand. These could be loaded into a diecasting machine in this state for injection into the die. This alternative process route is called “thixoforming,” and until recently, it was the preferred industrial process. For this reason, the microstructure developed during the reheating and melting for thixoforming will be considered first. Experimentally, it has been found that the most effective fraction solid f_s for thixoforming, lies between 0.5 and 0.6. Below this range, the semisolid slug becomes too soft to support its own weight and sags during remelting; above this range, it is too stiff to flow readily and fill the die. However, the slurry technologies used in rheocasting typically operate at lower fraction solids and rely on the ability to pour the semisolid alloy much like a liquid (see Chap. 4). It has been observed in practice that the fraction solid is in fact a critical factor for effective thixoforming, and therefore, both good temperature control and lack of sensitivity of f_s to small temperature variations of the alloy are essential to efficient manufacturing.

A determination of the change in f_s with temperature in a binary alloy system under strict equilibrium conditions may be obtained by referring to the phase diagram. For an alloy of overall composition C_o , conservation of solute requires that $C_o = C_l f_l + C_s f_s$, where the compositions are expressed in weight percentage and the fraction f as a weight fraction of liquid or solid. It reduces to $f_s = (C_l - C_o) / (C_l - C_s)$ (see Fig. 1.1), where C_s and C_l are the equilibrium compositions of solid and liquid, respectively, at temperature T . This is the familiar lever rule for obtaining the fraction solid; it allows one to calculate f_s where *general equilibrium conditions* prevail, that is, diffusion in the liquid and solid has removed all compositional gradients in the system. In particular that during solidification, the

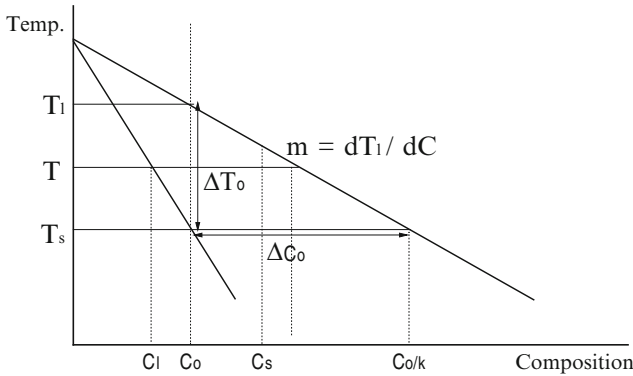


Fig. 1.1 Simple Binary Alloy Equilibrium Diagram

build-up of solute in the solid at the moving interface is continuously removed by back diffusion into the solid. However, a simple calculation of the time needed for diffusion to occur at the center of a $100\ \mu\text{m}$ diameter spherical particle, assuming a typical diffusion coefficient of $D = 10^{-13}\ \text{m}^2\ \text{s}^{-1}$, estimates that several hours are required. It is clear that under the fairly rapid cooling conditions employed in (Direct Chill) casting of commercial billets, equilibrium cannot prevail, nor during the soaking period prior to injection into the die.

The concept of *local equilibrium* is very often employed in transformation problems, as in solidification, where by the nature of things *general equilibrium* does not prevail. The assumption here is that the reaction kinetics at the interface (or interfaces) is very rapid (or there is negligible undercooling at the interface) compared with solute or heat transfer to or from the moving interface, and the latter therefore control the kinetics of transformation. Under these conditions, the interface compositions of both the liquid and solid may be obtained from equilibrium considerations, that is, by the use of phase diagrams. With this assumption, together with those of no diffusion in the solid and complete diffusion in the liquid, we obtain the other extreme prediction for f_s given by the Scheil equation: $f_s = 1 - (C_l/C_o)^{-1/(1-k)}$, which predicts a smaller value at a given temperature than the lever rule. Of course, some back diffusion into the solid will occur even for rapid cooling and a plot of f_s for Al–4.5%Cu over different cooling rates estimated by Flemings [1] is given in Fig. 1.2, which shows that Scheil prediction is quite accurate in the region of practical interest for semisolid processing ($f_s \sim 0.5$) and back diffusion has only a minor influence. The Scheil equation may be easily modified to take account the variation of k with temperature, and introducing more solutes, and solved using numerical methods. It should be added that the above predictions refer only to solutes that form substitutional solutions in the solid: in general, interstitial solutes, such as carbon in steels, diffuse very rapidly and for many purposes may be considered to be in *general equilibrium* between the phases.

