

Eutectic Solidification

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SUMMARY

Our present understanding of normal and anomalous eutectic solidification is assessed. Normal eutectic solidification which involves two non-faceting phases has been studied extensively and can be described quantitatively by the Jackson-Hunt analysis. Anomalous eutectic solidification which involves a non-faceting and a faceting phase, however, is more sensitive to solidification conditions and impurities and displays a much wider range of microstructures for which accurate quantitative analyses are not available. The range of such microstructures exhibited by Al-Si alloys is described, the coupled zone is defined and the dependence of the growth temperature of primary α (aluminium) and eutectic silicon on velocity, temperature gradient and strontium modifier content is described. Finally, the effect of impurities on the inoculation and growth of grey cast irons is described.

1. INTRODUCTION

The eutectic reaction is one of the oldest phenomena in solidification. Alloys of or close to this composition are of low melting point, are fluid and have a short freezing range. These characteristics promote castability. Casting of engineering components preceded understanding of the solidification process (e.g. the modification by sodium of Al-Si casting alloys was already practised at the turn of the century). Rapid developments in our understanding of eutectic solidification occurred in the 1960s and 1970s as a sequel to the single-phase and eutectoid studies of the 1950s and have now created the situation where understanding is helping to improve

practice. This is illustrated in the present paper by describing the major developments and their application to the control of cast microstructures.

2. THE EUTECTIC REACTION

In common with other solidification processes the eutectic reaction proceeds by nucleation and growth. The tendency in studying eutectic solidification has been to use the directional solidification technique to define eutectic growth structures. Nucleation should not be ignored, however, as it influ-

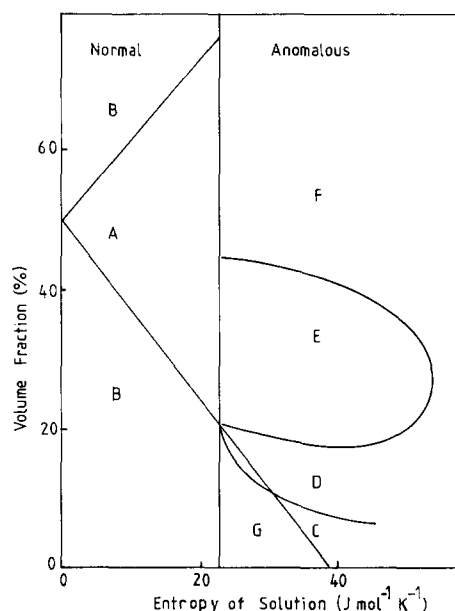


Fig. 1. Classification of eutectic microstructures in terms of the volume fraction and entropy of solution of second phase for a growth velocity of approximately $5 \mu\text{m s}^{-1}$ [1]: A, normal lamellar; B, normal rod; C, anomalous broken lamellar; D, anomalous irregular flake; E, anomalous complex regular; F, anomalous quasi-regular; G, anomalous fibrous.

ences structure and properties as discussed later with respect to the inoculation of cast iron. The first phase to form in eutectic solidification usually nucleates heterogeneously in the liquid. The second phase nucleates contiguously and heterogeneously but not necessarily epitaxially on the first phase even in eutectics showing a preferred orientation relationship between the phases. Directional solidification studies have led to the classification of structures shown in Fig. 1 [1]. Central to this classification in which one phase is non-faceting is the ability of the second phase to facet as measured by its entropy of solution. A critical value of $23 \text{ J mol}^{-1} \text{ K}^{-1}$ is used to distinguish the two main types of eutectic: (i) normal in which the second phase is non-faceting and (ii) anomalous in which the second phase is faceting.

