Crystallization from the melt

First, in order to illustrate some basic principles, we will consider the freezing behaviour of a melt of like metal atoms. The thermal history of a slowly cooling metal is depicted in Figure 1; the plateau on the curve indicates the melting point (m.p.), which is pressure-dependent and specific to the metal. Its value relates to the bond strength of the metal. Thus, the drive to develop strong alloys for service at high temperatures has stimulated research into new and improved ways of casting high-m.p, alloys based upon iron, nickel or cobalt.

The transition from a highly-disordered liquid to an ordered solid is accompanied by a lowering in the energy state of the metal and the release of thermal energy (latent heat of solidification), forming the arrest on the cooling curve shown in Figure 1. This ordering has a marked and immediate effect upon other structure-sensitive properties of the metal; for instance, the volume typically decreases by 1-6%, the electrical conductivity rises and the diffusivity, or ability of the atoms to migrate, falls.

Solidification is a classic example of a nucleation and growth process. In the general case of freezing within the bulk of pure molten metal, minute crystalline nuclei form independently at random points. After this homogeneous form of nucleation, continued removal of thermal energy from the system causes these small crystalline regions to grow independently at the expense of the surrounding melt. Throughout the freezing process, there is a tendency for bombardment by melt atoms to destroy embryonic crystals; only nuclei which exceed a critical size are able to survive. Rapid cooling of a pure molten metal reduces the time available for nuclei formation and delays the onset of freezing by a temperature interval of ΔT. This thermal undercooling (or supercooling), which is depicted in Figure 1, varies in extent, depending upon the metal and conditions, but can be as much as 0.1-0.3 Tm, where Tm is the absolute melting point. However, commercial melts usually contain suspended insoluble particles of foreign matter (e.g. from the refractory crucible or hearth) which act as seeding nuclei for so-called heterogeneous nucleation. Undercooling is much less likely under these conditions; in fact, very pronounced undercooling is only obtainable when the melt is very pure and extremely small in volume. Homogeneous nucleation is not encountered in normal foundry practice.

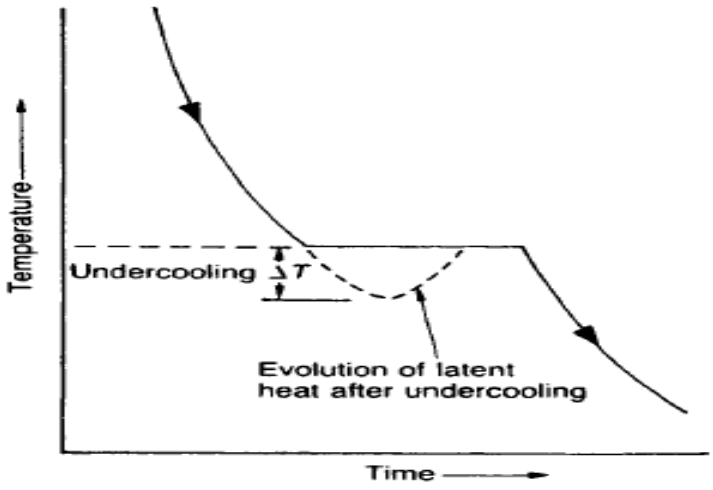

Fig. 1 Cooling curve for a pure metal showing possible undercooling.

When a pure metal solidifies, each crystal begins to form independently from a nucleus or 'centre of crystallisation'. The nucleus will be a simple unit of the appropriate crystal lattice, and from this the crystal will grow. The crystal develops by the addition of atoms according to the lattice pattern it will follow, and rapidly begins to assume visible proportions in what is called a 'dendrite' (a tree). This is a sort of crystal skeleton, rather like a backbone from which the arms begin to grow in other directions, depending upon the lattice pattern. From these secondary arms, tertiary arms begin to sprout, somewhat similar to the branches and twigs of a fir-tree. In the metallic dendrite, however, these branches and twigs conform to a rigid geometrical pattern. A metallic crystal grows in this way because heat is dissipated more quickly from a point, so that it will be there that the temperature falls most quickly leading to the formation of a rather elongated skeleton (Fig. 1).