Equilibrium phase diagrams assume planar interfaces exist between the phases represented, but may be modified to represent high interfacial curvatures. It may

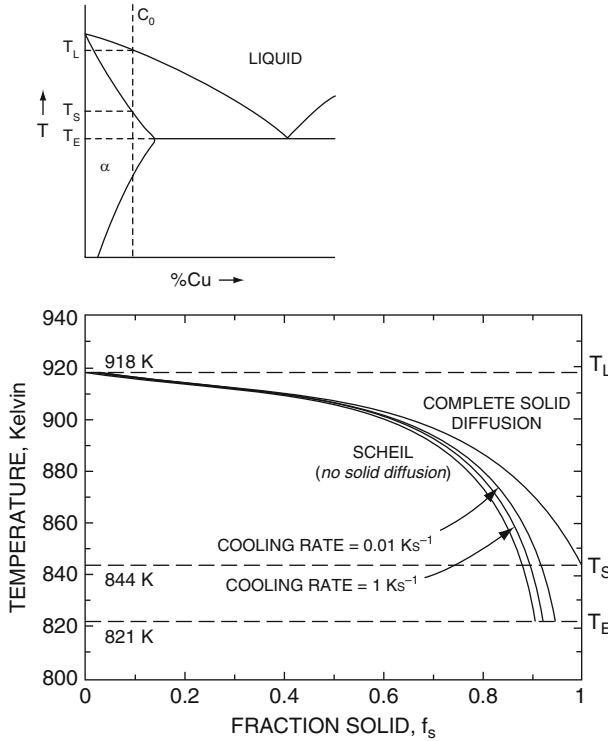


Fig. 1.2 The effect of Cooling Rate on the fraction of Primary Solid formed

be shown [2, 3] that the undercooling produced by interface curvature is given by $\Delta T_i = \frac{K\sigma}{\Delta S_f}$, where σ is the surface energy, ΔS_f the entropy of fusion and $K = 1/r_1 + 1/r_2$, where r_1 and r_2 are the two principal radii of curvature. For metal systems, ΔT_i only becomes important where the radius is less than $10 \mu\text{m}$, and will therefore affect processes, such as nucleation, interface instability, dendrite growth, and coarsening.

1.2 Nucleation

1.2.1 Homogeneous Nucleation

The Rate Equation

When a pure metal is cooled below its melting point, the liquid becomes undercooled and is in a metastable state with respect to the solid crystalline phase. There is a thermodynamic barrier to the formation of solid, since the first solid to appear

has to create an interface between the two phases that requires the expenditure of energy. We may write for the formation of a small spherical solid embryonic particle of radius r from the liquid melt:

$$\Delta G_r = \frac{4}{3} \pi r^3 \Delta G_v + 4 \pi r^2 \sigma,$$

where ΔG_v is the volume free energy change in transforming from liquid to solid, and σ is the interfacial energy between solid and liquid. It is clear that above the melting point both these terms are positive and ΔG_r must be also positive for all values of r and no solid particles can be stable. Below the melting point, ΔG_v becomes negative, and while ΔG_r remains positive for small solid particles (embryos), which will tend to dissolve back into the matrix, larger particles, however, that succeed in growing to the critical size r^* at $d \Delta G_r / dr = 0$ (see Fig. 1.3) can continue to grow further in size with an overall decrease in free energy of the system. Those particles larger than r^* are termed nuclei.

A simple approach to derive an expression for *homogeneous* nucleation rate I is to assume that growth occurs by single atom addition to nuclei and that the nucleation flux is given by the rate at which the critical embryos r^* grow by one atom jumping across the interface: $I = \nu S^* C^*$, where ν is the jump frequency of an atom, S^* is the number of atoms at the interface, and C^* is the number of critical embryos. This “equilibrium” number of critical embryos, C^* , may be estimated from the ideal entropy of mixing of embryos and single atoms, and the rate of atom transfer from diffusion of atoms in the liquid, to provide an estimate of nucleation rate:

$$I \approx 10^{39} \exp\left(-\frac{\Delta G^*}{kT}\right) \text{ s}^{-1} \text{ m}^{-3}. \quad (1.1)$$