3. NORMAL EUTECTIC STRUCTURES

A normal structure, either lamellar or rod, forms by the coupled growth of two similar phases at a near-isothermal interface. A full solution to the diffusion process that controls growth is difficult because the interface shape is not known *a priori* and must be obtained from the analysis. Jackson and Hunt [2] obtained an approximate quantitative solution by considering the interface composition to be that at a planar interface. They calculated contributions to the interface undercooling due to curvature and for the diffusion process. Atomic attachment occurs easily at the non-faceted interface and the kinetic undercooling is small. The interface undercooling is given by

$$\frac{\Delta T}{m} = V\lambda Q^L + \frac{a^L}{V} \quad (1)$$

where V is the growth velocity, λ is the interlamellar spacing and m , Q^L and a^L are constants for each system. A further condition is required for a unique solution of eqn. (1) and one possibility is that growth occurs close to the minimum undercooling. The movement and interaction of lamellar fault lines in addition to allowing interphase boundary orientation changes provide a competitive selection process by which the spacing can adjust to the value corresponding to this minimum under-

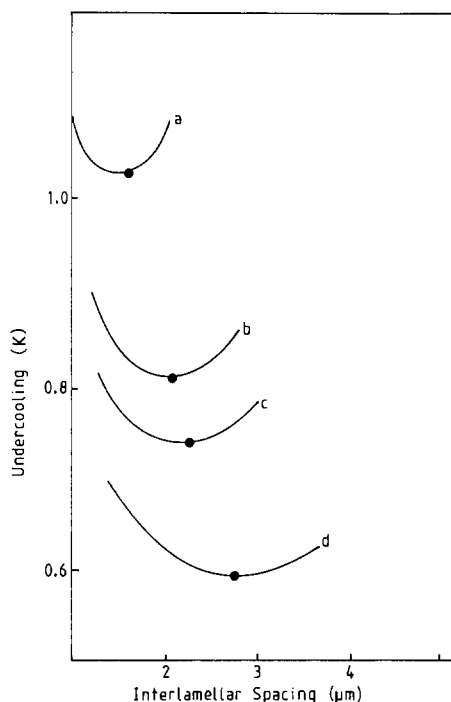


Fig. 2. The calculated growth curves for Al-CuAl₂ eutectic alloy and the position of the experimental point for four growth velocities [4]: curve a, $64 \mu\text{m s}^{-1}$; curve b, $39.2 \mu\text{m s}^{-1}$; curve c, $32.4 \mu\text{m s}^{-1}$; curve d, $21 \mu\text{m s}^{-1}$.

cooling at any velocity. The minimum of the growth curve corresponds to the relationships

$$\lambda^2 V = \frac{a^L}{Q^L}$$

$$\frac{(\Delta T)^2}{V} = 4m^2 a^L Q^L$$

$$\Delta T \lambda = 2ma^L$$

These relationships have been confirmed for several systems but a lack of knowledge of some of the constants prevents quantitative confirmation of the theory. Figure 2 shows calculated growth curves for the Al-CuAl₂ eutectic and the positions of the experimental points for several growth velocities. A similar growth curve has been proposed for the rod structure. A reasonable but intuitive criterion for lamellar or rod growth in a system is that the observed structure is the one that grows with the smaller undercooling. Rods should form if the volume fraction is less than 0.32 and if the solid-liquid and interphase boundary energies are considered to be equal for the two structures. If a low energy interphase

boundary forms in the lamellar structure, as will be the tendency as ΔS increases, the lamellar structure (Fig. 1, region A) will be stabilized and rods will form only at lower volume fractions.

The Jackson-Hunt analysis does not predict the conditions under which the planar eutectic interface becomes unstable. Such instability may occur as a result of constitutional undercooling due to the build-up of a third element ahead of the interface as for solute elements in single-phase solidification. The result is a cellular or colony structure with loss of phase alignment at the colony boundary. Furthermore, a competitive growth model has been used to predict instability with respect to the formation of primary phases. This transition defines the limits of the coupled zone. This is the range of growth velocities or temperatures for alloy compositions about the eutectic composition for which the structure is completely eutectic like. Several studies have shown that non-faceting dendrites follow an undercooling-velocity relationship of the form

$$\Delta T = \frac{GD}{V} + BV^{1/2} \quad (2)$$

where B is a constant and G and D are the temperature gradient and diffusion coefficient respectively in the liquid. The dependence on temperature gradient of dendritic growth explains why a wide coupled zone exists for growth with a high G/V ratio. This analysis, coupled with that for constitutional undercooling, allows prediction of the G/V ratio required for the successful growth of well-aligned *in situ* composites in material of off-eutectic composition.