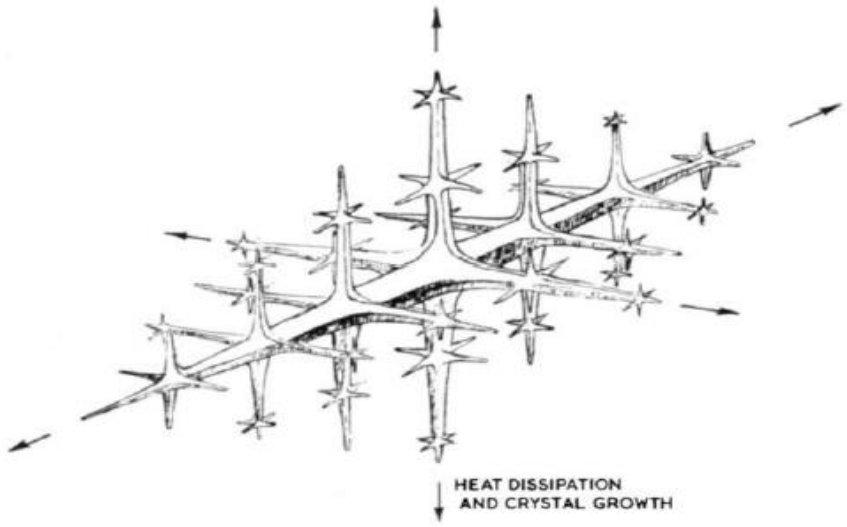

Fig. 2 The early stages in the growth of a metallic dendrite

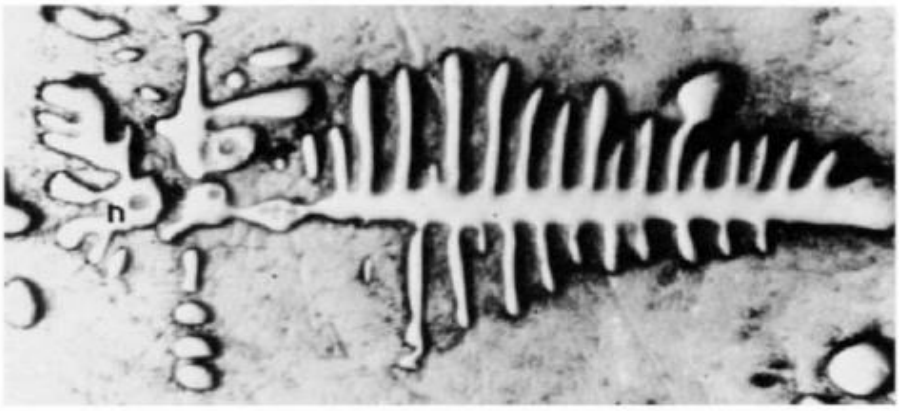

Fig. 3 Dendritic growth. This iron dendrite grew from a nucleus at 'n' in a molten mixture of iron and copper. After all the available iron had been used up the dendrite ceased to grow, and the molten copper solidified as the matrix in which the iron dendrite remains embedded. (In fact the iron dendrite will contain a little dissolved copper—in 'solid solution'—whilst the copper matrix will contain a very small amount of dissolved iron), x 300.

The dendrite arms continue to grow and thicken at the same time, until ultimately the space between them will become filled with solid. Meanwhile the outer arms begin to make contact with those of neighbouring dendrites which have been developing quite independently at the same time. All these neighbouring crystals will be orientated differently due to their independent formation; that is, their lattices will meet at odd angles. When contact has taken place between the outer arms of neighbouring crystals further growth outwards is impossible, and solidification will be complete when the remaining liquid is used up in thickening the existing dendrite arms. Hence the independent formation of each crystal leads to the irregular overall shape of crystals. The dendritic growth of crystals is illustrated in Fig. 4. In these diagrams, however, the major axes of the crystals are all shown in the same horizontal plane, ie the plane of the paper, whereas in practice this would not necessarily be the case. It has been shown so in the illustration for the sake of clarity.