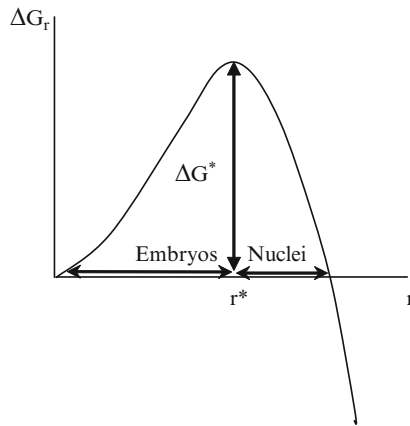


Fig. 1.3 Free energy of growing embryo/nucleus

The value of ΔG^* , the free energy barrier, in (1.1) depends on the undercooling ΔT below the melting point, and is directly proportional to $1/\Delta T^2$. Since this appears within the exponential term, the nucleation rate becomes extremely sensitive to the undercooling ΔT .

Using appropriate values to calculate ΔG^* for aluminum [2,4] in (1.1), the nucleation rate has been plotted against undercooling in Fig. 1.4. For a nucleation rate of $10^6 \text{ s}^{-1} \text{ m}^{-3}$, which is equivalent to one nucleus appearing per second in a volume of 1 cm^3 being the point at which nucleation can sensibly be observed under experimental conditions, this will occur from the figure at $\Delta T = 190 \text{ K}$, close to the experimental value given below. Figure 1.4 also demonstrates that over a further temperature decrease of 3 K , the rate increases by tenfold, illustrating the extreme sensitivity of nucleation to undercooling. Another way of expressing this sensitivity is to note that at 187.4 K undercooling, it would take 10 s for one nucleus to

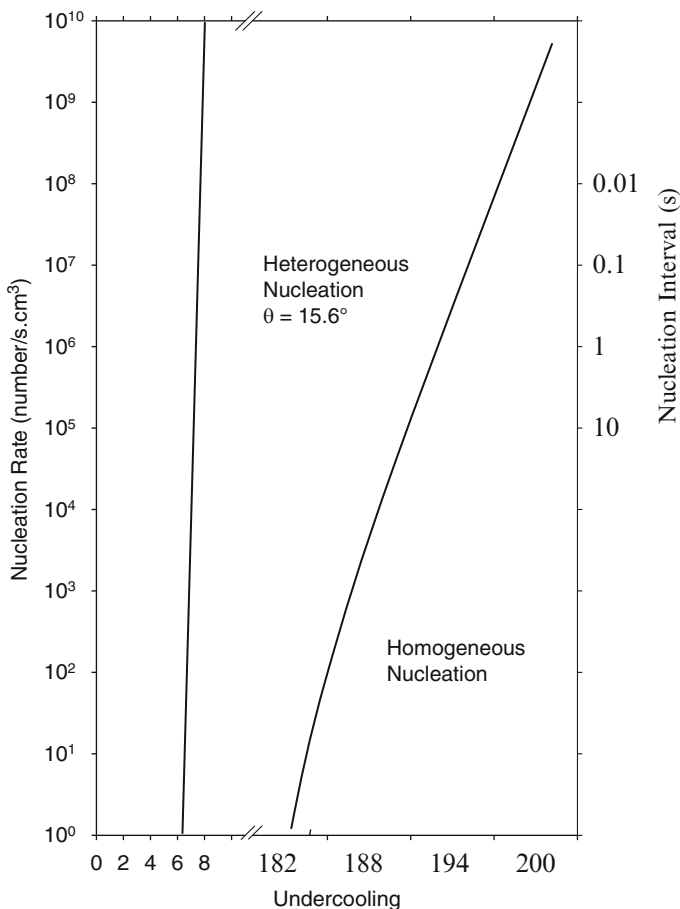


Fig. 1.4 Homogeneous and heterogeneous nucleation rates as a function of undercooling

appear in a melt of 1 cm^3 , whereas at 193 K it takes 0.1 s; effectively zero to copious nucleation over a temperature range of 6 K.

Holloman and Turnbull [4] carried out the classical work on homogeneous nucleation in pure metals, avoiding the problem of heterogeneous nucleation on impurity surfaces by dispersing the metal into very fine droplets whose numbers far exceeded the impurity particles present, and found that extremely high undercooling is required to achieve homogeneous nucleation: 195 K for aluminum and 295 K for iron, for example. From these results, they were able to derive the surface energies, which in some cases have been shown to be in good agreement with values derived using different techniques.

