

PROGRESS IN CAST METALS
INSTITUTION OF METALLURGISTS

• Series 2 Number 5

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SOLIDIFICATION AND STRUCTURE OF CASTINGS

by I. C. H. Hughes

GENERAL CONSIDERATIONS

A casting is a product of the solidification of liquid metal deliberately caused to assume a pre-determined useful shape and having a desired structure and properties. The ability of a casting to fulfil its planned function depends not only on its shape, but also on its macrostructure, microstructure and freedom from undesirable constituents, shrinkage defects and other discontinuities in the constituent phases, all of which are governed by the solidification process.

Solidification of liquid metal occurs by the nucleation and growth of crystals. Following the classic work of Turnbull and his associates¹, it is now certain that the nuclei involved in casting processes are heterogeneous, but their origins and natures are greatly variable. The shape and distribution of the crystals, and hence the properties of a casting are subject to considerable and controllable variation depending upon the constitution of the alloy being cast, the melt history and prior treatment, the thermal conditions in the mould and sometimes the mould material itself.

The change of state from liquid to solid is accompanied by the evolution of latent heat and a change in volume. Both the latent heat and the volume change must, during the solidification process, be transferred from the solidifying regions of the casting to a suitable sink. For latent heat this is ultimately the atmosphere or a cooling medium, with the mould as intermediary. For volume change the sink is generally a feeder head or a riser, but also sometimes the mould. The process of transfer of these by-products of solidification governs to a considerable degree the casting quality, and therefore its control is the business of the founder.

There is a considerable literature upon the above factors, and a number of good reviews have appeared.^{2,3,4} In this paper some important topics will be discussed; reference to background theory and other related subjects being made only in passing.

Understanding and control of the solidification and structure of cast metals is not naturally confined to castings as defined earlier, and although this paper is primarily concerned with solidification and structure of castings, some information and examples are included from ingot and billet production, and from certain other special spheres of solidification of particular relevance or interest.

CASTING CRYSTAL STRUCTURE

When liquid metal first enters a cold mould it is chilled at the interface, where numerous random fine crystals are nucleated, providing a thin layer of solid metal. Growth of the solid then continues inwards in a direction normal to the liquid isotherms in a uni-directional crystal growth mode, producing columnar crystals. Columnar crystals are generally considered to be a continued growth of those favourably orientated chilled surface crystals. Unfavourably orientated crystals will become suppressed. In pure metal castings the columnar crystals grow as a thickening skin with a substantially planar interface. Since heat is removed only from the surface of the casting the liquid will be hotter than the solid and there will be no incentive for further nucleation to occur in the interior of the casting. The columnar grains, therefore, ultimately reach the centre of the casting.

Impurities and alloying elements increase the freezing temperature range and, when the solubility of impurities is less in the solid than in the liquid, segregation of impurities take place into the liquid close to the growing interface. This makes possible a substantial super-cooling and a cellular or dendritic interface for the growing columnar grains. In the interior of the casting fresh nuclei become operative and an equiaxed region of crystals is favoured and may there replace the columnar crystal region.

Most metals shrink during solidification and the volume change is accompanied by a flow of liquid metal towards the solidified interface from the bulk of the liquid, the upper surface of which will consequently sink during solidification. The founder arranges for this surface to be in a feeder. If the metal expands, as is the case with bismuth, for example, then liquid will flow away from the interface and cause a rise in height of the top of the casting or the feeder surface.

If the metal shrinks and not enough excess liquid metal is available in the feeder there will finally be a region at the heat centre of the casting where a pipe, or void, exists along the centre-line intersection of the grains. The shape of pipes has been considered by Fell⁵.

During the columnar growth of crystals having a dendritic interface, solidification is continually occurring not only at the tips of the growing dendrites but also upon their side branches. Volume changes occur in these regions with a consequent flow of liquid into the inter-dendritic regions in most cases. If, for any reason, the flow of liquid metal fails there will be inter-dendritic porosity formed as an extension of the centreline pipe. If the solidifying metal involves an expansion then no such problem arises since the flow of liquid is outwards from the inter-dendritic channels.

The longer the freezing range of an alloy the longer will be the channels in the inter-dendritic regions, so that liquid flow during solidification will take place over a greater distance, and the concentration of impurities into the liquid will be greater. In longer freezing range alloys dendrites may stretch from the edge of the casting to the centre with liquid remaining between them for a considerable period before the casting is finally solid. Under these conditions there may be insufficient last liquid left to flow freely from one part of the casting to another, and widespread inter-dendritic porosity may result.

When equiaxed crystals form in the centre of the casting any contraction in volume accompanying solidification may be partly accommodated by settling of the crystals, or mass feeding. The finer these crystals, then the shorter the channels between them and the more easily mass feeding may take place, although any structural features hindering settling may lead to layer porosity.

Among the likely impurities in metals are the gaseous elements or elements which react together to produce gases. When these impurities are also concentrated into the last liquid during solidification the solubility or solubility product of the gaseous phases may be exceeded and bubbles produced. When this occurs in the inter-dendritic spaces the continuity of the remaining liquid is disrupted and porosity results.

Since the length of the columnar region is limited by the onset of multiple nucleation in the interior of a casting, the columnar crystallisation may be eliminated by deliberately promoting multiple nucleation in this region, and for some purposes such deliberate control of the structure of the casting is desirable, for example, to improve the distribution of shrinkage in long freezing range alloys or to achieve mechanical properties favoured by fine grain size. On the other hand, the properties of the casting are less directional when the grain size is fine, directional freezing to achieve localisation of solidification shrinkage in feeder heads may be more difficult and some properties, such as best creep resistance and magnetic behaviour, are best achieved with a coarse grain size, through avoidance of multiple nucleation.

In long-range freezing alloys of the solid solution type considerable coreing occurs. Last liquid may solidify at a considerably lower temperature than the first, and may solidify as a eutectic. In this case a new phase appears and requires fresh nucleation at some further degree of undercooling, in locations between the dendrite arms where the liquid will have remained throughout the casting. Eutectics are usually nucleated throughout a fairly broad region of the casting and grow in the undercooled last liquid in spherical colonies. There are some exceptions to this rule, notably in the metastable iron-carbide eutectic which grows in a columnar structure. Each eutectic grain or colony is itself surrounded by the last liquid which must be sucked towards the solid liquid interface to feed solidification contraction, for example, in lead-tin alloys, or pushed away from the solidifying eutectic front to accommodate its expansion, for example, in iron-graphite alloys.

There may be a further rejection of solute into the last liquid around the growing eutectic colonies, leading to a last low melting point liquid which will be in interconnected fine channels of very irregular form, often interrupted by dendrite arms remaining from the first stage of solidification. Shrinkage during the solidification of such last liquid poses a special feeding problem.

