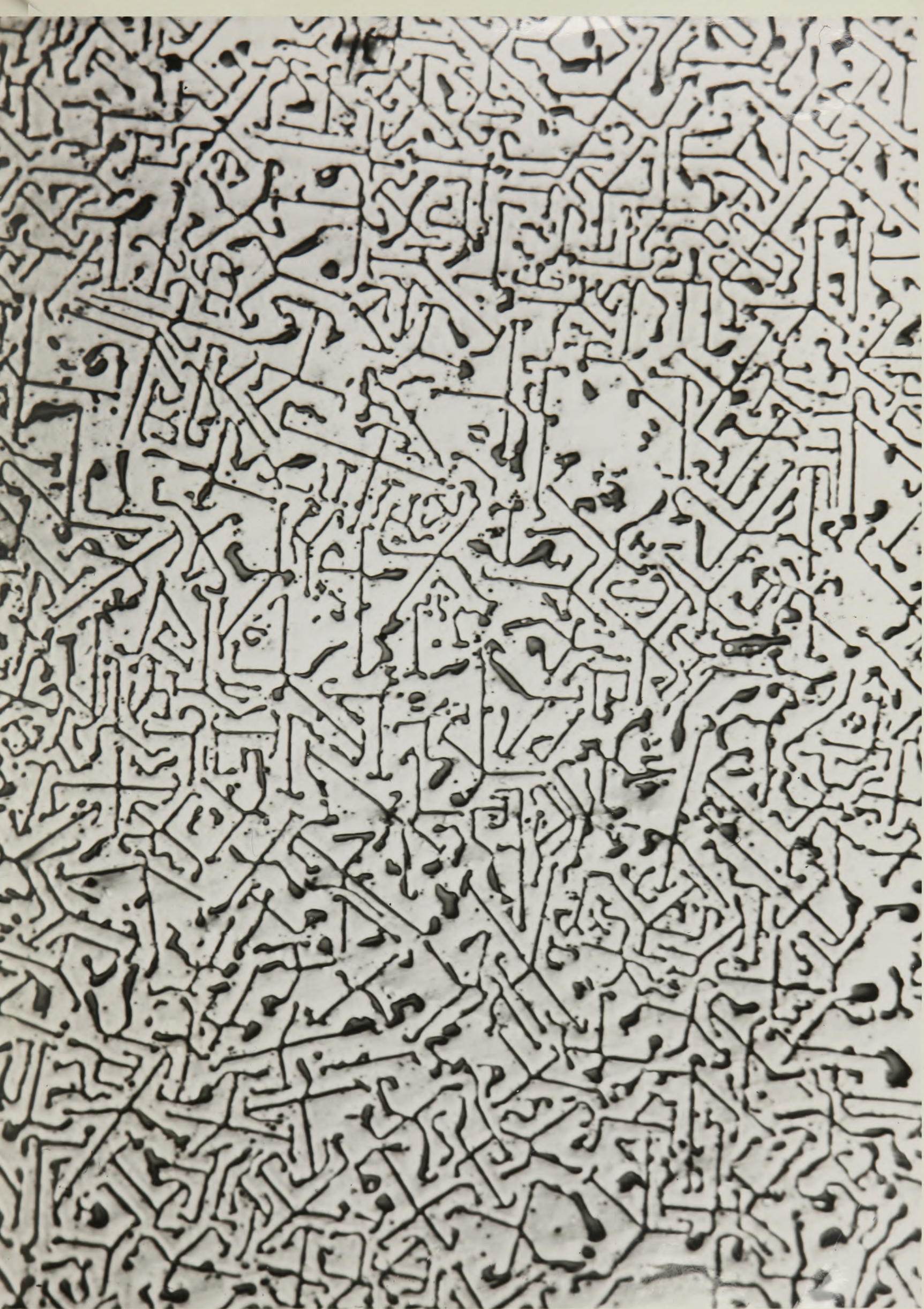
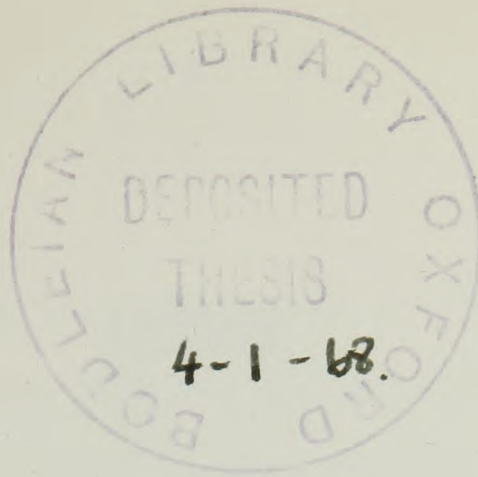