1.2.2 Heterogeneous Nucleation

It is clear then that homogeneous nucleation will occur only at very high undercooling in a melt that can never be achieved in normal industrial or even most laboratory solidification conditions. In fact solidification is commonly observed to start in metals within a few degrees of undercooling, and this strongly suggests that nucleation occurs on the surface of impurity particles (*nucleants*) present within the melt, or at the surface of the container, which helps to lower the thermodynamic energy barrier to nucleus formation, giving rise to *heterogeneous* nucleation. This has been treated theoretically [2, 3] by considering the formation of a small cap of solid upon the planar surface of the impurity having a contact angle θ (Fig. 1.5).

Balancing the surface tension forces along the surface, we have:

$$\sigma_{nl} = \sigma_{sn} + \sigma_{sl} \cos \theta.$$

Following a similar procedure used to calculate homogeneous nucleation, the heterogeneous nucleation rate can be determined approximately to be:

$$I_{\text{het}} \approx 10^{30} \exp\left(-\frac{\Delta G^*}{kT} f(\theta)\right) \text{ s}^{-1} \text{ m}^{-3}, \quad (1.2)$$

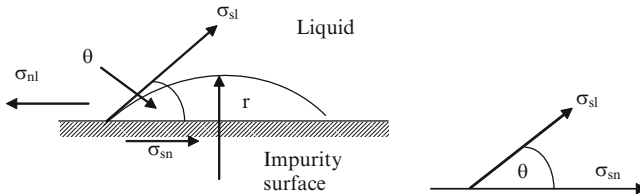


Fig. 1.5 Cap of solid phase forming from the liquid on an impurity surface by heterogeneous nucleation

where the reduced pre-exponential term takes some account of the potential sites on the nucleant surface available for nucleation, and the term $f(\theta) = (2 + \cos \theta)(1 - \cos \theta)^2 / 4$ allows for the reduction of the free energy barrier.

The heterogeneous nucleation rate has been plotted in Fig. 1.4 using the same data as previously, but for a nucleus cap, where $\theta = 15.6^\circ$. It shows that the onset of nucleation effectively now begins around $\Delta T = 7$ K undercooling, similar to common experimental observations.

The change of nucleation rate with undercooling for this situation is even more dramatic than in homogeneous nucleation as seen in Fig. 1.4, indicating that a 1 K change can produce a change in nucleation of four orders of magnitude.

1.2.3 Grain Refinement

The potency of some nucleant particles in promoting large numbers of nuclei during solidification is exploited industrially for grain refinement in castings. It has been shown recently (see review by Greer [5]) that grain refiners, such as Al-5wt% Ti-1wt% B added to aluminum melts, may result in a dramatic reduction in the undercooling to a maximum of 0.2 K before the onset of solidification. This indicates very potent catalysis for the nucleation of α -Al on the nucleant surface having a very low contact angle, in other words forming effectively a flat plate on its surface. Using an Al-based glass containing Al-5Ti-1B as a refiner, it has been possible to investigate the nucleation of solid α -Al on the nucleant or inoculant particles using transmission electron microscopy, since the process is slowed down due to the sluggish diffusion of aluminum atoms in the glassy matrix. This work reveals clearly that the aluminum solid nucleates only on the {0001} basal faces of TiB₂ particles, coated with a thin layer of Al₃Ti, which is the actual nucleation substrate and may be affected by the matrix chemistry.

However, only 1% of the TiB₂ particles in the system produce Al grains in spite of possessing α -Al nuclei on their surfaces and the question arises concerning the inefficiency of grain production. Maxwell and Hellawell [6] assumed this occurred because the latent heat released by the initial nuclei raised the melt temperature causing the nucleation rate to fall. However, Greer has suggested a further barrier exists to the growth of the nuclei already formed, illustrated in Fig. 1.6. This involves the size of the inoculant particle and the surface area available for the nucleus growth. For a small particle, once the nucleus has been covered its surface, further growth of the nucleus cap may require a decrease in its radius (see Fig. 1.6(2)) and further undercooling is needed to achieve this. Eventually, a minimum radius r^* is achieved for a hemispherical nucleus ($2r^* = d$) at an undercooling for free growth, given by $\Delta T_{fg} = 4\sigma / \Delta S d$, where ΔS is the entropy of fusion per unit volume and d is the nucleant particle diameter. At this undercooling, the nucleus will grow without further restraint (free growth) as its radius then increases with size to form a new grain. This is illustrated in Fig. 1.6, where for particles of size less than 6 μm growth is impeded after nucleation until undercooling has increased

