

Fig. 4.10 Heterogeneous nucleation in mould-wall cracks. (a) The critical nuclei. (b) The upper nucleus cannot grow out of the crack while the lower one can. (After P.G. Shewmon, *Transformations in Metals*, © 1969 McGraw-Hill. Used with the permission of McGraw-Hill Book Company.)

So far it has been assumed that the mould wall is microscopically flat. In practice however it is likely to contain many microscopic cracks or crevices. It is possible to write down equations for the formation of a nucleus on such a surface but the result can be obtained more easily as follows. In both of the nucleation types considered so far it can be shown that

$$\Delta G^* = \frac{1}{2} V^* \Delta G_v \quad (4.23)$$

where V^* is the volume of the critical nucleus (sphere or cap). This equation, as well as Equation 4.7, are in fact quite generally true for any nucleation geometry. Thus, if a nucleus forms at the root of a crack the critical volume can be very small even if the wetting angle θ is quite large. Figure 4.10 shows an example where $\theta = 90^\circ$. Therefore nucleation from cracks or crevices should be able to occur at very small undercoolings even when the wetting angle θ is relatively large. Note however that for the crack to be effective the crack opening must be large enough to allow the solid to grow out without the radius of the solid/liquid interface decreasing below r^* .

In commercial practice heterogeneous nucleation is often enhanced by the addition of *inoculants* to the melt in order to refine the final grain size. The inoculating agent forms a solid compound with one of the components of the melt which then acts as a site for nucleation. According to the theory of heterogeneous nucleation outlined above the effectiveness of an inoculant should depend on the wetting angle and the surface roughness. Low values of θ are favoured by a low-energy interface between the inoculant and solid nucleus, γ_{SM} , which should in turn be favoured by good lattice matching between the particle and solid. However lattice matching alone is unable to account for the effectiveness of nucleants. Other contributing factors include chemical effects, as well as surface segregation and roughness. It is thus

difficult at present to predict the effectiveness of a given nucleant. In practice the aim of inoculant additions is of course not to reduce undercooling but to achieve a fine grain size, and then other variables such as the concentration of nucleating particles also becomes important.

4.1.4 Nucleation of Melting

Although nucleation during solidification usually requires some undercooling, melting invariably occurs at the equilibrium melting temperature even at relatively high rates of heating. This is due to the relative free energies of the solid/vapour, solid/liquid and liquid/vapour interfaces. It is always found that

$$\gamma_{SL} + \gamma_{LV} < \gamma_{SV} \quad (4.24)$$

Therefore the wetting angle $\theta = 0$ and no superheating is required for nucleation of the liquid. In fact this interfacial energy relationship implies that a thin liquid layer should even be able to form below T_m (see exercise 4.10). This phenomenon has not, however, been verified for metals as yet.

It is interesting to note that although T_m is a well-defined parameter in metallurgy, the actual atomic *mechanism* of melting is still not properly understood (for a good discussion of this phenomenon see, e.g. Cahn, 1978²). The solid \rightarrow melt transformation in metals corresponds to an equivalent increase in vacancy concentration of as much as 10%, which is difficult to explain in the usual terms of defect structures. The melt, on this basis, might simply be considered to consist of an array of voids (condensed vacancies) surrounded by loose regions of disordered crystal (Frenkel's theory³). The sudden change from long-range crystallographic order to this loose, disordered structure may be associated with the creation of avalanches of dislocations which effectively break up the close-packed structure as melting occurs, as proposed by Cotterill *et al.* (1975)⁴ on the basis of computer simulation experiments. There are, however, problems of quantifying this dislocation mechanism with dilatometric observations, and a more refined theory of melting is awaited.

4.2 Growth of a Pure Solid

It was shown in Section 3.4.6 that there are basically two different types of solid/liquid interface: an atomically rough or diffuse interface associated with metallic systems, and an atomically flat or sharply defined interface often associated with non-metals. Because of the differences in atomic structure these two types of interface migrate in quite different ways. Rough interfaces

migrate by a *continuous growth* process while flat interfaces migrate by a *lateral growth* process involving ledges.