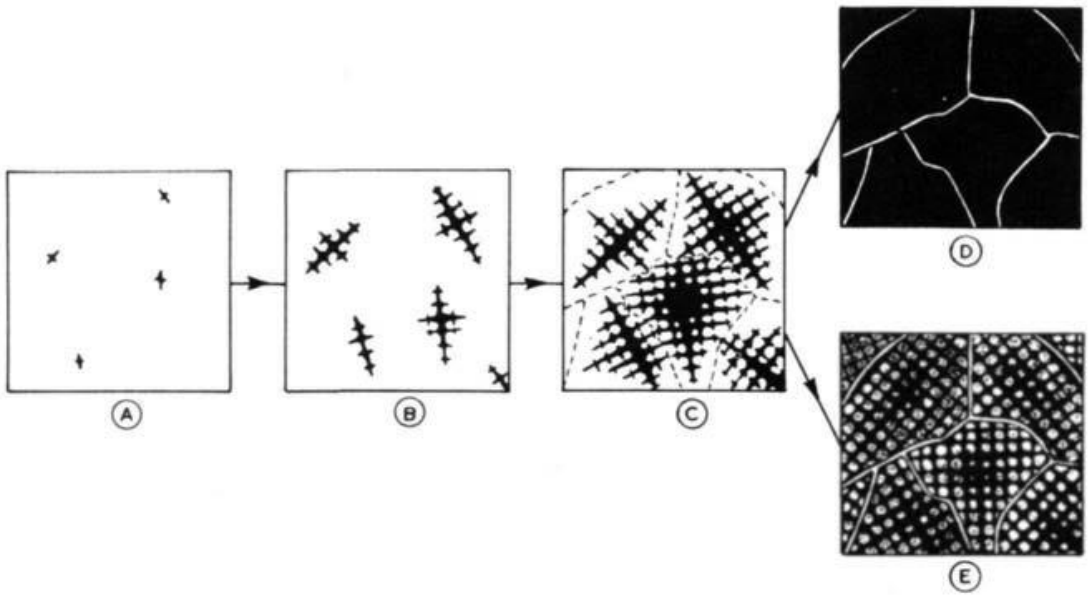

Fig. 4. The dendritic growth of metallic crystals from the liquid state. A solid pure metal (D) gives no hint of its dendritic origin since all atoms are identical, but an impure metal (E) carries the impurities between the dendritic arms, thus revealing the initial skeleton.

If the metal we have been considering is pure we shall see no evidence whatever of dendritic growth once solidification is complete, since all atoms are identical. Dissolved impurities, however, will often tend to remain in the molten portion of the metal as long as possible, so that they are present in that part of the metal which ultimately solidifies in the spaces between the dendrite arms. Since their presence will often cause a slight alteration in the colour of the parent metal, the dendritic structure will be revealed on microscopical examination. The areas containing impurity will appear as patches between the dendrite arms (Fig. 4.E). Inter-dendritic porosity may also reveal the original pattern of the dendrites to some extent. If the metal is cooled too rapidly during solidification, molten metal is often unable to 'feed' effectively into the spaces which form between the dendrites due to the shrinkage which accompanies freezing. These spaces then remain as cavities following the outline of the solid dendrite. Such shrinkage cavities can usually be distinguished from blow-holes formed by dissolved gas. The former are of distinctive shape and occur at the

crystal boundaries, whilst the latter are quite often irregular in form and occur at any point in the crystal structure (Fig. 5).

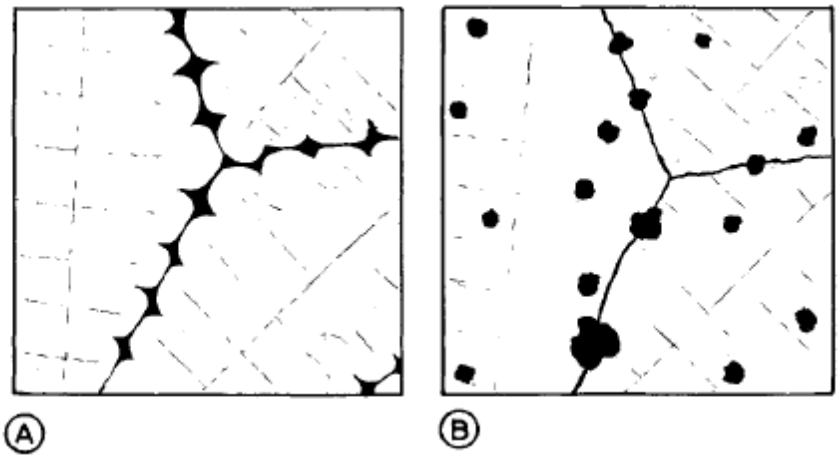

Fig. 5 Porosity in cast metals. Shrinkage cavities (A) tend to follow the shape of the dendritic arms and occur at the crystal boundaries, whilst gas porosity (B) is usually of irregular shape and occurs at almost any point in the structure.

The rate at which a molten metal is cooling when it reaches its freezing point affects the size of the crystals which form. A slow fall in temperature, which leads to a small degree of undercooling at the onset of solidification, promotes the formation of relatively few nuclei, so that the resultant crystals will be large (they are easily seen without the aid of a microscope). Rapid cooling, on the other hand, leads to a high degree of undercooling being attained, and the onset of crystallisation results in the formation of a large 'shower' of nuclei. This can only mean that the final crystals, being large in number, are small in size. In the language of the foundry, 'chilling causes fine-grain casting'.Thus the crystal size of a pressure die-casting will be very small compared with that of a sand-casting. Whilst the latter cools relatively slowly, due to the insulating properties of the sand mould, the former solidifies very quickly, due to the contact of the molten metal with the metal mould. Similarly, thin sections, whether in sand- or die-casting, will lead to a relatively quicker rate of cooling, and consequently smaller crystals.