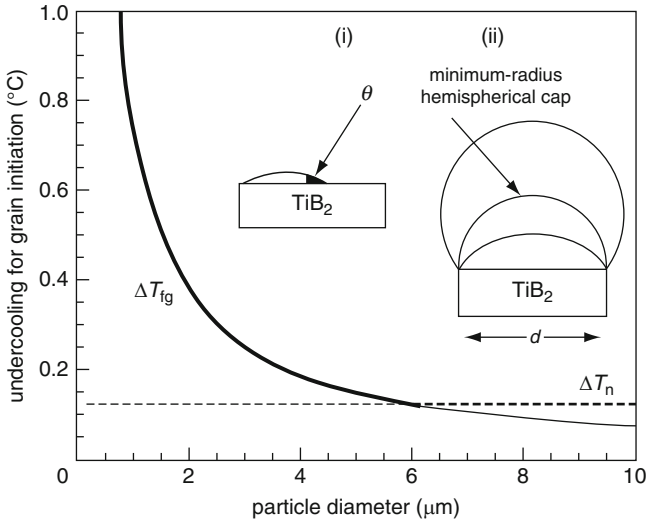


Fig. 1.6 The *bold line* indicates the undercooling necessary for grain initiation. The free-growth undercooling is calculated; the nucleation undercooling is schematic only. *Inset (1)* shows the classical spherical-cap model for heterogeneous nucleation. *Inset (2)* shows a cap of α -Al growing on an inoculant particle through the critical hemispherical condition [5]

to ΔT_{fg} to permit free growth; this is a region of free growth control. However, for large nucleant particles over $6 \mu\text{m}$, growth of nuclei will occur spontaneously after nucleation (i.e., nucleation controlled).

Greer has checked the proposition that the free growth requirement may frequently control grain density under certain conditions by measuring the number of grains formed in a small melt, where isothermal conditions may be assumed during cooling controlled by constant heat loss from the system. The number of grains formed was measured as a function of the number of inoculant particles introduced into the melt. Predictions of the number of grains were made firstly on the basis of heterogeneous nucleation control and the effect of undercooling alone, as proposed by Maxwell and Hellawell [6]. This shows a linear increase in grain density with number of nucleant particles, (Fig. 1.7, region (A)), since at low particle concentrations, there is time for all particles to act as a nucleation source. However, nucleation is eventually unable to cope with high levels of nucleant particles and the number of grains formed falls off to form a plateau (region (B)). The second prediction assumes the criterion of free growth and uses the measured distribution of inoculant size in the melt, and shows the calculated number of grains does not fall off with the addition of particles but continues to rise providing good agreement with measured grain densities as shown in the Fig. 1.7.

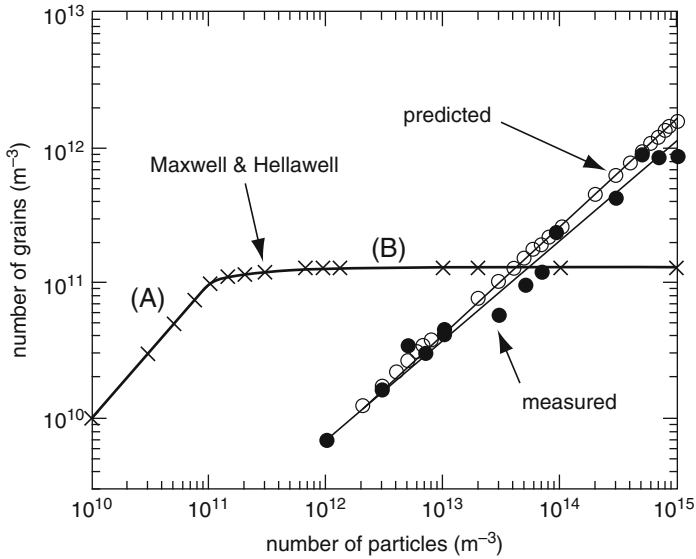


Fig. 1.7 The number of grains per unit volume as a function of the number of refiner particles per unit volume, showing a general trend to lower efficiency at higher addition level. Data from grain diameters measured in TP-1 tests (*closed circles*) are compared with predictions of the free-growth model (*open circles*) [5]. The predictions are qualitatively different from those of Maxwell and Hellawell [6] and are a much better fit to the data [5]

Another way of producing a fine grain size during solidification without introducing foreign particles, which may be deleterious to mechanical properties, is through grain multiplication as a result of the breakup of dendrites. This process will be discussed later (Sects. 1.5, 9.6, and 9.7).