4.2.1 Continuous Growth

The migration of a diffuse solid/liquid interface can be treated in a similar way to the migration of a random high-angle grain boundary. The free energy of an atom crossing the S/L interface will vary as shown in Fig. 3.24 except one solid grain is replaced by the liquid phase. The activation energy barrier ΔG^a should be approximately the same as that for diffusion in the liquid phase, and the driving force for solidification (ΔG) will then be given by

$$\Delta G = \frac{L}{T_m} \cdot \Delta T_i \quad (4.25)$$

where L is the latent heat of melting and ΔT_i is the undercooling of the interface below the equilibrium melting temperature T_m . By analogy with Equation 3.21 therefore, the net rate of solidification should be given by an equation of the form

$$v = k_1 \Delta T_i \quad (4.26)$$

where k_1 has the properties of boundary mobility. A full theoretical treatment indicates that k_1 has such a high value that normal rates of solidification can be achieved with interfacial undercoolings (ΔT_i) of only a fraction of a degree Kelvin. For most purposes therefore ΔT_i can be ignored and the solid/liquid interface is assumed to be at the equilibrium melting temperature. In other words the solidification of metals is usually a diffusion controlled process. For pure metals growth occurs at a rate controlled by heat conduction (diffusion) whereas alloy solidification is controlled by solute diffusion.

The above treatment is applicable to diffuse interfaces where it can be assumed that atoms can be received at any site on the solid surface, i.e. the accommodation factor A in Equation 3.22 is approximately unity. For this reason it is known as continuous growth. Such a mode of growth is reasonable because the interface is disordered and atoms arriving at random positions on the solid will not significantly disrupt the equilibrium configuration of the interface. The situation is, however, more complex when the equilibrium interface structure is atomically smooth as in the case of many non-metals.

4.2.2 Lateral Growth

It will be recalled that materials with a high entropy of melting prefer to form atomically smooth, close-packed interfaces. For this type of interface the minimum free energy also corresponds to the minimum internal energy, i.e. a