Series *et al.* [3] have modified the Jackson-Hunt analysis to correct for discrepancies between theory and experiment at high growth velocities. As discussed elsewhere [4], although other theories have been proposed, the Jackson-Hunt analysis predicts the relationships observed between structural and solidification parameters and is the most easily applied of the available theories.

4. ANOMALOUS EUTECTIC STRUCTURES

Many important engineering alloys including Al-Si and cast irons fall into the category

of anomalous eutectic structures. They display a range of microstructures even in a single alloy system with a corresponding range of properties. The extensive range of structures in the anomalous class can be traced to the different and anisotropic characteristics of the high entropy phase. Whereas the low entropy phase grows at a rate controlled by diffusion with all atoms incorporated into the solid, the high entropy phase grows at a rate determined by the manner in which the interface incorporates atoms into the solid. Consequently, at the same undercooling a low entropy phase will usually grow at a higher velocity than a high entropy phase. The growth of the latter, however, is very sensitive to the nature and stability of its solid-liquid interface which is influenced by structural defects, adsorption of impurities and temperature. The growth of the two dissimilar phases of an anomalous eutectic alloy is cooperative rather than coupled and occurs at a non-isothermal interface. It can be anticipated that the diffusion process at such an interface will require a larger driving force. It has been shown that the interface undercooling and particle spacing are much larger than predicted by the Jackson-Hunt analysis. Figure 1 represents typical microstructures formed in high purity alloys containing different volume fractions of the high entropy phase. If this phase forms the matrix, the interface curvature is such that steps are readily available at its growth interface and the growth structure (Fig. 1, region F) is more like that of a normal alloy as in white cast irons. With a slightly lower volume fraction the different growth behaviours of the two phases can lead to the formation of a compositional boundary layer at the growth interface and constitutional undercooling. This is relieved by the formation of a faceted cellular interface, and coupled growth can occur in the cells as with the complex regular structure (Fig. 1, region E) found in Al-Ge, Pb-Bi and silicon-rich Al-Si alloys. With a further reduction in the volume fraction to approximately 20%, the high entropy phase relieves any growth restriction by branching as in the flake structures (Fig. 1, region D) of Al-Si and grey cast irons. When the volume fraction is less than 10%, branching is restricted to the plane of the flake as in the broken lamellar structure (Fig. 1, region C).

Figure 1, region G, defines the fibrous structure often found at higher velocities in alloys that otherwise show broken lamellar, flake or complex regular structures. Anomalous structure formation is also sensitive to the growth velocity, the temperature gradient in the liquid and impurities. Consequently, structural control to produce the desired properties requires a detailed study of each system. Studies of Al-Si and grey cast irons are described below.

5. Al-Si STRUCTURES

The structures observed in directionally solidified eutectic alloys are represented in Fig. 3 as a function of the temperature gradient and growth velocity and illustrate the range of structures that may form in one system [5]. The very high G/V ratio in Fig. 3, region A, prevents constitutional undercooling of either phase and the phases grow independently at a planar interface by a long-range diffusion process. The high entropy phase, silicon, displays a range of morphologies reflecting the different ways in which the interface incorporates the silicon atoms during growth. The lower G/V ratios in Fig. 3, region B, render this interface unstable, leading to cooperative semicoupled growth of the two phases by a short-range diffusion process. The silicon phase leads at the interface and develops a $\{100\}$ preferred orientation. The silicon morphology is sensitive to the solidification conditions. A rod structure forms at the highest temperature gradients. As the gradient falls and the growth velocity increases, the silicon phase develops side plates (Fig. 4) the number of which decreases with further decrease in the G/V ratio. The angular silicon structure in Fig. 4 shows three side plates and is observed in sand castings. The growth of angular silicon particles may be aided by growth at dislocation steps and the side plates are separated by $\{210\}$ twins. The aluminium interface between the side plates is planar at higher G/V ratios but, as the ratio decreases, the interface develops a pocket.