1.3 Solid-Liquid Interface Structure

Some crystals, especially those in which directional bonding exists or possess complex structures, grow from the liquid phase with clear faceted surfaces, i.e., bounded by simple crystallographic planes. It is believed that these crystals have atomically smooth surfaces and growth proceeds either by the nucleation of two dimensional islands on such surfaces and subsequent growth by atomic attachment to the edges of this layer, or more likely by the growth at a ledge on the crystal surface produced by a crystal defect (e.g., a screw dislocation), which cannot be eliminated by the process.

In general, most pure metals and alloys possessing simple crystallographic structures do not grow with faceted interfaces, and these interfaces are considered to be diffuse, that is, the atoms at the interface are not clearly within either the solid or

the liquid phases, but over a region, say of three atoms thick, move from one state to the other [2]. At this type of diffuse or rough interface, every atom in the region can migrate from one phase to the other and there are no special sites at the interface, such as atomic ledges in faceted growth. The consequence is that the interface moves forward continuously and uniformly at all points along it, with essentially a constant velocity in all crystallographic directions. To a first approximation, these structureless interfaces must also possess little anisotropy of surface energy, although some must still remain to determine the dendritic structure that evolves in alloy crystals during growth.

The type of interface is reflected in the entropy of fusion ΔS_f of the material [3]. It has been shown that for those materials with values of $\Delta S_f/R$ less than 1 (which includes all metals), that the interface between solid and liquid are diffuse (or rough), and give rise to non-faceted growth. Also the kinetic undercooling required for normal growth conditions is extremely small (~ 0.001 K), and for most growth calculations may be safely ignored compared with heat and solute diffusion. However, where $\Delta S_f/R$ is high (>2), as in silicon precipitating from Al-Si alloys or graphite from Fe-C, faceted growth may occur in which relatively high undercoolings are required for appreciable growth, and highly anisotropic growth rates and surface energies will exist.

1.4 Morphological Instability

In the last section, it was demonstrated that at the interface of a growing metal crystal, the kinetic undercooling is negligible and growth is essentially controlled by the transfer of heat or solute, to or from the moving interface. Local equilibrium is then said to exist at the interface. Under these conditions, however, the moving interface may become morphologically unstable: that is small perturbations formed at the interface, arising possibly from local disturbances in heat flow, can in certain circumstances become amplified, eventually developing a cellular or dendritic structure. In the case of pure metals, this can only occur when isolated free crystals grow into an undercooled melt (equiaxed growth); in columnar growth of crystals from the ingot surface, however, where a positive temperature exists into the melt, the interface is always stable to accidental growth fluctuations, since perturbation tips would move into hotter liquid and will melt back to restore a planar interface.

However in alloys, a different situation prevails for a moving planar interface. In this case, where the partition coefficient $k < 1$, solute is rejected by the solid into the liquid, forming a concentration profile as in Fig. 1.8a. Eventually, a steady-state solute distribution is established in the liquid as the rate of solute rejection is balanced by the diffusive flow below the composition gradient into the bulk liquid. It may be shown [3] that at this stage, the solute gradient at the interface $G_c = -(V/D) \Delta C_o$, where V is the growth velocity, D the diffusion coefficient in the liquid, and ΔC_o the difference between the interface and bulk solute concentrations. The interface concentration in the liquid (C_o/k) will possess a liquidus