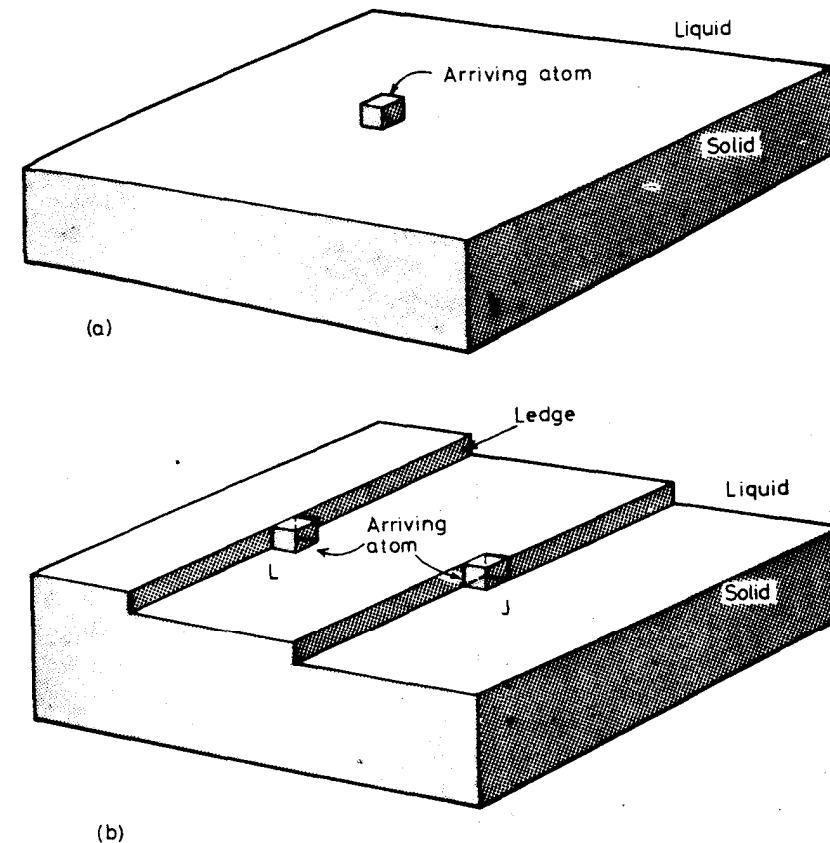


Fig. 4.11 Atomically smooth solid/liquid interfaces with atoms represented by cubes. (a) Addition of a single atom onto a flat interface increases the number of 'broken bonds' by four. (b) Addition to a ledge (L) only increases the number of broken bonds by two, whereas at a jog in a ledge (J) there is no increase.

minimum number of broken 'solid' bonds. If a single atom leaves the liquid and attaches itself to the flat solid surface, Fig. 4.11a, it can be seen that the number of broken bonds associated with the interface, i.e. the interfacial energy, will be increased. There is therefore little probability of the atom remaining attached to the solid and it is likely to jump back into the liquid. In other words, atomically smooth interfaces have inherently low accommodation factors. However, if the interface contains ledges, Fig. 4.11b, 'liquid' atoms will be able to join the ledges with a much lower resulting increase in interfacial energy. If the ledge contains a jog, J, atoms from the liquid can join the solid without any increase in the number of broken bonds and the interfacial energy remains unchanged. Consequently the probability of an atom remaining attached to the solid at these positions is much greater than for an atom joining a facet. Smooth solid/liquid interfaces can therefore be

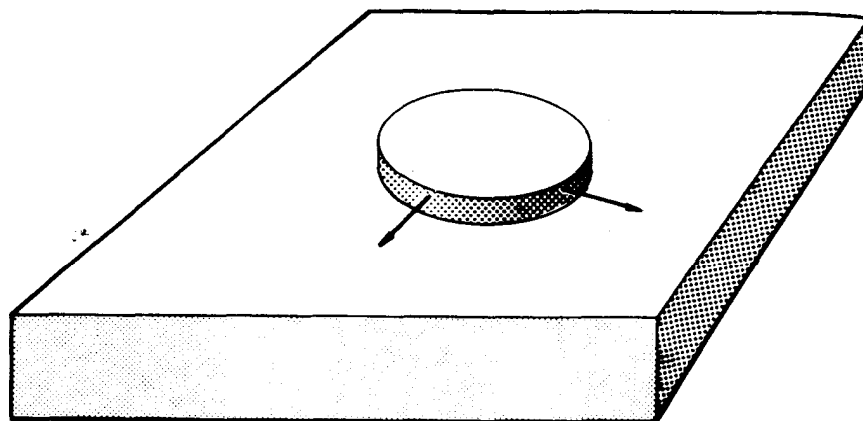


Fig. 4.12 Ledge creation by surface nucleation.

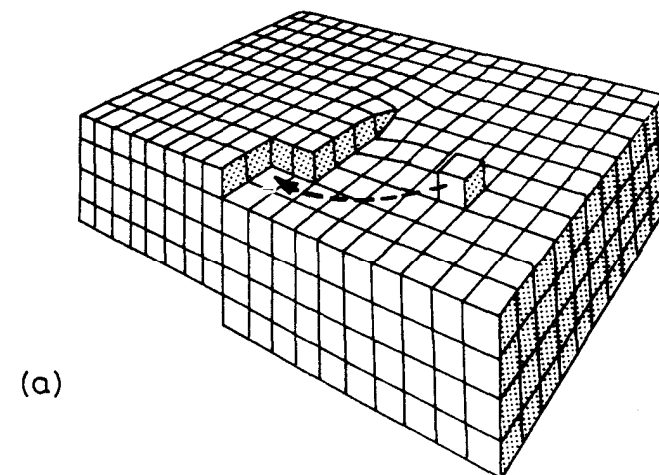
expected to advance by the lateral growth of ledges similar to that described for coherent solid/solid interfaces in Section 3.5.1. Since the ledges and jogs are a non-equilibrium feature of the interface, growth will be very dependent on how the ledges and jogs can be supplied. It is thought that there are basically three different ways in which this can be achieved. These are (i) by repeated surface nucleation, (ii) by spiral growth, and (iii) from twin boundaries.