When considering grain size it is necessary to clearly distinguish between several different concepts. There is the grain size of primary crystals nucleated as columnar or equiaxed grains throughout the casting and generally having grown as dendritic colonies. The dendrites themselves have an arm spacing or cell size which is important when segregating impurities are present, in the control of mechanical properties. Super-imposed on the primary crystals size there may be a eutectic structure in which the size of the eutectic colonies is of importance. The dispersion of the eutectic constituents is a further feature of eutectiferous cast alloys and may be one which dominates the structure and properties of the casting, as in cast irons. Of these grain sizes only those of the primary crystallisation or of eutectic colonies are controlled by nucleation. Dispersion of dendrite spacing and eutectic constituents is controlled by growth considerations.

The general solidification process and its progress on a macroscopic scale in castings of simple shape has been studied by many workers using thermal analysis, pour-out techniques and quenching experiments.³

THERMAL AND MECHANICAL EFFECTS DURING SOLIDIFICATION In general, the lower the pouring temperature the finer the grain size both of the primary crystals and of any eutectic grains. High pouring temperatures favour columnar grain structures and in some cases a casting may be changed from a wholly columnar to a wholly fine grained equiaxed structure simply by lowering the pouring temperature.

The metal first entering the gates and the casting will be locally undercooled where it encounters the walls, and fine crystallites will be nucleated there and some of them swept around in a cloud by the initial turbulence of the metal as it fills the mould. At higher pouring temperatures most of these crystallites will be re-dissolved by the bulk of the metal still well above its liquidus, but at lower temperatures re-solution will be much slower and when the temperature is at or below the liquidus they serve to nucleate crystals throughout the casting, resulting in a fine equiaxed structure. At the lowest pouring temperatures this effect can be very pronounced and it has been referred to by some as the "Big Bang" effect. A striking illustration of nucleation in this way has been recorded in films produced by Jackson and co-workers using transparent organic materials.⁶

At the surface of a casting made in a metal mould the local high cooling rate leads to a thin layer of fine randomly orientated chill crystals, and those more favourably orientated continue to grow into the casting as a columnar region with preferred orientation along the directions of maximum thermal gradient. A chill crystal layer is not usually evident in sand moulds, though random crystal nucleation at the mould face still occurs, but has received less study. The extent of the columnar zone increases with increase in pouring temperature partly because of an increase in thermal gradients in the hotter metal, leading to less constitutional supercooling and therefore less chance of nucleation of fresh grains, and partly because in hot metal the crystallites formed in the early stages of mould filling are rapidly re-dissolved. The initial strong circulation of liquid also dies down in hot metal before nucleation temperatures are reached.

That fluid circulation is an essential feature of the distribution of multiple nuclei for the equiaxed zone has been discussed by Reynolds and Preece⁷ and demonstrated by a number of workers, whose work has been recently reviewed.^{8,9} Fig.1, due to Uhlmann and others,¹⁰ shows how suppression of fluid flow by means of a magnetic field promotes columnar crystallisation in Al-Cu alloys. Conversely, electro-magnetic stirring has long been known to refine the grain size of cast metals. Langenberg and co-workers,¹¹ developed the technique for stainless steels and it is illustrated in Fig.2.

Fluid flow also arises naturally by convection, as well as during mould filling, and may, in addition to circulating crystallites nucleated in the colder parts of the casting and equalising temperature gradients, cause mechanical fragmentation of the tips of growing dendrites and so produce more crystallites. This effect, suggested in a rudimentary way by Genders and Bailey,¹² has received considerable recent support¹³ and is generally considered to be a principal factor in nucleation of equiaxed grains.

Fragmentation of crystallites may not be solely a matter of mechanics, since Jackson and co-workers have shown that dendrite secondary arms may become detached through a remelting process in which the inter-dendritic liquid becomes so enriched in solute that it is able to re-dissolve part of the dendrite limb. This effect, too, has been illustrated on film for non-metallic transparent crystals, and seen for tin alloys directly by Schaefer and Glicksman.¹⁴

The top surface of a casting open to the atmosphere, or the open surface of a feeder head, cools very fast and acts in fact as a chilled surface.¹⁵ Early solidification in this top region can be a source of fine crystallites which become detached through liquid circulation and may provide a prolific source of nuclei. Southin¹⁶ has proposed that instead of the usual 3-zone concept of casting structure, containing respectively chill, columnar and equiaxed regions, a fourth, top crystallisation zone should be recognised in castings, as shown in Fig.3.

From time to time over the last 30 years workers have shown how, by vibrating a solidifying casting or its top surface, nucleation can be promoted by mechanisms which are thought now to be essentially multiplication by fragmentation of initially solidifying crystals. Other methods of agitation, such as by bubbling gases through the casting during the early stages of solidification, have been shown to have a similar effect.⁸

Crystallites circulating through the liquid may become entrapped in the columnar zone and, under unfavourable thermal conditions, not give rise to new equiaxed grains nor cause the columnar zone to cease growth. When they do they have been distinguished by a characteristic elongated shape and referred to as "comet" grains. A particular example in zinc has been illustrated by Southin⁸ (Fig.4.)

More recently even the mechanism of formation of the fine chill crystal zone at the casting surface has been re-examined by Bower and Flemings¹⁷ for ingots made in metal moulds. They showed that fluid flow plays some part in causing the large number of small chill crystals formed and that by application of a static magnetic field in the initial stages of solidification the number of chill crystals was greatly reduced. They inferred that these crystals originated in a process of crystal multiplication and circulation of liquid along the mould wall in the first stages of solidification.

Irrespective of the above effects, the grain structure, be it columnar or equiaxed, becomes coarser the slower the solidification rate of the casting, so that high pouring temperatures, and large castings have coarser grain structures. In precision castings heated moulds cool slower and have coarser grain structures as the mould temperature rises. Fig. 5 illustrates some of these thermal effects in castings made in precision moulds.¹⁸

Columnar crystals may bend and slope in a variety of ways and have been shown to lean towards the direction from which any liquid flow originates. All these effects may probably be explained in terms of the crystals growing with preferred maximum growth direction normal to the isotherms in the liquid.

Eutectic colonies seem to be influenced by thermal conditions in much the same way as equiaxed primary grains. Low pouring temperature increases their number throughout the casting, as shown for cast iron in Fig. 6¹⁹. Vibration during solidification has been shown to increase the eutectic colony number in poorly nucleated cast iron sufficiently to change a magnesium-treated white cast iron into a graphitic spheroidal graphite iron^{20,21} but Stubbs²² has shown that the final number of colonies after vibration of a given iron is constant for the particular treatment and composition, and may be lower than that obtained without vibration when the melt has previously been well nucleated by an inoculating addition. It would be interesting to study the inter-relationship of the effects upon grain size of vibration and deliberate nucleation by addition of a nucleant for other metals. Vibration has been used both at low and ultrasonic frequencies for grain refinement of metals, for example in permanent moulds, but its use is restricted by practical problems.

Dendrite arm spacing is of importance to mechanical properties, especially when the solidification range is long and inter-dendritic segregation pronounced. Its fineness is influenced by alloy constitution (Fig.7) and by solidification rate, and hence by factors such as mould thermal properties and pouring temperature in as far as they influence solidification rate^{23,24}. Fig.8 illustrates this feature²⁵. A relationship of the form

$$Y = 0.002X^{-.337}$$

Where X = solidification rate in °F per sec., and

Y = cell size in inches,

was found by Spear and Gardner²⁴.