This creates a solute diffusion problem as silicon accumulates in the liquid in the depression. The situation may be relieved either by the development of perturbations in the

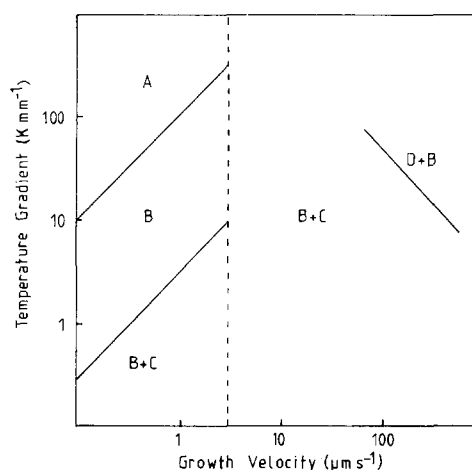


Fig. 3. Type of microstructure as a function of growth conditions in a directionally solidified Al-Si eutectic alloy [5]: A, independent growth; B, rod or angular silicon growth; C, flake silicon; D, fibrous silicon.

aluminium phase, leading to branching of the silicon side plate as occurs at higher velocities in quench modification or by the nucleation of silicon in the interface depression. The nucleation of silicon is relatively easy in the Al-Si system and at growth velocities in the range $3\text{--}400\ \mu\text{m s}^{-1}$ it is the favoured process. Twinning occurs under these conditions and the silicon displays a flake morphology which forms by the rapid extension of the flake edge at twin-plane re-entrant edges resulting from the intersection of multiple $\{111\}$ twins with the interface. This mixed eutectic structure is shown in Fig. 4 and forms over a wide range of solidification conditions. Quench modification (Fig. 3, region D) occurs at higher velocities. The transformation occurs in two stages. At lower velocities the angular silicon side plates branch within their plane as a result of aluminium overgrowth. At higher velocities the flake silicon transforms to a fibrous structure. Transmission microscopy of samples grown at increasing velocities shows a progressive reduction in multiple and single twinning until finally no twins are observed. This indicates that fibrous growth can occur without the aid of twins and is considered to occur by the continuous incorporation of silicon atoms at the interface as with normal structures. The fibrous structure shows a colony structure at high velocities, a characteristic of normal alloys. This sequence of microstructural