Surface Nucleation

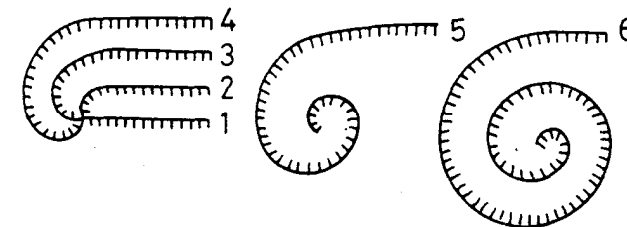
It was pointed out above that a single atom 'solidifying' on to a flat solid surface will be unstable and tend to rejoin the melt. However, if a sufficiently large number of atoms can come together to form a disc-shaped layer as shown in Fig. 4.12 it is possible for the arrangement to become self-stabilized and continue to grow. The problem of disc creation is the two-dimensional analogue of cluster formation during homogeneous nucleation. In this case the edges of the disc contribute a positive energy which must be counterbalanced by the volume free energy released in the process. There will therefore be a critical radius (r^*) associated with the two-dimensional nucleus which will decrease with increasing interface undercooling. Once nucleated the disc will spread rapidly over the surface and the rate of growth normal to the interface will be governed by the surface nucleation rate. A full theoretical treatment shows that

$$v \propto \exp(-k_2/\Delta T_1) \quad (4.27)$$

where k_2 is roughly constant. This is shown schematically in Fig. 4.14. Note that this mechanism is very ineffective at small undercoolings where r^* is very large.



(a)



(b)

Fig. 4.13 Spiral growth. (a) A screw dislocation terminating in the solid/liquid interface showing the associated ledge. (After W.T. Read Jr., *Dislocations in Crystals*, © 1953 McGraw-Hill. Used with the permission of McGraw-Hill Book Company.) Addition of atoms at the ledge causes it to rotate with an angular velocity decreasing away from the dislocation core so that a growth spiral develops as shown in (b). (After J.W. Christian, *The Theory of Phase Transformations in Metals and Alloys*, Pergamon Press, Oxford, 1965.)

Spiral Growth

If the solid contains dislocations that intersect the S/L interface the problem of creating new interfacial steps can be circumvented.

Consider for simplicity the introduction of a screw dislocation into a block of perfect crystal. The effect will be to create a step or ledge in the surface of the crystal as shown in Fig. 4.13a. The addition of atoms to the ledge will cause it to rotate about the point where the dislocation emerges, i.e. the ledge will never run out of the interface. If, on average, atoms add at an equal rate to all points along the step the angular velocity of the step will be initially greatest nearest to the dislocation core. Consequently as growth proceeds the ledge will develop into a growth spiral as shown in Fig. 4.13b. The spiral