Much literature has grown up on gating, on thermal analysis of solidifying castings and on risering and feeding. Obviously, the casting design and the way in which liquid metal is introduced into the casting, as well as the placing of feeders and chillers, will influence the overall temperature of the metal in the castings, the variations in temperature and cooling rate from place to place and the convected flow of metal within the casting. A great deal of this literature has been reviewed by Ruddle.³

With the exception of ingots in which top or bottom casting influences segregation patterns, little attention has been paid to the measuring of thermal effects of using different runner systems in sand castings. These are usually designed on the basis of cleanliness of metal and freedom from turbulence or entrapped air, yet their influence on casting structure is of great importance. Many articles on foundry practice contain advice on the location of gates and feeders to achieve directional or uniform solidification or a controlled graduation of structure.

GRAIN SIZE CONTROL BY ADDED NUCLEANTS To be able to add to the liquid metal before casting a powerfully nucleating substance to achieve a fine macroscopic grain size in the casting, irrespective of melt history, casting temperature and mould conditions, is an

attractive objective for foundrymen. Cibula^{26,27} postulated that to achieve nucleation most effectively by this means throughout the casting it would be necessary to combine a supply of nucleating particles with a soluble alloying addition; the particles acting as a nucleating substrate should have a low interfacial energy with the solid phase which they nucleate, which may arise because of a similar lattice spacing or because of some affinity such as compound formation. The function of the alloying addition would be to promote supercooling through being less soluble in the solid than the liquid, and so restrict grain growth, thus favouring nucleation. A further mechanism of nucleation may be the promotion by the additive of a peritectic reaction, creating the facility for higher temperature nucleation of the primary phase. A well-known example of this latter mechanism is the nucleation of certain magnesium alloys by zirconium. The effect of an added nucleant may be very powerful, and an example is shown in Fig.9.²⁸

There have been some excellent recent reviews of nucleating additions for grain refinement,^{29,30} and the practice is widespread throughout the foundry world where it is often carried out with great consistency, though with a good deal of technical skill, especially since many of the nucleating additives consist of complex substances and proprietary mixtures supplied by companies peripheral to the industry. Table 1 contains a list of some of the nucleating additives which have been claimed to produce most powerful effects upon the primary structures in casting alloys. Nucleants for eutectic grain structures are mentioned, though these are specifically referred to again later.

One might reasonably expect that for most potent nucleation the nucleating additive providing a substrate would do so in the finest and most concentrated dispersion through first dissolving, and then by precipitation of a compound, as in the addition of titanium-rich fluxes to magnesium and aluminium alloys. Similarly, refinement of copper alloys by iron probably involves precipitation of iron-rich crystals as nuclei during cooling prior to solidification. At the same time, if the additive is soluble, an excess over that needed to precipitate the nucleating compound may function as an alloy to promote constitutional supercooling. Nucleating additives of this kind may remain in the alloy and have their effects even after remelting. This effect has been variously referred to as the recollection or heredity effect.

Although in Table 1 some suggestions are made concerning the compositions or natures of the nuclei in certain cases, this has been a subject of controversy for many years and still poses one of the principal uncertainties in the modern understanding of the solidification process. Nuclei can seldom be expected to be large enough to be easily isolated for identification. Experimental techniques have often involved centrifuging or otherwise segregating, followed by chemical analysis of the unsegregated and segregated regions to determine the segregating elements or compounds. In some cases there may be statistical evidence of a particular grain refining process leading to more than one kind of nucleus, as shown by Emley²⁹ in Fig. 10. In magnesium and aluminium alloys coring of the grains may occur and the central "pips" examined and analysed. For example, in aluminium-titanium-boron alloys a core of Al_3Ti has recently been detected.³¹

Campbell³² has demonstrated impressively the grain refining effect of titanium boride powder additions to 3 per cent silicon-iron, electro-slag remelted to preserve very clean conditions. The addition of titanium oxide alone caused some refinement, but titanium boride (TiB_2) produced a very fine grain, as shown in Fig.11. The number of grains nucleated was often 10^3 more than the number of TiB_2 particles added, so that it was postulated that the added particles dissolved and re-precipitated TiC or TiN as a fine nucleating dispersion, the boron acting as an alloy to promote constitutional undercooling. Fig.12 shows in more detail the potent grain refinement achieved by addition of TiB_2 .

Once the primary phase has been nucleated and begins to grow, any of the crystal multiplication processes already discussed may operate. In some cases the phase being nucleated can be promoted by a powder addition of the same phase, though this seldom proves to be a very potent effect, as might be anticipated, since the addition would be expected to dissolve and not re-precipitate as a fine dispersion. However, graphite, added to grey cast iron, is a very potent nucleant for the eutectic grains which are thought to originate by nucleation of the graphite phase. One explanation for this could be that the added graphite may suffer from a crystal fragmentation process during dissolution, the fragments being then carried around the casting by fluid flow and promoting crystal nucleation.

An interesting feature of the nucleating substances tabulated lies in the frequency with which the transition metals, such as titanium and iron, recur as nucleants for several

metals, as well as the other strong oxide and carbide formers. Carbon also features in magnesium and aluminium nucleation. A comprehensive range of substances has been established as potent nucleants for magnesium alloys.^{29,33}

One of the more difficult primary phases to nucleate has proved to be austenite in iron and steel. In spite of reports that titanium will nucleate low alloy steels and that bismuth will nucleate austenite in white cast irons, these effects are probably limited to special cases. Most success has been achieved in highly alloyed austenitic steels, in which titanium may have some useful effects, but considerable refinement has been produced by calcium cyanamide, high nitrogen ferrochrome or by powders containing, for example, titanium, niobium and zirconium, introduced as additions in the presence of increased nitrogen content.²⁸ Hall and Jackson have suggested that the function of the increased nitrogen content is to retard the solution of nitrides formed by the powdered addition, which act as substrate nuclei, while added elements such as zirconium, niobium and vanadium also act as alloys restricting grain growth.

The successful use of powder additives involves overcoming practical problems of their incorporation into liquid metal. On the other hand, some authors have claimed success in introducing steel powder into steel to produce grain refined castings by the technique of micro-chilling.^{34,35} Berry³⁶ has reviewed methods for grain refinement of high speed steel castings, where the need to produce a fine dispersion of constituents, especially carbides in the interdendritic spaces, is of great importance to performance.