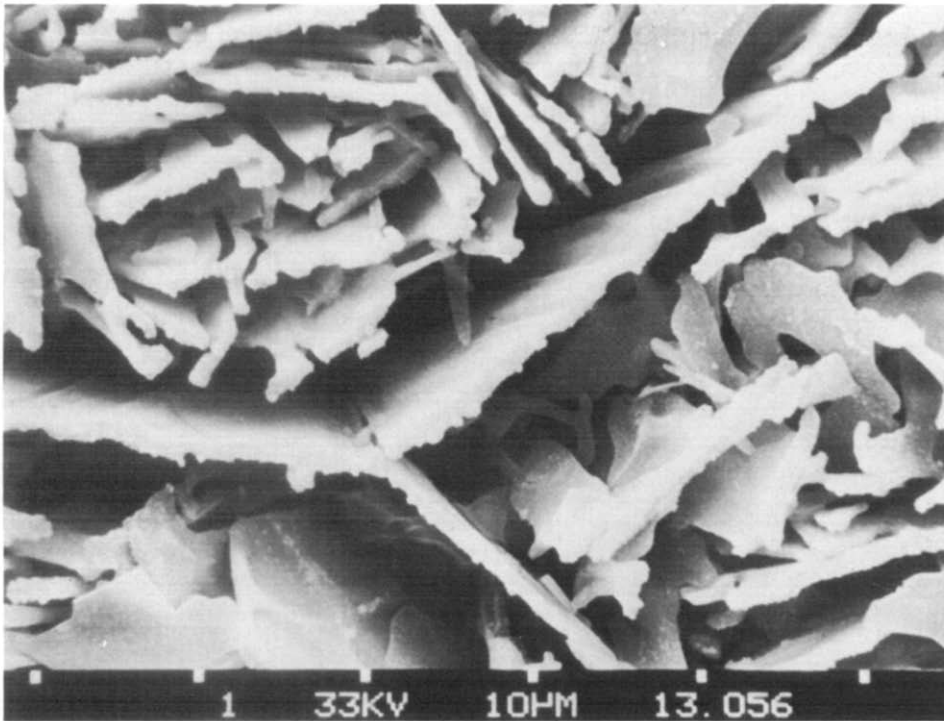


Fig. 4. Scanning electron micrograph of deeply etched Al-Si eutectic alloy grown in the B + C region of Fig. 3. (From ref. 5.)

changes is for an alloy of eutectic composition. Figure 5 shows the effect of silicon concentration and growth velocity on microstructure for a temperature gradient of 12.5 K mm^{-1} . This zone shows the broadening at high values of G/V described earlier and the asymmetrical shape that is characteristic of anomalous alloys.

The mechanical properties of aluminium castings depend on the morphology of the eutectic silicon. The coarse branched dendrite-like structure in Fig. 5, region B, causes premature crack initiation and fracture in tension but gives maximum compressive strength. The cleavage plane of silicon is (111); hence flakes permit easy crack propagation. The tensile strength increases gradually as increased growth velocity refines the flake size but significant strengthening is achieved only when the structure is modified.

Quench modification only occurs in die castings; sodium and more recently strontium have been used for modification. Figure 6 shows that small concentrations of strontium are sufficient to broaden the coupled zone in Fig. 5 by raising the upper zone boundary.

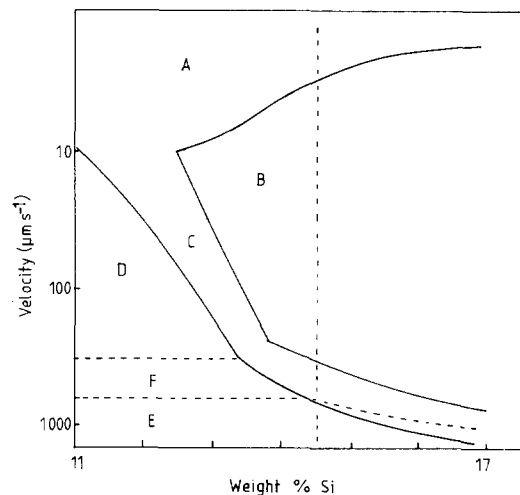


Fig. 5. Microstructure as a function of growth velocity and silicon content in high purity Al-Si alloys grown at a temperature gradient of 12.5 K mm^{-1} [5]: A, plate-like, angular and complex regular silicon; B, complex regular star-like polyhedral silicon (greater than 14.5 wt.% Si), angular and flake eutectic silicon; C, flake and angular silicon, zone of coupled eutectic growth; D, α (aluminium) dendrites and flake eutectic silicon; E, α (aluminium) dendrites and fibrous eutectic silicon; F, transition of flake and angular silicon to fibrous silicon.

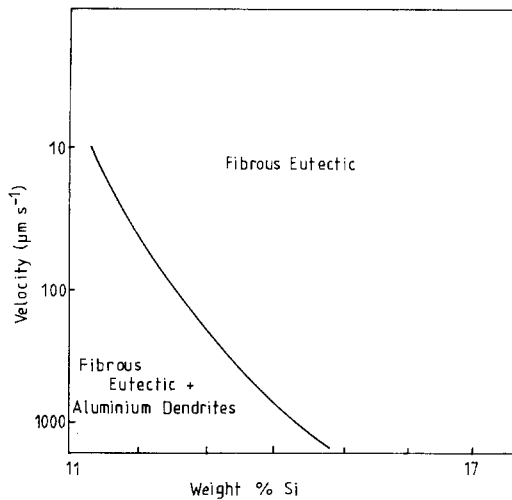


Fig. 6. The influence of 0.01 wt.% Sr on the structure of Al-Si alloys (*cf.* Fig. 5). (From ref. 6.)