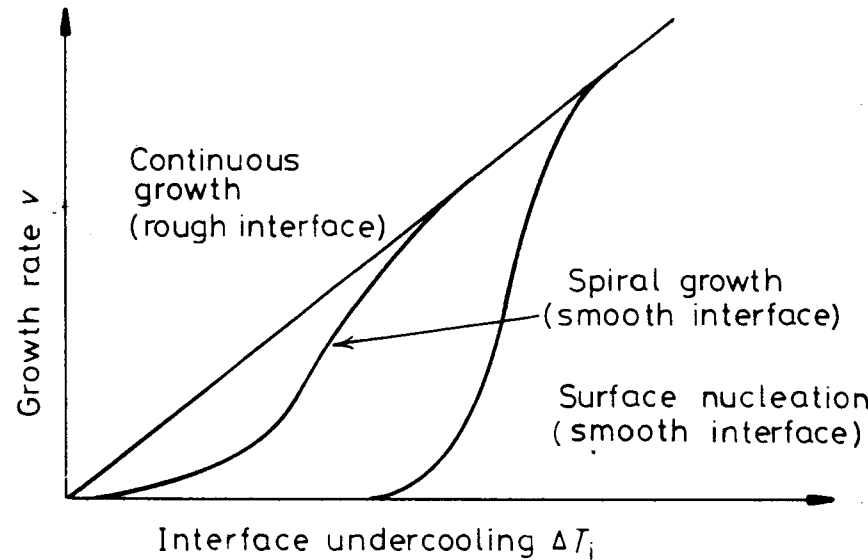


Fig. 4.14 The influence of interface undercooling (ΔT_i) on growth rate for atomically rough and smooth interfaces.

tightens until it reaches a minimum radius of curvature r^* at which it is in equilibrium with the surrounding liquid and can decrease no more. Further out the radius of curvature is less and the spiral can advance at a greater rate. Eventually a steady state is reached when the spiral appears to be rotating with a constant angular velocity. A complete theoretical treatment of this situation shows that for spiral growth the normal growth rate v and the undercooling of the interface ΔT_i are related by an expression of the type

$$v = k_3(\Delta T_i)^2 \quad (4.28)$$

where k_3 is a materials constant. This variation is shown in Fig. 4.14 along with the variations for continuous growth and two-dimensional nucleation. Note that for a given solid growth rate the necessary undercooling at the interface is least for the continuous growth of rough interfaces. For a given undercooling, faceted interfaces are much less mobile and it is to be expected that the spiral growth mechanism will normally be more important than repeated nucleation.

Growth from Twin Intersections

Another permanent source of steps can arise where two crystals in different orientations are in contact. In solidification it is quite common for materials showing faceting to solidify as two crystals in twin orientations. Interfacial facets will therefore intersect at the twin boundary which can act as a permanent source of new steps thereby providing an easy growth mechanism similar to the growth spiral mechanism.

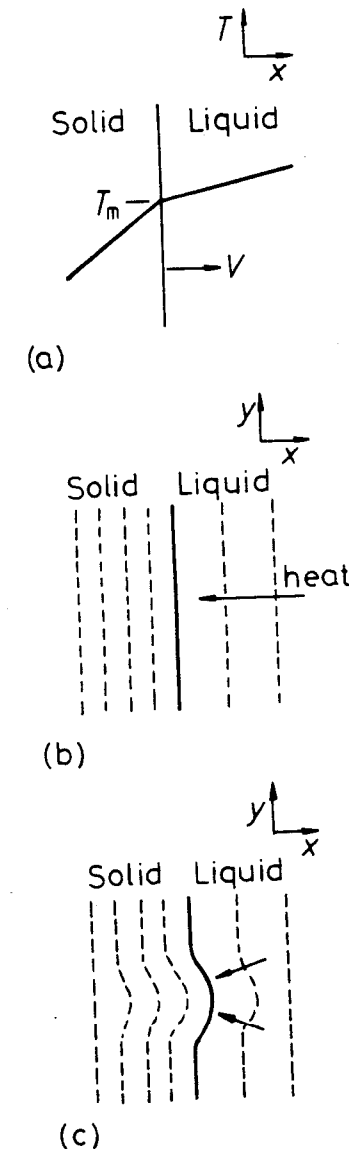


Fig. 4.15 (a) Temperature distribution for solidification when heat is extracted through the solid. Isotherms (b) for a planar S/L interface, and (c) for a protrusion.

