

Lecture 8: Growth Morphologies

Geometry of Solidification

Fig. 1 shows the grain structures possible when molten metal is poured into a cold metal mould. The *chill zone* contains fine crystals nucleated at the mould surface. There is then selective growth into the liquid as heat is extracted from the mould, *i.e.* crystals with their fast-growth directions parallel to that of heat flow grow rapidly and stifle others. If the liquid in the centre of the mould is undercooled sufficiently, grains may nucleate and grow without contact with any surface. Such grains grow to approximately equal dimensions in all directions, *i.e.* are *equiaxed*.

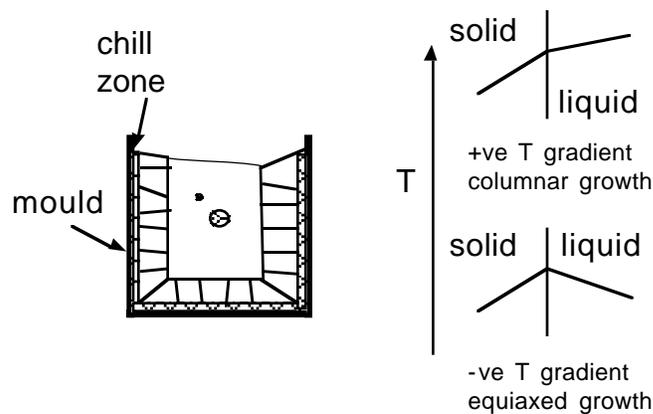


Fig. 1: Geometry of solidification

Equiaxed growth in a pure metal can show morphological instabilities, *i.e.* thermal dendrites (Fig. 2). This is because a small perturbation at the interface ends up in even more supercooled liquid so the interface becomes unstable. Dendrites have preferred growth directions relative to their crystal structure.

Solidification of Alloys

Solute is partitioned into the liquid ahead of the solidification front. This causes a corresponding variation in the liquidus temperature (the temperature below which

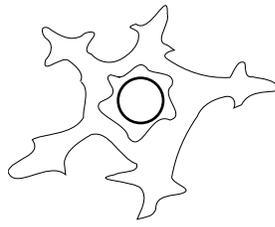


Fig. 2: Thermal dendrite formation when the temperature gradient in the liquid is negative.

freezing begins)[†]. There is, however, a positive temperature gradient in the liquid, giving rise to a supercooled zone of liquid ahead of the interface (Fig. 3). This is called constitutional supercooling because it is caused by composition changes.

A small perturbation on the interface will therefore expand into a supercooled liquid. This gives rise to dendrites.

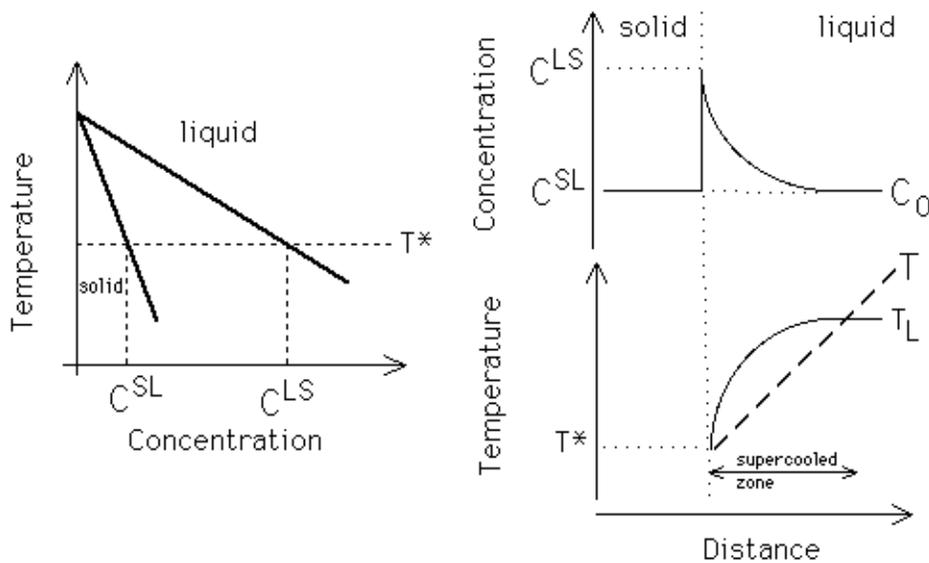


Fig. 3: Diagram illustrating constitutional supercooling.