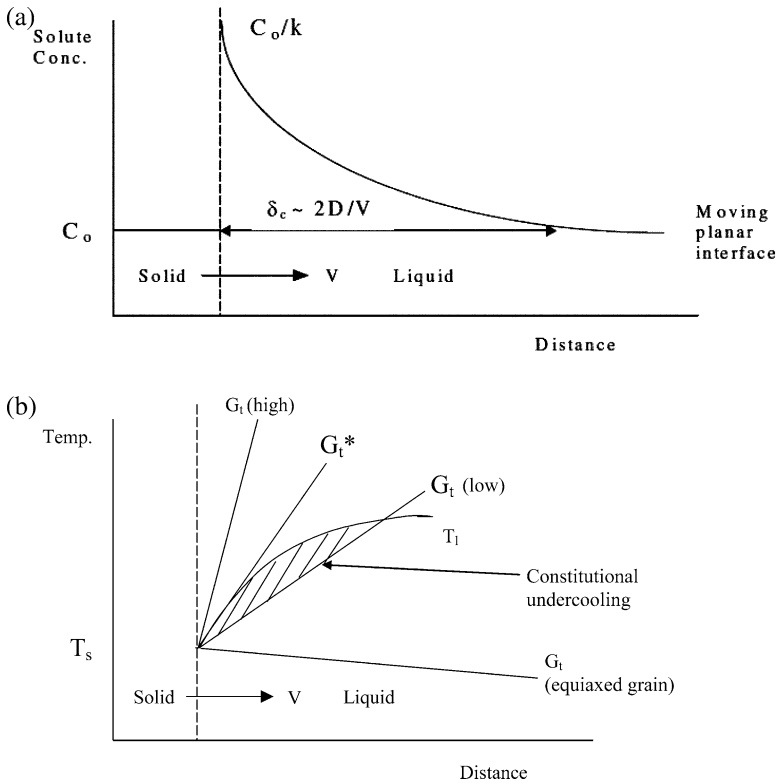


Fig. 1.8 Distribution of (a) solute and (b) temperature ahead of a moving planar interface showing the development of Constitutional Undercooling.

temperature, according to the phase diagram, below the liquidus temperature for the bulk of the liquid that is still at the original alloy composition C_o (see Fig. 1.8a). A liquidus temperature (T_l) may be constructed in the region ahead of the moving interface, as in Fig. 1.8b and the gradient of T_l at the liquid interface may be obtained by multiplying the solute gradient G_c above by m , the liquidus slope in the phase diagram. Where a steep temperature gradient actually exists within the liquid, G_t (high), it is clear that no undercooling exists ahead of the interface to encourage solid to grow. A low temperature gradient, G_t (low), however, produces a region that is metastable with respect to the formation of solid, and this is termed “constitutional undercooling.” We might expect that for a surface perturbation in which solid enters this constitutionally undercooled region, it will be encouraged to grow and therefore, the planar interface is unstable. The critical condition will then occur when the liquidus temperature gradient equals the actual temperature gradient: that is $G_t^* = mG_l = -\frac{mV}{D} \Delta C_o$, and instability should occur when G_t is below this critical value. It should be noted that where equiaxed grains are growing within a melt, the temperature gradient must be negative (the latent heat must flow away into the surrounding liquid). As a consequence, an enhanced and extended region of

undercooled liquid exists around each equiaxed grain in which dendritic growth is favored.

This approach considers only the thermodynamic restraint on interface instability and neglects the effect of surface tension, which might be expected to further constrain the development of instability, and furthermore the treatment provides no estimate of the scale of the perturbation. Applying a small sine wave perturbation to the interface, which is at local equilibrium but contains a surface tension modification, and examining whether the perturbation grows or shrinks, allows one to examine the effect of surface tension on stability. It transpires [3] that there exists a critical wavelength, $\lambda_c = 2\pi (\Gamma/\varphi)^{1/2}$, where Γ is the Gibbs–Thomson coefficient and φ is the degree of undercooling, below which the perturbation disappears and above which it grows increasingly rapidly. At the thermodynamic limit to instability, the perturbation wavelength approaches infinity and therefore, the planar surface is effectively stabilized by surface tension. A more detailed consideration of interface stability is given in [3].

1.5 Grain Multiplication

The generation of fine equiaxed grains by stirring during solidification in order to develop a thixoformable microstructure has much in common with the formation of equiaxed structures in conventional chill castings.

In chill castings, an outer columnar structure is formed at the mould wall of elongated dendrites growing into the melt with a specific crystallographic direction parallel to the direction of heat flow. Equiaxed dendrites may then develop in the ingot center with random orientation, growing approximately uniformly in all directions. It is known that this region of equiaxed grains is particularly sensitive to the superheat of the melt before pouring, and to the flow in the melt after pouring: high superheat reduces the volume of the equiaxed region, and flow tends to increase it. It has been shown that to prevent fluid flow by applying a strong magnetic field also reduces the amount of equiaxed structure.