4.2.3 Heat Flow and Interface Stability

In pure metals solidification is controlled by the rate at which the latent heat of solidification can be conducted away from the solid/liquid interface. Conduction can take place either through the solid or the liquid depending on the temperature gradients at the interface. Consider for example solid growing at

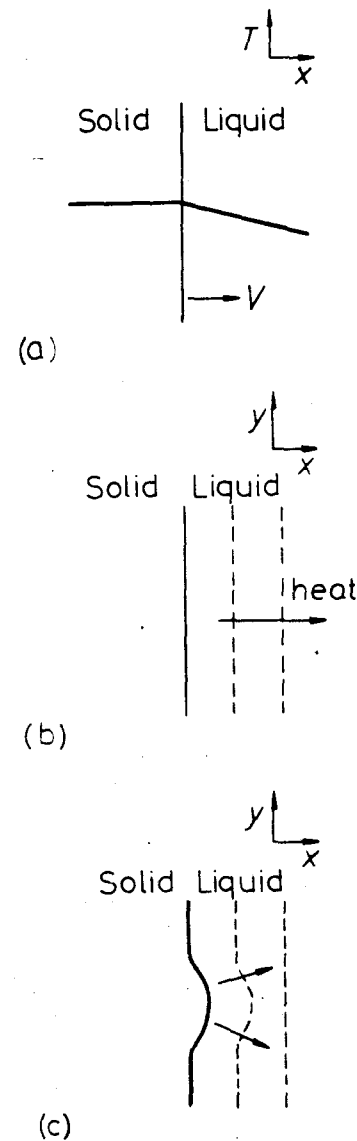


Fig. 4.16 As Fig. 4.15, but for heat conduction into the liquid.

a velocity v with a planar interface into a superheated liquid. Fig. 4.15a. The heat flow away from the interface through the solid must balance that from the liquid plus the latent heat generated at the interface, i.e.

$$K_S T'_S = K_L T'_L + v L_v \quad (4.29)$$

where K is the thermal conductivity, T' is the temperature gradient (dT/dx), the subscripts S and L stand for solid and liquid, v is the rate of growth of the

solid, and L_v is the latent heat of fusion per unit volume. This equation is quite general for a planar interface and even holds when heat is conducted into the liquid ($T'_L < 0$), Fig. 4.16a.

When a solid grows into a superheated liquid, a planar solid/liquid interface is stable. This can be shown as follows. Suppose that as a result of a local increase in v a small protrusion forms at the interface, Fig. 4.15a. If the radius of curvature of the protrusion is so large that the Gibbs-Thomson effect can be ignored the solid/liquid interface remains isothermal at essentially T_m . Therefore the temperature gradient in the liquid ahead of the nodule will