Emphasis is generally laid on a sufficient addition of the grain refining substance to produce the desired fine grain structure, but a relationship between the amount of addition and the fineness of the grain size produced may be expected. Fig.13 illustrates such a relationship for silicon inoculation of grey cast iron eutectic grains.³⁷ Similar, though logarithmic, relationships are observed between titanium content and grain size in aluminium alloys,³¹ and between zirconium content and grain size in magnesium alloys.³³

Although successful grain refinement by a late addition of added nucleant will override effects of pouring temperature or previous history, there is still usually some effect of such variables, though for the best nucleants in practice it may be negligible compared with the unrefined condition. Figs.14 and 15 illustrate the consistency of grain size achieved with good nucleants.³⁰ In general, the effects of a nucleant will fade on holding the liquid metal before pouring, or superheating the liquid metal after making the addition, and also on remelting the alloy. Fig. 16.³⁸ illustrates time-temperature relationships for cast iron eutectic grain number. Agitation of the liquid metal by bubbling gas through it often reduces or removes the grain refinement effect of a nucleant, for example by bubbling nitrogen or chlorine through titanium-nucleated aluminium alloys or bubbling many gases through cast iron. Much of the progress in nucleating additives has been aimed at making them resistant to the effects of holding time and temperature and in some cases to remelting, and several examples have been mentioned above.

One of the most interesting grain refining processes is the superheating of magnesium-aluminium alloys containing a trace of carbon, which has a most potent effect due, it has been suggested, to aluminium-carbide formation, though the evidence may imply alternative, or more complex possibilities.³³ Fig.17 illustrates the effect.³⁹ Even for these alloys however, prolonged heating and excessive temperature cause grain coarsening.

In a number of non-ferrous systems poisoning or neutralisation of nucleants can occur, for instance by elements combining with zirconium in magnesium-zirconium alloys or with carbon in aluminium alloys. Nucleants may also be limited in the ranges of alloy compositions in which they are effective and there is always interest in developing substances which overcome these limitations. For example, zirconium additives have been developed which are effective over a wide range of tin contents in tin bronzes.

CONTROL OF GRAIN STRUCTURE BY MOULD TREATMENT The possibility of deliberately influencing grain structure of cast metals by treatment of the mould was envisaged by Reynolds and Tottle,⁴⁸ who applied a number of metal powders to the surface of small sand and metal moulds and thereby achieved marked grain refinement of a number of metals cast into them. Some of their results are summarised in Table 2, and Fig.18 illustrates the degree of refinement achieved in aluminium cast into a mould, the surface of which was coated with titanium powder. Three main classes of substances were suggested as effective for this purpose; namely, powder made from the metal being cast, which nucleated by a simple mechanism of providing small fragments on which growth occurred. Powders made from a metal having some degree of similarity of lattice spacing with the metal being cast, which could

act as a substrate for growth, and thirdly a reactive substance which would decompose the oxide skin on the metal being cast and precipitate fine particles of that metal on which further growth could occur. Generally, the size of Reynold's and Tottle's castings was not great enough to reveal how deeply the effect could be felt, but Cibula³⁰ has suggested that, being a mould surface epitaxial effect, the grain refinement would essentially be confined to near-surface regions.

On the other hand, Genders and Bailey¹² reported that coating a mould with a volatile dressing produced extensive grain refinement in small brass ingots, as is shown in Fig.19. This effect is explainable in terms of modern views on mechanical crystal fragmentation and dispersion of fragments throughout the melt to provide a source of nuclei for equiaxed crystals.

In castings of superalloys, for high temperature turbine components, the requirements of fatigue resistance, good machinability and freedom from hot tears has led to a need for a means of producing fine equiaxed crystal structures. This has been particularly difficult to achieve by thermal means since most of the castings in question are precision cast in heated moulds. A technique very similar to that explored by Reynolds and Tottle has been developed for such castings⁴⁹ by which various substances based upon cobalt, iron and nickel in metallic or compound form have been found to be effective when incorporated in the surface layers of the mould, and it has been claimed that oxides and other compounds, when used in this way, may be reduced either to the metal or oxides which are most effective nucleants during processing of the mould prior to casting.

Particularly successful has been cobalt aluminate (cobalt blue colour), which may be combined with the first dip-coat applied to wax patterns used to produce precision moulds. This process has been described by Feagin⁵⁰ and has been successful for a range of cobalt and nickel-based alloys, and Table 3 refers to some of the mould coatings which he has found most potent.

Fig.20 shows a section through a precision mould for casting small turbine vanes and reveals the dark interior which is composed of a zircon-based dip coat containing 4 per cent of cobalt aluminate. Fig.21 shows vanes made with such a coating and those made using a plain zircon coating with their surfaces etched to disclose the grain size, which was considerably refined by the cobalt aluminate.

Although some claims have been made from time to time for melt additions which could be made to white cast irons to refine the primary austenite grain structure, no substance has yet been found which will consistently do so. Until recently only control of the pouring temperature has been found to influence greatly the characteristics of this structure in ordinary commercial castings. Bryant and Moore⁵¹ have shown, however, that cobalt metal powder applied to the surface of the ordinary sand mould or core will cause a powerful refinement of the grain structure. The effect is most potent at the surface but extends throughout castings up to 2 or more inches thick. This effect is of great practical significance since it is associated with the elimination of fine hot tears or checks when the coating is applied to the point on the mould where they occur. Micro-probe analysis has shown that the effect is associated with dispersion of cobalt throughout much of the casting, suggesting a mechanism involving epitaxis, melting of dendrite arms and circulation of dendrite fragments. Thermal analysis has shown that the solidification sequence at the surface in treated moulds is associated with more rapid skin solidification when a cobalt coating is applied.

The commercial importance of the development of mould coatings for iron castings necessitates the use of a cheaper substance than cobalt, and zinc-containing coatings have been developed^{52,53} which are at least as potent. Fig.22 shows the effect of such a coating on white iron dendrite structure. The coating may be applied by spraying or by painting critical portions of sand cores.

As might be expected, refining the dendrite grain size of cast irons improves the soundness of these relatively long-freezing range alloys. Cobalt coatings have this effect on both grey and white irons though not chromium-containing white irons which solidify with primary dendrites. On the other hand, zinc-containing mould coatings have been found to refine chromium-containing white irons solidifying as either primary austenite or ferritic dendrites.⁵³ It seems probable that the grain refinement effect of zinc-containing mould coatings depends at least in part on some surface agitation of the metal due to volatilisation of zinc, so that grain refinement may be due, in part, to an effect similar to that demonstrated by Genders and Bailey, which would explain why both ferrite and austenite grain structures can be nucleated using this substance.

It has also long been known that tellurium metal powder, used in mould coatings, can be used to improve local soundness of grey cast irons.⁵⁴ The effect of tellurium used as a mould coating in this way is shown in Fig.23. Tellurium in the presence of hydrogen (from water present in most kinds of sand mould) is a powerful carbide eutectic promoter⁵⁵ and produces a thin white iron layer on the extreme casting surface, visible in Fig.23, which has been assumed to be in some way responsible for the effect. Tellurium mould coatings do not have a grain refinement effect upon the dendrite structure⁵⁶ so that the reason for their effect remains obscure. More recently bismuth, which in many respects behaves similarly to tellurium, has been developed as a basis for mould coatings to improve local soundness in grey iron castings,⁵⁷ and such a mould coating, containing metallic bismuth does, in fact, have a small dendrite refining effect.