It follows that a supercooled zone only occurs when the liquidus–temperature (T_L)

[†] The liquidus phase boundary defines the temperature below which solidification begins under equilibrium conditions

gradient at the interface is larger than the temperature gradient:

$$\left. \frac{\partial T_L}{\partial x} \right|_{x=0} > \frac{\partial T}{\partial x}$$

It is very difficult to avoid constitutional supercooling in practice because the velocity required to avoid it is very small indeed. Directional solidification with a planar front is possible only at low growth rates, for example in the production of silicon single crystals. In most cases the interface is unstable (Fig. 4):

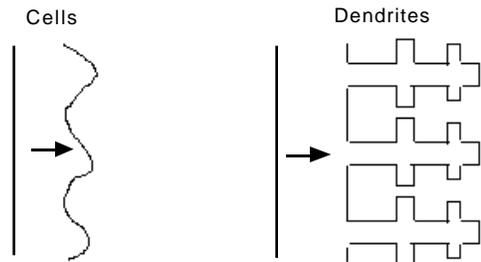


Fig. 4: Cells and dendrites. Cells form when the size of the supercooled zone is small and dendrites when the size is large.

Solid–State Transformations

The atomic arrangement in a crystal can be altered either by breaking all the bonds and rearranging the atoms into an alternative pattern (*reconstructive* transformation), or by homogeneously deforming the original pattern into a new crystal structure (*displacive* transformation), Fig. 5.

In the displacive mechanism the change in crystal structure also alters the macroscopic shape of the sample when the latter is not constrained. The shape deformation during constrained transformation is accommodated by a combination of elastic and plastic strains in the surrounding matrix. The product phase grows in the form of thin plates to minimise the strains. The atoms are displaced into their new positions in a coordinated motion. Displacive transformations can therefore occur at temperatures where diffusion is inconceivable within the time scale of the experiment. Some solutes may be forced into the product phase, a phenomenon known as solute trapping. Both the trapping of atoms and the strains make displacive transformations less favourable from a thermodynamic point of view.

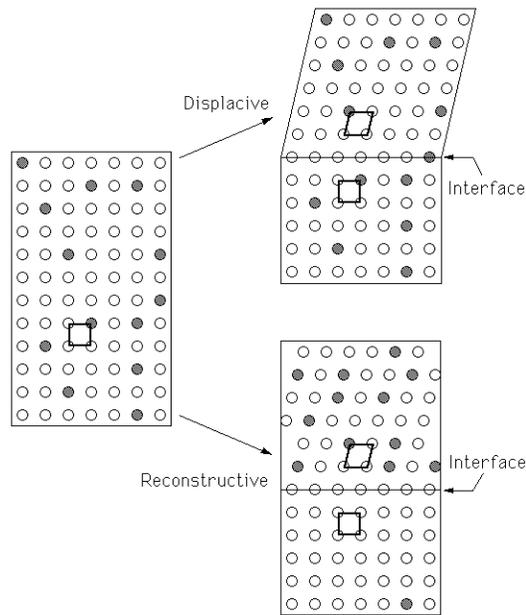


Fig. 5: The main mechanisms of transformation. The parent crystal contains two kinds of atoms. The figures on the right represent partially transformed samples with the parent and product unit cells outlined in bold. The transformations are unconstrained in this illustration.

Fig. 6 shows how the shape of the product phase changes when the transformation is constrained, because a thin-plate then minimises the strain energy.