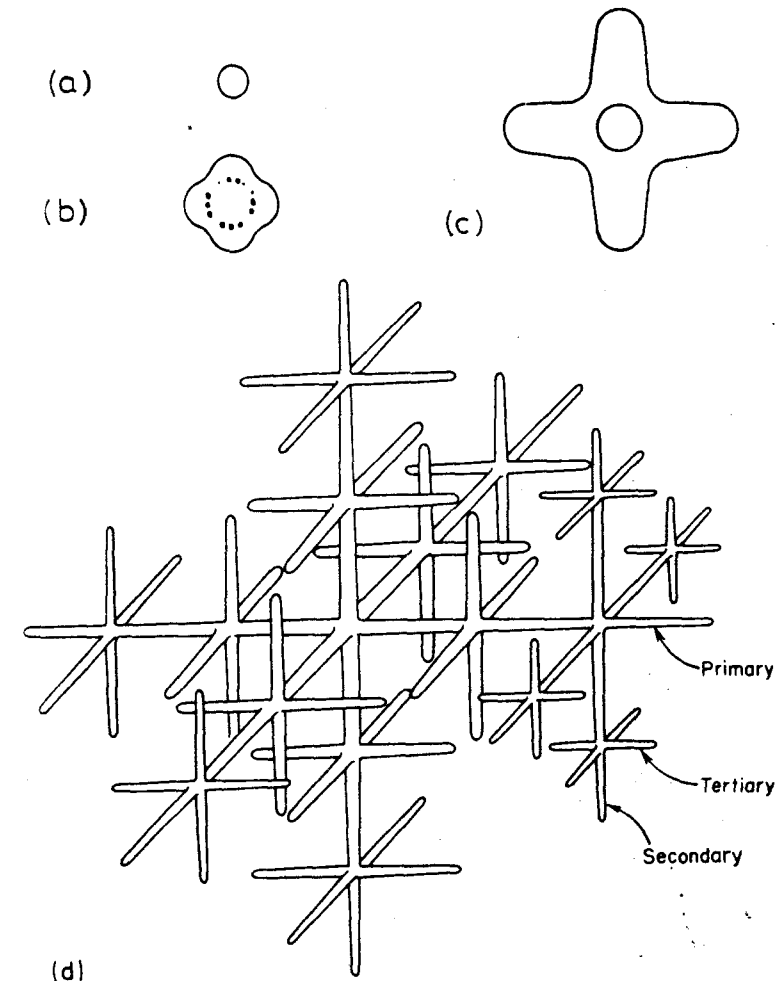


Fig. 4.17 The development of thermal dendrites: (a) a spherical nucleus; (b) the interface becomes unstable; (c) primary arms develop in crystallographic directions ($\langle 100 \rangle$ in cubic crystals); (d) secondary and tertiary arms develop (after R.E. Reed-Hill. *Physical Metallurgy Principles*, 2nd. edn., Van Nostrand, New York, 1973).

increase while that in the solid decreases. Consequently more heat will be conducted into the protruding solid and less away so that the growth rate will decrease below that of the planar regions and the protrusion will disappear.

The situation is, however, different for a solid growing into supercooled liquid, Fig. 4.16. If a protrusion forms on the solid in this case the negative temperature gradient in the liquid becomes even more negative. Therefore heat is removed more effectively from the tip of the protrusion than from the surrounding regions allowing it to grow preferentially. A solid/liquid interface advancing into supercooled liquid is thus inherently unstable.

Heat conduction through the solid as depicted in Fig. 4.15, arises when solidification takes place from mould walls which are cooler than the melt. Heat flow *into* the liquid, however, can only arise if the liquid is supercooled below T_m . Such a situation can arise at the beginning of solidification if nucleation occurs at impurity particles in the bulk of the liquid. Since a certain supercooling is required before nucleation can occur, the first solid particles will grow into supercooled liquid and the latent heat of solidification will be conducted away into the liquid. An originally spherical solid particle will therefore develop arms in many directions as shown in Fig. 4.17. As the primary arms elongate their surfaces will also become unstable and break up into secondary and even tertiary arms. This shape of solid is known as a *dendrite*. *Dendrite* comes from the Greek for *tree*. Dendrites in pure metals are usually called *thermal dendrites* to distinguish them from dendrites in