On an experimental scale it has been possible to practically eliminate the nucleation of metals by the mould walls through containing the solidifying metal in a liquid glass layer.⁵⁸ When no reaction between the glass and the metal occurred very considerable undercooling resulted, partly because of the lack of nucleating substrate at the walls and partly, it is postulated, through absorption of heterogeneous nuclei by the glass, and undercooling approaching that for homogeneous nucleation was observed. No practical use of this practice seems yet to be in sight.

CONTROL OF EUTECTIC STRUCTURE The microscopic appearance of eutectics, and their mechanical properties, are usually dominated by the dispersion and shapes of their individual phases. Attempts to classify eutectics according to the structures which they exhibit and the way in which they are thought to solidify have produced a considerable literature, much of which has been reviewed by Chadwick,^{59,60} by Rumball and Kondic⁶¹ and by Hogan, Kraft and Lemkey⁶². In most metal/metal eutectics the phases grow as more or less regular lamellae, but in some cases one phase is present as rods or more complex shapes. Eutectics grow in colonies which, in castings, are nucleated, usually at sites ahead of the growing solidification interface, and on nuclei which may be one of the primary phases of the eutectic or some other substance,⁶³ but about which relatively little is clearly known. The size of the eutectic colonies is governed by the number of operating nuclei and this is an essential feature of the structure of the eutectic alloys. An instance when eutectic colony structure becomes obvious is in the lead-tin eutectic when this alloy is cast as sheets of "spotted metal" used for making organ pipes, shown in Fig.24. It is easy to verify that the number of colonies increases for a given alloy with increased cooling rate.

Within each eutectic colony the dispersion of the phases is related to frequency of branching and it is becoming accepted that all regular eutectics,⁶⁴ and perhaps even those having irregular shaped phases, are wholly interconnected within each colony. The dispersion of the phases, and hence the fineness of the eutectic structure, depends upon alloy composition, and also on rate of growth which is illustrated by Fig.25. This relationship for the lead-tin eutectic,⁶⁵ is of the general form $\lambda = AR^{-n}$. Growth rate, in turn, is related to undercooling resulting from the cooling rate of the casting.

With strong undercooling, especially when the alloy contains impurities, the colony interfaces may breakdown to solidify with a cellular interface yielding a sub-structure which, while very well documented for controlled directional solidification, is not well recorded for castings.

The two most important commercial eutectic systems are based upon the aluminium-silicon and the iron-carbon (graphite) systems, each of which has one phase appearing as irregular non-metallic particles. Considerable recent progress has been made in understanding and controlling each of these systems.

Aluminium-silicon alloys The silicon phase in aluminium-silicon eutectic alloys normally appears as irregular, angular plates, long regarded as separate from one another and arising by repeated nucleation. More rapid cooling leads to finer structures, and very rapid cooling to a very fine structure which, under the light microscope, appears to contain silicon in the form of fine granules. Sodium modification produces a similar structure at slow cooling rates, and this structure has improved strength and ductility. Modification leads to undercooling of the eutectic temperature at a given cooling rate, but how far this can be regarded as consequent upon a change in nucleation or of growth conditions has been disputed. The literature on this subject has been summarised by Smith.⁶⁶

Following the work of Ghosh and Kondic,^{67,68} Bell and Winegard⁶⁹ and of Day,⁷⁰ it is now becoming clear that in both unmodified and modified aluminium-silicon alloys the eutectic silicon plates are wholly interconnected within eutectic colonies. The interphase

spacing is governed by solidification rate in a manner similar to that of other eutectics. The relationship found by Day⁷¹ for directionally solidified alloys was $\lambda = AR^{-0.56}$. Truly convincing evidence for this view of the structure has had to await the study of deeply etched samples by the scanning electron microscope, illustrated by Figs. 26 and 27. In the modified alloys the silicon crystals are obviously heavily branched and no longer angular in appearance.

The eutectic colonies themselves are usually difficult to reveal in microspecimens, but Day,⁷² by alloying with copper, has been able to delineate them through segregation of the Al-Si-Cu Al₂ ternary eutectic, Fig. 28. The copper containing alloys, which behave, and may be modified with sodium, in the same way as aluminium-silicon alloys, enabled a plot of colony count against cooling rate to be made, as shown in Fig. 29. Sodium modification, while increasing undercooling and producing a much finer dispersion of eutectic silicon, does not influence the number of colonies. From these observations Day was able to conclude that the effect of sodium is not to influence the nucleation of the melt but to cause a change in the growth process. The observed depression of the eutectic temperature by sodium is thus that required to drive the growth process in the modified alloy at a given cooling rate.

Sodium modification is not preserved on re-melting and fades quite quickly after the addition. Non-fading modifying additions are, therefore, of great concern. A number of other metals of the alkaline and alkaline earth groups are known to be effective modifiers, and of these strontium seems to have the greatest promise as a non-fading modifier.⁷³

Directional solidification studies⁷⁰ have shown that in slowly grown unmodified alloys silicon crystals have strongly preferred [100] growth directions and are occasionally [111] twinned. Increased growth rate involves an increase in twin density, and sodium modification was shown to have a similar effect. It may be concluded that the increased twinning is responsible for the ability of the silicon phase in modified alloys to assume the branched, fibrous form. Sodium also modifies the structure of primary silicon crystals in hypereutectic alloys, causing them to assume a compact, rounded outline and finally, when about 1 per cent of sodium is present, a spherulitic form with a clearly defined radial structure which may be seen in polished and etched microspecimens. Fig. 30.⁷⁴ shows such a structure. The eutectic silicon, though modified as described above, does not become spherulitic in such alloys. Fig. 30 also shows the presence of large NaAlSi particles. Day has suggested that the spherulitic silicon crystals also contain a high twin density and that it is the ability to produce multiple twins which makes possible the growth of the spherulites.

Grain refinement of the aluminium-silicon eutectic by deliberate nucleating additions will, according to the above picture, lead to an increase in eutectic colony number, and not, as has often been assumed, to a direct decrease in size of silicon particles. The nucleation of these alloys has been discussed by Crosley and Mondolfo⁷⁵ who have noted that an AlP is a nucleant for primary silicon and that NaAlSi may form a suitable substrate in very high sodium alloys. There is little recorded information, however, on nucleation of eutectic colonies, presumably because of the difficulty of revealing them. Phosphorus additions have a well known potent nucleating effect on primary silicon in hypereutectic alloys⁴⁷ which is of great importance in producing finer and more uniform structures in alloys which have been developed for automobile engines, but evidence of whether phosphorus additions will increase the eutectic colony number is lacking.

Cast Irons For practical purposes cast irons may be regarded as alloys based upon the binary iron-carbon eutectic, though the constitution of alloyed cast irons may become very complex. In the stable iron-carbon system the carbon in the eutectic is present as graphite, and the metastable iron carbide-containing eutectic occurs as a consequence of undercooling resulting from inadequate nucleation or growth of the stable eutectic structure.⁷⁶ Since 1953^{77,78} it has been clear that the graphite eutectic is wholly interconnected within eutectic colonies. Cast iron metallurgists have referred to these colonies as eutectic cells for more than 30 years, but this nomenclature must not be confused with that describing substructures resulting from a cellular interface during solidification. Such a substructure can occur in iron-carbon alloys and it has been described by Lakeland.⁷⁹ Segregation of impurities to colony boundaries usually makes it possible for eutectic colonies to be easily observed and counted in cast irons, and this number has an important influence on soundness, which improves as the number decreases.⁸⁰ Fig. 31 shows the increase in colony number with increased cooling rate and may be directly compared with Fig. 29 for aluminium silicon alloys.