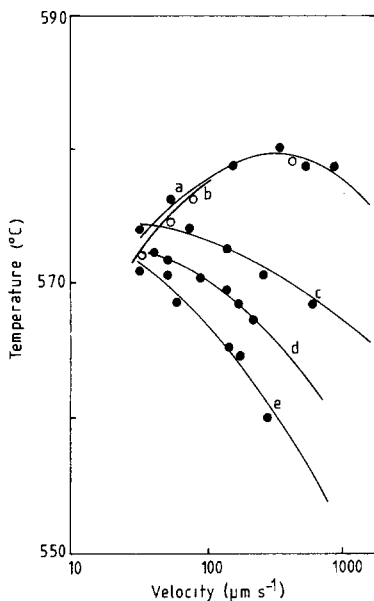


Fig. 7. Growth temperature *vs.* velocity relationships: curve a, α (aluminium) dendrites in an Al-11.7wt.%Si alloy at $G = 12 \text{ K mm}^{-1}$; curve b, α (aluminium) dendrites in an Al-11.7wt.%Si alloy modified with strontium at $G = 12 \text{ K mm}^{-1}$; curve c, eutectic Al-Si at $G = 12 \text{ K mm}^{-1}$; curve d, eutectic Al-Si at $G = 0.8 \text{ K mm}^{-1}$; curve e, strontium-modified eutectic at $G = 12 \text{ K mm}^{-1}$.

Strontium adsorption at the growth interface poisons twin-plane re-entrant edge sites on the silicon interface, increasing the interface undercooling until continuous growth is possible [6]. Figure 7 shows growth temperature measurements made during directional solidi-

fication for α (aluminium) dendrites, flake silicon eutectic and strontium-modified eutectic. These show that, while strontium only marginally increases the undercooling for α (aluminium) dendritic growth, the modified eutectic grows at a much larger undercooling than the unmodified eutectic. A decrease in temperature gradient from 12 to 0.8 K mm^{-1} also increases the undercooling for eutectic growth but without modifying the flake morphology. The measurements also confirm the competitive growth model for the lower boundary of the coupled zone. The growth temperature for the silicon phase could not be determined because silicon nucleates ahead of the interface during directional solidification.

The theory of the growth of anomalous structures is not as advanced as for normal structures. Attempts have been made to account for the discrepancy in flake undercooling and spacing between experiment and the predictions of the Jackson-Hunt theory by assuming a mixed diffusion and interface kinetic control. This is described in more detail in relation to cast irons. Fisher and Kurz [7] have used an alternative approach in which only minor attention is given to the growth kinetics. They consider that flakes grow at the limit of stability of the high entropy phase so as to allow it to branch. The observed spacing will vary between this upper limit and the value corresponding to the minimum undercooling and is greater than that predicted by the Jackson-Hunt analysis. The influence of the temperature gradient is related to its effect in flattening the solid-liquid interface. Solute rejection from the flake tip is more difficult, promoting morphological instability, increasing the frequency of branching and reducing the average flake spacing. A reduced spacing will mean easier diffusion and a reduced undercooling. Although this model predicts the observed form of relationship for Al-Si, quantitative agreement is poor.