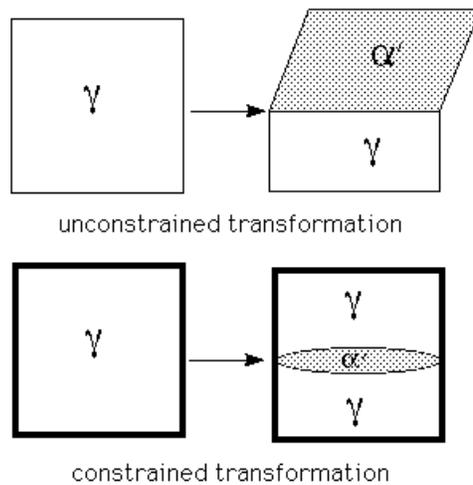


Fig. 6: The effect of strain energy on the morphology of the transformed phase during displacive transformation involving shear deformation.

It is the diffusion of atoms that leads to the new crystal structure during a reconstructive transformation. The flow of matter is sufficient to avoid any shear components of the shape deformation, leaving only the effects of volume change. This is illustrated phenomenologically in Fig. 7, where displacive transformation is followed by diffusion, which eliminates the shear. This *reconstructive diffusion* is necessary even when transformation occurs in a pure element. In alloys, the diffusion process may also lead to the redistribution of solutes between the phases in a manner consistent with a reduction in the overall free energy.

Virtually all solid–state phase transformations can be discussed in the context of these two mechanisms.

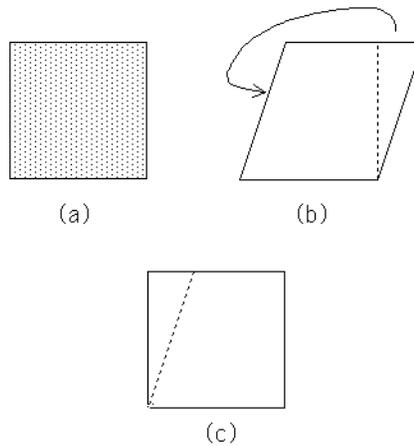


Fig. 7: A phenomenological interpretation of reconstructive transformation. (a) Parent phase; (b) product phase generated by a homogeneous deformation of the parent phase. The arrow shows the mass transport that is necessary in order to eliminate the shear component of the shape deformation; (c) shape of the product phase after the reconstructive–diffusion has eliminated the shear component of the shape deformation.

Equilibrium Shape

The equilibrium shape of a particle is frequently determined by the minimisation of interface energy. If the interface energy does not depend on the orientation of the boundary, then the shape which gives the minimum surface to volume ratio is a

sphere (Fig. 8a). In crystalline materials the interface energy is always dependent on the orientation of the interface. The latter is defined by its normal. The orientation dependence of the interface energy can be represented by a radial vector whose magnitude is proportional to the energy. This is the so-called gamma-plot. The equilibrium shape can then be found by drawing surfaces normal to the cusps in the gamma-plot as illustrated in Fig. 8b.

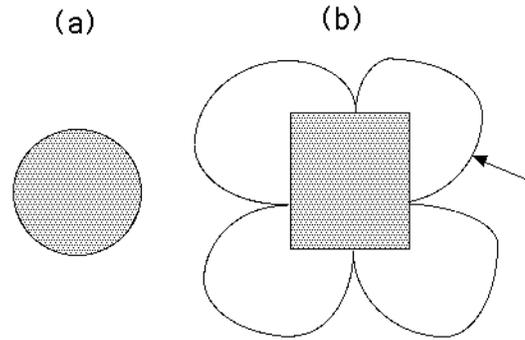


Fig. 8: (a) Equilibrium shape when the interface energy is isotropic. (b) Equilibrium shape when the interface energy varies with the orientation of the boundary. The arrow shows the plot of interface energy (proportional to radial distance from the centre) as a function of orientation of the interface plane (defined by the plane-normal which is parallel to the radial vector on the plot).