Much is known about controlling the number of eutectic colonies by deliberately added nucleants (referred to as inoculants). The most potent of these is graphite itself, but alloys of iron and silicon, containing aluminium, calcium or various other alkaline earth and rare earth elements, are also very effective. Their behaviour is complex since some minor element combinations promote nucleation while others do not.⁸¹ The significance of the minor elements in silicon-based inoculants has been discussed by Lux,⁸² who has proposed that salt-like carbides, such as Al_4C_3 , may act as a nucleus for the graphite phase, and if this is so they would appear to fulfil Cibula's proposal that a nucleant should contain both a nucleating substance and an alloying element which would promote undercooling (in this case the carbide-forming minor element and the silicon respectively). As with nucleants for other systems, the need is not only for the most powerful additive, but also for one having persistence, and recent improvements have concentrated upon the minor elements strontium for maximum effect and barium for minimum rate of fade. Most potent inoculation has been achieved by adding the inoculant actually in the mould or the sprue.⁸³

Increasing the rate of growth of the iron-carbon eutectic tends to decrease the dispersion of the graphite, and this is promoted by a decrease in sulphur content, as is shown in Fig. 32. Sulphur may also be neutralised by titanium additions to achieve a similar fine structure. When the sulphur content is below 0.01 per cent it is very difficult to obtain coarse graphite in castings. In directional solidification experiments yielding results similar to those in Fig. 32 the relationship between dispersion and growth rate is similar to that expected for other systems; it has been reported⁸⁴ that $\lambda = AR^{-n}$ where n lies between 0.3 and 0.4.

At even lower sulphur contents, below 0.002 per cent, and with rapid cooling a change to a very fine graphite structure occurs. This form of graphite, when examined in deeply etched samples using the scanning electron microscope, is seen to be in the form of fine, branched fibres,^{85,86} as shown in Fig. 33. It has been termed 'coral' or 'fine vermicular' graphite. The similarity between the structure shown in Figs. 33 and 27 for modified aluminium-silicon alloys is striking. Each of the structures is favoured by rapid cooling, each has conferred strength and ductility on the alloy, but the fine graphite structure presents practical production difficulties which, as yet, have prevented it from becoming a commercial product.

The characteristic structures of grey cast irons and other alloys containing graphite in eutectic flake form, for example, cobalt-carbon, nickel-carbon, platinum-carbon and uranium-carbon alloys, are due to the fact that graphite lamellae have a considerable ability to bend and branch, unlike silicon crystals in unmodified aluminium-silicon alloys. It has been shown^{87,88} that in nickel-carbon alloys graphite sheets are composed of crystallites which are related to one another by rotation twins. Day⁸⁴ has further explored the structure of graphite in cast irons and has revealed similar structures in them. Figs. 34 and 35 show substructures in flake graphite and it is apparent that misfits between the crystals are the source of bending of the graphite flakes and, it may be postulated, of branching. The known ability of graphite flakes to curve with a smaller radius and to branch more frequently in finer structures may be related with the observation that as the solidification rate increases the crystal substructure becomes finer. Thus, the external structure of graphite appears to be governed by its internal structure. The ability of elements such as sulphur to modify the graphite structure may, therefore, stem from their influence on the fineness and degree of misfit of the elements of the substructure.

Spherulitic graphite results when magnesium, cerium or a variety of other alkaline earth and rare earth elements are present in cast iron. By analogy with silicon spherulites in aluminium-silicon alloys it may be that graphite in spherulites has a high density of growth mistakes and a particularly fine crystallite substructure. Perhaps magnesium, or other elements, have their effect through promoting multiple growth mistakes in this fine substructure. Contrary to some suggestions it does not, therefore, seem that spheroidisation of graphite by magnesium is directly analogous to modification of eutectic silicon by sodium. Strong desulphurisation without adding magnesium may, however, produce an effect analogous to modification of aluminium-silicon alloys.

Each graphite spherulite, together with its surrounding austenite, is a single eutectic colony and the number of these varies with rate of solidification in the same way as for eutectic colonies already described.

The need to examine eutectic microstructures in three dimensions in order to evaluate them correctly is further emphasised by recent work on improvements of the strength of grey

cast irons. Nitrogen additions cause rounding of the edges of the graphite flakes and a reduction in their area of spread, which provides an appreciable increase in strength but cannot be detected microscopically. The scanning electron microscope clearly reveals the changing structure in deeply etched samples, as shown in Fig.36.^{84,89}

Other Alloys There have recently been a number of papers showing^{90,91} how eutectic structures of complex alloys containing eutectic carbides can be varied in ways which cause the carbides to become more compact or dispersed in compacted forms. Most of the additives claimed to do this have been present in amounts of several percent and similar effects have long been known in iron-chromium-carbon alloys.

THE PRODUCTION OF CRYSTAL-ORIENTATED STRUCTURES Permanent magnet alloys, based upon nickel or cobalt, together with major amounts of iron and several other metals, have the highest coercive force and other desirable properties when the grains are uniformly orientated with respect to the magnetic axis. Great attention has, therefore, been paid in recent years to the directional solidification of such alloys to achieve a columnar structure with the $[100]$ growth direction deliberately aligned within the casting.

A simple approximation of directional solidification can be achieved by incorporating a metal chiller at the base of the mould, and steeper temperature gradients can be promoted by a large hot feeder head at the top of the casting, or by a heated mould, or both. In this way a number of simple alloys may be made to solidify with columnar structures. This practice has been applied not only for magnetic purposes but also to achieve improved impact and fatigue strength and other properties in steel.^{92,93}

Most magnet alloys, however, contain several percent of titanium as well as aluminium. When this combination is present the alloys are very resistant either to the growth of large equiaxed crystals or to the formation of columnar crystals.⁹⁴ This may be an example of a combination of constitutional supercooling in highly alloyed material, together with the effect of titanium-rich nuclei such as oxides and nitrides, and the subject has been discussed by Palmer and Shaw.⁹⁵ Harrison showed that the addition of such alloys to sulphur,⁹⁶ selenium⁹⁶ or tellurium⁹⁷ in amounts in the range 0.2 to 0.8 per cent greatly facilitates the production of columnar crystals in simple directional solidification mould arrangements. Sulphur is more effective when a small amount of carbon is present or when the alloy is vacuum melted, and indeed, vacuum melting can promote columnar crystallisation in alloys containing 5 per cent titanium or less.⁹⁵ These effects seem to depend upon the removal or neutralisation of titanium-rich nucleating compounds, and Palmer and Shaw have illustrated sulphide inclusions which appear to have absorbed small particles which may have otherwise constituted nuclei. Nevertheless, the behaviour is not entirely straight forward and they showed that the effect of sulphur was most pronounced when it was added as a late addition and that there was an advantage in holding and superheating a metal for a period after its addition. Figs.37 and 38 illustrate the effect of sulphur.