In a large ingot the crystal size may vary considerably from the outside surface to the centre (Fig. 6). This is due to the variation which exists in the temperature gradient as the ingot solidifies and heat is transferred from the metal to the mould. When metal first makes contact with the mould the latter is cold, and this has a chilling effect which results in the formation of small crystals at the surface of the ingot. As the mould warms up, its chilling effect is reduced, so that the formation of nuclei will be retarded as solidification proceeds. Thus crystals towards the centre of the ingot will be larger. In an intermediate position the rate of cooling is favourable to the formation of elongated columnar crystals, so that we are frequently able to distinguish three separate zones in the crystal structure of an ingot, as shown in Fig. 7. More recent research into rapid solidification processes (RSP) has been carried out with the object of obtaining metals and alloys with extremely tiny crystals, and in some cases retaining the amorphous structure of the original liquid at ambient temperatures.

Fig. 6 A Dendrites on the surface of an ingot of antimony. Antimony is one of the few metals which expand during solidification. Hence the growing dendrites were raised clear of the remaining liquid so that their growth could not be completed.

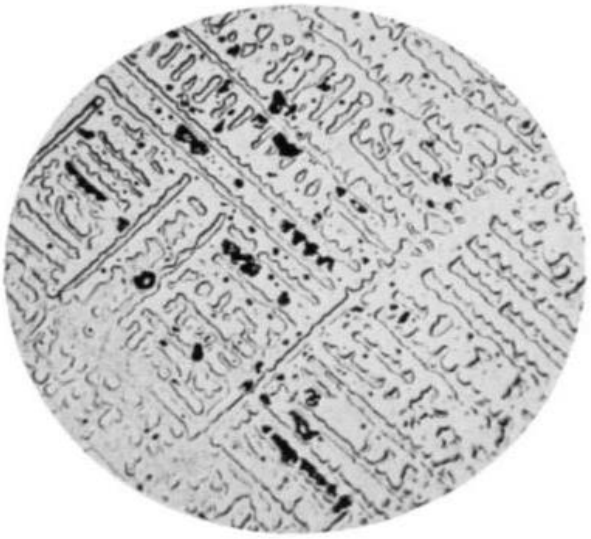

Fig. 6B Shrinkage cavities (black areas) in cast tin bronze. These roughly follow the shape of the original dendrites and occur in that part of the alloy to solidify last, x 200.

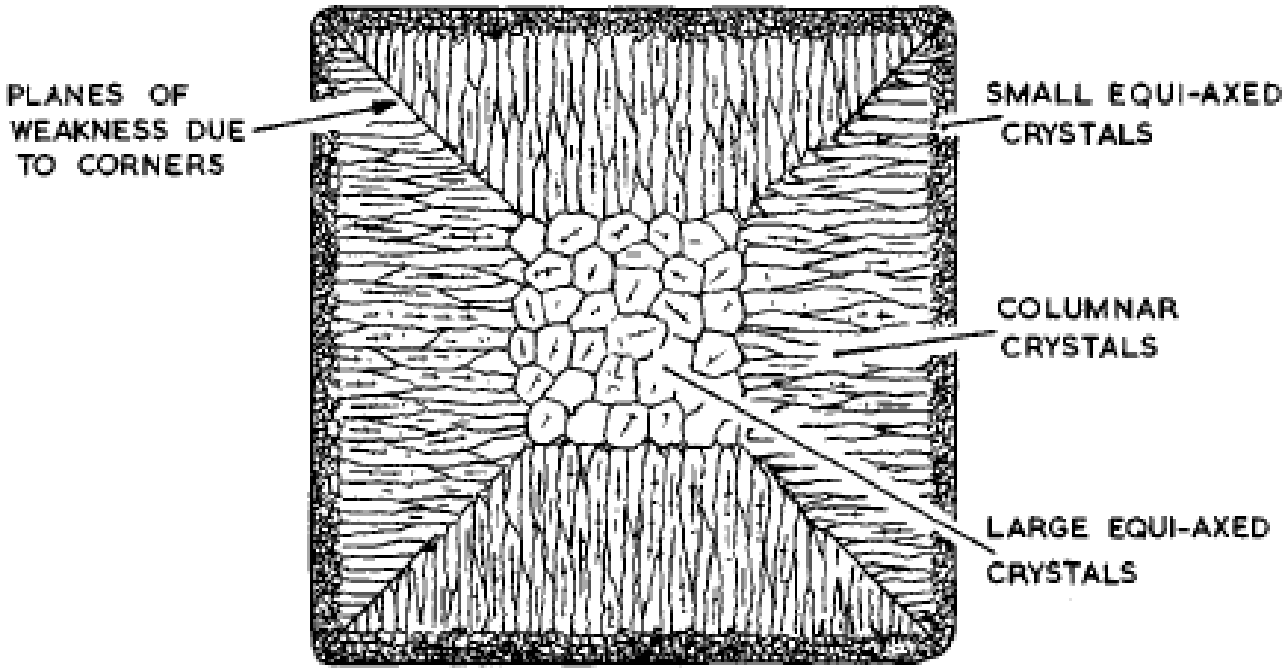

Fig. 7. The crystal structure in a section of a large ingot.