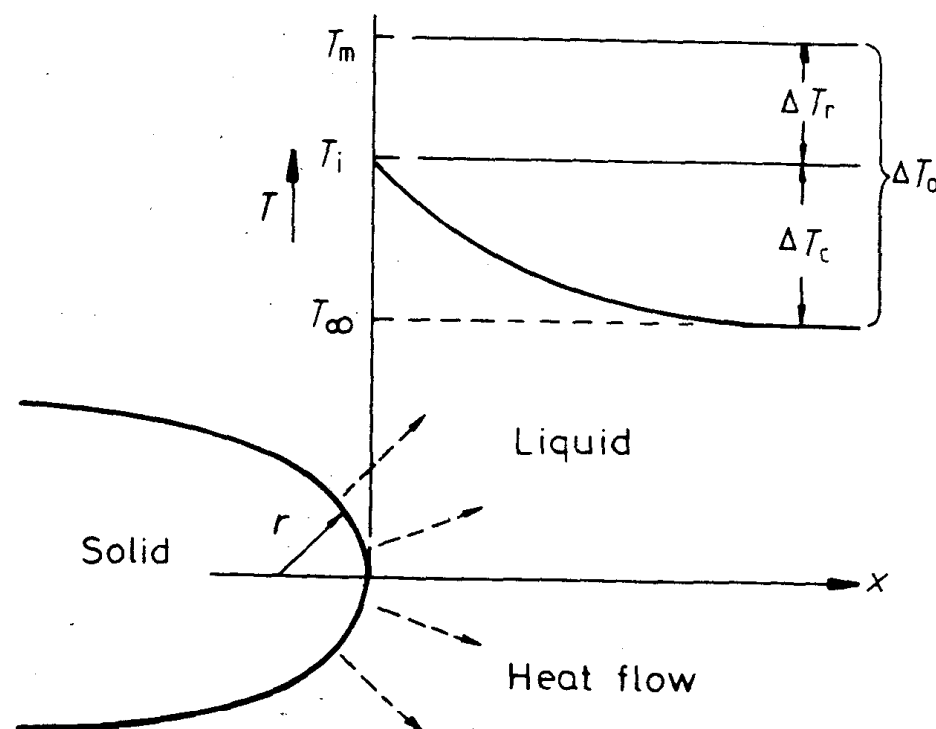


Fig. 4.18 Temperature distribution at the tip of a growing thermal dendrite.

alloys (see below). It is found experimentally that the dendrite arms are always in certain crystallographic directions: e.g. $\langle 100 \rangle$ in cubic metals, and $\langle 1\bar{1}00 \rangle$ in hcp metals⁵.

Let us now take a closer look at the tip of a growing dendrite. The situation is different from that of a planar interface because heat can be conducted away from the tip in three dimensions. If we assume the solid is isothermal ($T_s = 0$) the growth rate of the tip v will be given by a similar equation to Equation 4.29 provided T'_L is measured in the direction of v . A solution to the heat-flow equations for a hemispherical tip shows that the (negative) temperature gradient T'_L is approximately given by $\Delta T_c/r$ where ΔT_c is the difference between the interface temperature (T_i) and the temperature of the supercooled liquid far from the dendrite (T_∞) as shown in Fig. 4.18. Equation 4.29 therefore gives

$$v = \frac{-K_L T'_L}{L_v} \approx \frac{K_L}{L_v} \cdot \frac{\Delta T}{r} \quad (4.30)$$

Thus for a given ΔT , rapid growth will be favoured by small values of r due to the increasing effectiveness of heat conduction as r diminishes. However ΔT is not independent of r . As a result of the Gibbs-Thomson effect equilibrium across a curved interface occurs at an undercooling ΔT_r below T_m given by

$$\Delta T_r = \frac{2\gamma T_m}{L_v r}$$

The minimum possible radius of curvature of the tip is when ΔT_r equals the total undercooling $\Delta T_0 = T_m - T_\infty$. This is just the critical nucleus radius r^* given by $(2\gamma T_m / L_v \Delta T_0)$. Therefore in general ΔT_r is given by $\Delta T_0 r^*/r$. Finally since $\Delta T_0 = \Delta T_c + \Delta T_r$ Equation 4.30 becomes

$$v \approx \frac{K_L}{L_v} \cdot \frac{1}{r} \left(1 - \frac{r^*}{r} \right) \quad (4.31)$$

It can thus be seen that the tip velocity tends to zero as $r \rightarrow r^*$ due to the Gibbs-Thomson effect and as $r \rightarrow \infty$ due to slower heat conduction. The maximum velocity is obtained when $r = 2r^*$.

4.3 Alloy Solidification

The solidification of pure metals is rarely encountered in practice. Even commercially pure metals contain sufficient impurities to change the characteristics of solidification from pure-metal to alloy behaviour. We now develop the theory a step further and examine the solidification of single-phase binary alloys. Following this we then consider the solidification of eutectic and peritectic alloys.