Zone melting has also been applied as a means of producing highly orientated columnar crystals in magnet alloys.⁹⁸

Although a fine equiaxed structure is favoured by many for turbine vanes, when high temperature creep resistance of the alloy is paramount it is desirable to avoid transverse grain boundaries, and a number of workers, notably Pearcey and Versnyder,^{99,100} have developed methods for producing castings in high temperature alloys with wholly columnar grain structures. Erickson and co-workers have further refined the technique.¹⁰¹ Such alloys are normally cast in heated precision moulds and the technique of directional solidification has progressed from standing the mould on a mould chiller to passing the mould slowly from a heated chamber into a cool chamber with quite elaborate temperature gradient control. Fig.39 illustrates a casting arrangement and Fig.40 shows etched directionally solidified turbine vanes. By appropriate selection of crystals of correct alignment in the lower part of the mould the technique can be developed to achieve single crystal castings with no grain boundaries, which are claimed to have the best properties for high temperature turbines.¹⁰² Fig.41 shows the cross-section of a vane with dendrite wholly orientated as a single crystal. Bower and Flemings¹⁰³ have pointed out that by extending the principle of direction solidification, poly-crystals having preferred orientations in two dimensions can be produced, for simple castings.

The control of directional solidification of eutectic alloys has now been a popular laboratory study for more than a decade, though the tendency to supercooling and loss of directionality of eutectic structure has made the experimental requirements somewhat

exacting. Even under moderate production temperature gradients most eutectics prefer to grow as more or less spherical colonies with repeated nucleation ahead of the growing interface. A common exception to this rule is the iron-carbide eutectic which readily grows in a columnar crystal form in castings, but its structure normally shows cellular degeneration, as was shown by Wilkinson and Helawell.¹⁰⁴

When eutectics are grown with their lamellae parallel throughout the casting, the mechanical properties in the axial direction will be different from those in the transverse direction. Lemky and co-workers,¹⁰⁵ and later Crossman and co-workers,¹⁰⁶ have shown that CuAl₂-Al single grain eutectic has a maximum strength in the direction of the lamellae.

Certain eutectics, notably some of those having a low volume fraction of one phase, can be made to crystallise with that phase in a rod-like form. The possibility that such eutectics could be grown directionally to produce a fibre strengthened structure was recognised by Lemky and co-workers¹⁰⁷ who found that Al-Al₃Ni grown in this way, and illustrated in Fig.42, showed a strengthening factor of three times in the axial direction compared with randomly orientated crystals. The best chance of developing a fibre-strengthened alloy by the growth of a rod-like eutectic would be where the rod-like phase is one having an inherent high strength. Carbides may satisfy this requirement and Lemky and co-workers¹⁰⁸ have shown that Ta₂C and Nb₂C carbides in eutectic structures can be grown in a rod-like form to achieve strengthening of 2 or 3 times compared with that of the non-directional alloy. Fig.43 shows carbide rods in a Ta-Ta₂C directionally grown alloy. These workers showed that on single directional solidification the carbides appeared as blade-like crystals, but after several recrystallisations the rods were obtained. More recently it has been shown how cobalt-chromium carbides can be grown directionally as rods with a matrix of cobalt,¹⁰⁹ in cobalt chromium-carbon alloys.

The possibility of fibre-strengthening castings has also been considered on the basis of casting the metal around fibres previously placed in the mould. The process may be carried out by continuous casting or by infiltration under pressure,¹¹⁰ and the fibres may have to be specially treated to enable them to be wetted by the metal.¹¹¹ Carbon fibres have been introduced in aluminium alloys in this way, and Fig.44 shows carbon fibres in an aluminium alloy.¹¹² Cooling channels are created in turbine vanes for use at high temperatures by inserting fine tubes of silica or metal in the precision moulds prior to casting. Silica tubes are subsequently removed from the solid casting by reaction with caustic soda or pickle liquids containing hydrofluoric acid.

SEGREGATION, STRUCTURE AND MOULD DIMENSIONAL STABILITY Segregation is a feature of the solidification of all cast alloys and arises during solidification when the solubility of impurities and deliberate alloying elements is different in the solid from that in the liquid. Flemings and his associates¹¹³ have defined the segregation ratio as the ratio of maximum to minimum content of an alloying element during dendritic solidification measured across a maximum distance of one dendrite arm spacing. Generally, this ratio depends upon the dendrite arm spacing, which is independent of macro grain size, although in some cases grain refinement can be so potent, for example in magnesium-zinc alloys, that the grain size is reduced below the dendrite arm spacing^{114,115} so that grain refinement actually reduces the segregation ratio in these alloys. Increased undercooling before solidification decreases dendrite arm spacing and so promotes a low segregation ratio.¹¹³ (See Fig.45).

During solidification, flow of liquid between the growing dendrites will lead to concentrations of solute not only in inter-dendrite arm locations but also in inter-grain boundary regions, giving heavier segregates there, which increase in severity with increased grain size. These grain boundary segregates become more severe in heavy castings where grain refinement normally reduces their severity. For example, Jolley and Gilbert¹¹⁶ have illustrated how chromium and manganese segregate in this way in heavy-section spheroidal graphite iron castings where there is difficulty in producing a sufficiently high graphite nodule number, (eutectic grain number). This subject has received much attention recently, since the availability of the micro probe analyser has enabled a great deal of information on segregation to be obtained.

At the end of freezing in long range freezing alloys, and in eutectics solidifying at a fairly high degree of undercooling, the last liquid is likely to be distributed widely throughout the casting, in inter-connected channels. The liquid in these channels may solidify at a much lower temperature than the surrounding solid and will outline the grains. Three-dimensional radiography¹¹⁷ has demonstrated the continuous channels of tin in aluminium-tin alloys, as shown in Fig.46. Emley¹¹⁸ has shown a similar network of last liquid by radiography of magnesium alloys, while Nicholas,¹¹⁹ using deep etching techniques

and stereo-micrography, has illustrated networks of phosphide eutectic in spheroidal graphite cast irons. The free flow of such low-melting point liquids is demonstrated by the ease with which tin sweat can occur on bronzes and phosphide sweat can occur on cast irons, giving rise to extreme examples of inverse segregation. Fig.47 illustrates phosphide sweat on cast iron.¹²⁰ The long period for which the last low-melting point liquid can exist throughout the entire casting in fine channels before solidification is clearly shown by diagrams relating progress of freezing with time throughout a casting. Fig.48 shows such a diagram for a phosphoric grey cast iron.¹²¹

The extent of the literature on inverse segregation is a clear indication of the fascination which this subject has held for metallurgists, though today the subject is fairly clearly understood. Following the work of Masing and Haase, Adams¹²² produced a very credible account of the phenomenon and recent articles have shown how the segregating elements progressively build up in the last liquid, and during the time when the casting is nearly completely solidified and contracting this liquid may be caused to flow outwards from the interior through the fine network of channels already existing.^{123,124} In commercial castings exudation of low melting point last liquid, including eutectics, may appear all over smooth surfaces, but may be particularly concentrated into re-entrant angles and near to hot spots.