6. GREY CAST IRONS

One of the most important cast materials is grey cast iron and the control of its structure for property requirements is complex. The morphology of the high entropy phase, graphite, varies from coarse flake through

various intermediate forms such as coral and compacted to nodular iron in which the graphite grows independently in the liquid. Each graphite form confers its own characteristic properties. Flake irons for example have a good thermal conductivity but a moderate strength whereas nodular irons have a high strength but a moderate thermal conductivity. In common with other anomalous alloys the graphite morphology varies with solidification conditions but is most sensitive to impurities present in the liquid and compositional control is the method used commercially to obtain a desired structure. Minkoff [8] has studied graphite growth extensively and places emphasis on interface kinetics correlating the various types of cast iron with graphite growth instabilities. The flake form is bound by (0001) and (10 $\bar{1}$ 0) faces, and atom incorporation at the (10 $\bar{1}$ 0) growth interface is more rapid because steps are produced by twist or rotation boundaries. Branching from the (10 $\bar{1}$ 0) face in response to austenite overgrowth produces the typical eutectic cell (*i.e.* grain) structure. The intermediate graphite forms are attributed to instabilities on (0001) faces, either because steps on these faces become unstable or because the faces themselves become unstable. Nodular growth is observed to have its origin in a pyramidal instability. These progressive changes in graphite form occur with progressive increase in interface undercooling promoted by the effect of different solutes. The effect of individual solutes can be rationalized as follows.

(i) Elements from groups I, II and III, plus lanthanum and rare earths, are strongly reactive to graphite, adsorb strongly at the growth interface interfering with atom incorporation and promoting kinetic undercooling.

(ii) Elements of group IV and boron concentrate ahead of the interface, leading to constitutional undercooling.

(iii) Surface-active elements from group VI such as sulphur adsorb at the interface and lower the interfacial energy; this raises the growth temperature, producing an effect opposite to that of (i) and (ii).

The influence of solutes in solution is additional but can be modified by interaction and will vary because of segregation during solidification. For example magnesium and cerium may be added together so that both contribute to the kinetic undercooling but the strong

influence of magnesium will be moderated. Titanium will react with magnesium and then promote constitutional undercooling. The net result of adding an Mg-Ce-Ti mixture is to extend the range of composition of added elements for the production of a desired structure, in this case compacted irons. Minkoff [8] has quantized and formulated these ideas into his "delta tee" method for compositional control of cast iron. The analysis at melt-down is fed into a computer. This processes the data to calculate the graphite undercooling allowing for melt interactions and segregation during solidification and predicts the graphite morphology from the calculated undercooling. It is claimed that the method can predict compositional adjustments necessary for the production of flake, compacted or nodular irons.

Finally, as a further example of how understanding is helping to promote better practice, a similar approach may be used to develop more powerful inoculants for nodular irons. Using an inoculation model of graphite-enveloped substrates which form in silicon-rich areas of high carbon activity during the solution of the inoculant, and inoculant fade as being the restoration of the equilibrium state in the liquid by dissolution of graphite layers round the heterogeneous nuclei, it is possible to assess the dependence of both processes on impurity-induced effects by means of simple nucleation and growth theory. Impurities reducing the liquid-graphite interfacial energy and promoting constitutional undercooling enhance inoculation, while impurities promoting kinetic undercooling retard it. Reduction in the interfacial energy is particularly effective because of the small size of the nuclei. Consequently to promote inoculation and to increase the nodule count it is beneficial to incorporate elements such as bismuth into the inoculant so that on dissolution they reduce the interfacial energy. Bismuth is favoured because it decreases the energy appreciably at very low concentrations. However, careful control over inoculant composition is necessary to ensure that, if the bismuth causes flake formation initially, the impurity undercooling during subsequent growth is such as to promote nodule formation. Lietaert *et al.* [9] have used this model to develop a new and more efficient inoculant combining the beneficial

effects of alkaline and rare earth metals with bismuth without the risk of nodule degeneration.

7. CONCLUSIONS

It has been shown that an adequate quantitative description of normal eutectic solidification is given by the theory of Jackson and Hunt. The situation, however, is not as well defined for anomalous eutectic solidification. This solidification process is more sensitive to solidification conditions and impurities as shown for Al-Si and cast irons and produces a wide range of microstructures. Solidification occurs at a non-isothermal interface and contributions to the undercooling might be expected from diffusion, curvature and interface kinetics in the absence of impurities. Quantitative analyses have been attempted for the flake morphology. They place a different emphasis on the various contributions to the undercooling and, as yet, none provides good agreement with experiment.

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