Three possible mechanisms have been put forward to explain the presence of the equiaxed grains (see review by Flood and Hunt [7]):

- (a) Constitutional undercooling ahead of the columnar grains, resulting in heterogeneous nucleation
- (b) The so-called Big Bang theory, and
- (c) Dendrite arm detachment

The possibility of heterogeneous nucleation occurring in the constitutionally undercooled region ahead of the columnar grains (which must be small given that the solute can diffuse very efficiently sideways from the growing dendrite tips) has been ruled out for two reasons. It has been shown by Chalmers [8] by imposing a mechanical barrier in the form of a thin metal cylinder between the inner and outer regions in the casting, which prevented the transportation of solid fragments from the outer columnar region to the center but did not affect the heat flow or the development of a

constitutionally undercooled region ahead of the growing tips (see Fig. 1.8(a)), that the central equiaxed region then contained much fewer but coarser equiaxed grains compared to the identical experiment carried out without the barrier. The other piece of evidence against this nucleation theory is that experiments carried out containing alloy free of foreign nucleants still develop equiaxed structures. Although it is felt that constitutional undercooling cannot explain the origin of equiaxed grains (except where potent inoculants have been purposely added), nevertheless it must still play a part in their growth.

The Big Bang theory proposes that during pouring of the liquid alloy into the chill mould, crystals nucleate on the mould surface and are then washed into the center of the casting, some of which survive to grow into the equiaxed region at a later stage of solidification. The dendrite arm detachment concept is that remelting at the roots of arms on the columnar dendrites growing from the mould walls, resulting from local recalescence or thermal fluctuations from fluid flow, or from the forces created by flow, causes the arms to become detached from the mother dendrite crystal and carried into the bulk liquid. Essentially these two are similar mechanisms, distinguished only by time and place at which they occur. The Big Bang takes place during the pouring stage and is completed on the filling of the mould, whereas the dendrite remelting mechanism continues throughout the solidification process as long as circulation of the fluid by convection occurs. But both involve grain multiplication by the melting off (or detachment) of dendrite arms and their transport into the bulk of the melt. Once transported to the ingot center, growth of these free crystals occurs because the melt is constitutionally undercooled, and this eventually limits the growth of the columnar grains from the mould walls. It is thought that both these mechanisms may operate in the same system, perhaps at different stages in solidification. It is clear that the effect of superheat in reducing equiaxed grain formation is readily explained by the Big Bang, since most of the free grains formed at this stage will be remelted. However, continued stirring of the melt, after the superheat has dissipated, will assist dendrite arm detachment and encourage equiaxed grain growth.

Both these mechanisms are active in the recent slurry generation processes: the new rheocasting (NRC) process of Ube in which liquid alloy is poured into stainless steel cups and subjected to controlled cooling; and the semisolid rheocasting (SSR[®]) developed at MIT and now under license to Idra-Prince in which a spinning cold finger is introduced into the alloy melt to generate large amounts of small solid particles by dendrite fragmentation (see Chap 4, and Chap Sects 10.61 and 10.62).

1.6 The Growth and Spheroidization of Equiaxed Grains

It has often been claimed that the near spheroidal or rosette morphology of grains growing within the stirred melt arises from their circulation in the semisolid region, passing through hot and cold zones, alternately melting and growing, which results in degenerate dendrites when solidification is complete. However, it is also possible that such morphologies might develop under steady growth conditions.

It has been stated already that under the growth conditions experienced by equiaxed grains in alloys, constitutional undercooling will exist around them leading to dendritic growth. It might be supposed, therefore, that convective flow across the solid–liquid interface produced by stirring would help to remove the solute build-up around them, reducing the constitutional undercooling, and so might restore planar (or spherical) stability. However, the theoretical investigations by Vogel and Cantor [9, 10] into this problem of growth in alloy systems under laminar flow conditions, by modeling heat and solute diffusion away from a perturbed spherical particle using boundary layer approximations, demonstrated that not only did the growth rate of the interface increased (resulting from increased heat transfer), but the interface became more unstable, breaking down into a finer dendritic structure. However, these conclusions are based on the assumption of laminar flow in the liquid and recently, Qin and Fan [11] have carried out similar theoretical computations but including turbulent flow. Their results support Vogel and Cantor for laminar flow but show that under turbulent conditions flow is able to penetrate inside the perturbed interface and remove the accumulated solute. This can lead then to restabilizing of the interface, first under less intense flow to generate a rosette morphology and eventually at greater turbulence to promote the rapid growth of spherical particles. It is claimed that such behavior is observed in “twin-screw rheomolding” [12].