The contraction during cooling and solidification of last liquid will involve considerable forces causing flow, and fresh liquid cannot replace it by the normal feeding technique, involving the provision of reservoirs of still-liquid metal of average casting composition, because of its high liquidus temperature compared with the solidification temperature of the last liquid. Consequently in long freezing range alloys which contract on solidification, the flow of low melting point last liquid out of central pipes and from other surface connected hot regions, will often lead to fine porous regions. The occurrence of porosity elsewhere within the casting involves the creation of voids, which Campbell has pointed out^{125,126} must involve considerable energy to nucleate, though when gaseous elements are among those segregating the occurrence of gas pressure, when bubbles are nucleated, will be a factor promoting such porosity. The occurrence of voids containing gas pressure may assist outward flow of inversely segregated liquid, and the creation of a fine grain size will assist in reducing this flow by creating many more channels and dispersing voids, as well as favouring mass feeding. This may not stop inverse segregation but is likely to greatly reduce its localisation. In cast irons, however, grain refinement reduces phosphide sweat by another mechanism, discussed later.

The formation of segregates in ingots and castings in V and A patterns has recently been the subject of fresh views by Hunt and co-workers.^{127,128} It has long been recognised that such segregates are formed by convective processes. Recently Hunt¹²⁷ has shown, in transparent models, that when the solute elements segregating to the liquid between dendrites lead to a lower density liquid, then thermosolutal convection currents may be set up in the growing mushy zone between dendrite arms, leading to channelling of liquid, rich in impurities, which flows out in the familiar segregate patterns. Fig.49 is an illustration from Hunt's work.¹²⁷ Because this flow is channelled it may cause more discrete segregating regions than would be expected from a continuing uniformly-distributed thermal-convection at the solid/liquid interface.

A type of channelled segregation in directionally-solidified castings has been termed "freckle" formation and these channels, too, have been ascribed to thermo-solutal convection during solidification.^{128,129}

When hot metal is poured into a sand mould the influence of heat and of hydrostatic pressure causes the cavity to change dimensions, and this influences the final size of the casting and the extent to which it requires feeding to ensure its soundness. This applies to all castings and sand moulds.^{130,131,132,133} Greensand and clay-bonded dried sand mould cavities enlarge continuously after casting, but hardened sand moulds show much less movement, while cement sand mould cavities may actually contract, squeezing the solidifying castings. In alloys which must be fed the mould cavity instability may be of relatively little consequence except in influencing the final casting weight, though one might expect there to be more problems in achieving soundness in greensand moulds than in hardened moulds when a long freezing range alloy is being cast, especially if there is a low melting point last-freezing phase. On the other hand, many non-ferrous alloys are more affected by the influence of greensand moulds in promoting gas porosity due to reaction or absorption than by mould dimensional stability. Nevertheless, white cast irons have been shown to need more feeding in greensand than in dried sand moulds.¹³³

The eutectic in grey cast iron expands on solidification and the expansion is transmitted with some force to the mould wall, so that the ability of a casting to be sound is greatly influenced by mould dimensional stability and ability to resist the expansion forces.¹²⁰ Increasing the number of eutectic grains increases the expansion force on the mould, and this can be shown to be of greater effect than is describable solely in terms of more dispersed solidification. Phosphide sweat in phosphoric grey cast irons is promoted by large eutectic grain size and by rigid moulds. It is reduced by soft moulds, or a finer grain size, both of which lead to an increase in casting size and hence less tendency to squeeze last liquid from the casting.

Castings made from spheroidal graphite cast iron, which constitutionally is similar to flake graphite cast iron, show a much higher eutectic grain number and a much greater expansion force, and for this reason require more feed metal. The origin of the outward pressure during solidification has been discussed by Rieter,¹³⁴ who has suggested that a liquid capillary type of action supplies the force causing it. If this hypothesis is correct, then similar forces might be expected to originate in other cast metals, and some evidence for this has already been offered for zinc alloys.¹³⁵

Castings made in permanent moulds either as gravity die castings, pressure die castings or die-pressings do not suffer from mould dimensional instability of the kind shown by sand moulds, though they show changes in dimensions if they are not clamped strongly and if they contain sand cores which are not rigid. Castings tend to be sounder in such moulds but sweat of low melting point last liquids can be a problem in some cases.

SOME PROCESSES OF SPECIAL INTEREST

Cast-in inserts When making castings for wear-resisting applications, which also have to be machined, it has long been the practice of foundrymen to place solid inserts of machinable metal in the mould where machining is to be undertaken, and to cast around them the metal intended to be difficult to machine. Steel, or grey iron inserts, may be used in high alloy wear resistant castings in this way. Cooling tubes may be cast into large castings such as those intended for dies or furnace cooling panels. If inserts fuse into the metal poured around them an intermediate composition layer may be produced with poor properties. For example, a carburised and over-heated layer may occur at the surface of a steel insert in a cast iron casting. Often the foundryman will deliberately avoid fusing the surface of the metal insert by coating it with an inert refractory wash, while in smaller castings where insufficient heat is available to fuse the insert a clean metal surface alone is sufficient, and the inserts are then maintained in position by a friction fit, sometimes assisted by machined serrations on the surface of the insert. This need for a good friction grip is sometimes extremely important. For example, fine cooling channels may be created in high temperature turbine vanes by inserting fine metal tubes into precision moulds. Centrifugal force has been known to eject these tubes because of insufficient frictional retention.

Sometimes the foundryman has to support the cores and mould parts by the use of studs and chaplets which must either fuse into the metal of the casting or form a perfect friction joint. The use of foamed polystyrene chaplets in such instances is a new technique with interesting possibilities, since these vapourise when the metal enters the mould and their support is no longer required, thus eliminating the problem of fusion or continuity of solid metal where chaplets have to be used.

Duplex and composite castings The need to combine quite different properties in different parts of a casting arises when part of the casting is to be hard and part soft, or part strong and part weak. The use of metal inserts or chillers in a mould for cast iron can create local hard regions and is well known. Some of the most important castings traditionally made by this process are rolls for steel mills, which are made in vertical metal chillers; and by careful control of composition and conditions of casting they have a hard chilled surface containing the metastable iron-carbide eutectic to a controlled depth, with a soft, tougher interior containing the stable iron-graphite eutectic. The fractured cross-section of such a roll is shown in Fig. 50. During the last fifteen years or so a number of methods have been devised for exercising greater control over the structure of such rolls by double-pouring displacement techniques. The mould is first filled with an expensive alloy which solidifies at the surface to yield a hard, wear resistant material. At a pre-determined time the central liquid is displaced by a low alloy iron which yields a soft, grey, and much tougher core. Fig. 51 shows the cross-section structure of a double poured alloy iron roll.¹³⁶