THE NUCLEATION AND GROWTH OF SOME EUTECTICS

Volume I

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ABSTRACT

A survey of the current literature on binary eutectic systems shows that, although the simpler eutectic morphologies produced between phases of low entropy of fusion are now fairly well documented and understood, the same is not true when one of the phases has a high entropy of fusion. This thesis is an attempt to partially rectify this dearth of fundamental information on metal/non-metal eutectic systems.

The system aluminium/silicon was chosen as being one typical of this class of eutectic alloys. High purity specimens were unidirectionally solidified under carefully controlled and measured growth conditions. The resultant microstructures were then classified in terms of the growth variables of

R - the growth rate

G - the temperature gradient in the liquid
ahead of the growing interface

C - the alloy composition

The growth variables were found to greatly affect the mode of the eutectic reaction and to cause not only changes in the scale of the eutectic microstructure but to alter the form of the microstructure as well.

The unidirectionally grown specimens were subjected to detailed morphological and crystallographic analyses and in this way information was obtained about the possible growth mechanisms of these various forms of the eutectic microstructure. The various eutectic forms were as follows:

a) Long Range Diffusion

When the Al/Si specimens were unidirectionally solidified above a certain critical G/R value ($G/R = 10^7 \text{ sec.}^\circ\text{C.cm}^{-2}$), the two eutectic phases grew by means of a relatively long range diffusion process. The aluminium phase grew with an isothermal interface and the silicon grew with a non-isothermal interface, to produce a massive form of the eutectic. The interconnected silicon phase grew by a twin plane reentrant edge growth mechanism.

b) Short Range Diffusion

Below this critical G/R value, the two eutectic phases grew by a short range diffusion process, which could be either steady or non-steady state depending on the growth conditions.

The form of these short range diffusion types depended upon the growth kinetics of the silicon phase and the ease of aluminium overgrowth.

i) $\langle 100 \rangle$ Si growth textured form

At low growth rates ($R \sim 10^{-5}$ cm/sec.) the silicon phase grew by means of a screw dislocation kinetic mechanism and this produced interconnected silicon crystals elongated in the growth direction which had a $\langle 100 \rangle$ Si growth texture; the width of these particles being affected by both growth rate and temperature gradient. This form of the eutectic silicon normally grew by a steady state and short range diffusion process. Corrugated silicon particles were observed, however, indicating that a non-steady state growth mechanism could also operate.

ii) $\{111\}$ Spinel twin related form

When the pure eutectic alloy was unidirectionally grown at higher growth rates ($R > 3 \times 10^{-4}$ cm/sec.) the eutectic silicon phase grew by a different kinetic mechanism which involved the use of $\{111\}$ spinel twins. Growth was normally by a non-steady state process and this produced an irregular microstructure. The eutectic silicon in this form of the alloy was always found to be interconnected, even at the highest attainable growth rates, (i.e. rapid quenches) and it was shown that many of the irregular

silicon particles grew by means of a twin plane reentrant edge mechanism and that the various particles were related to each other via multiple $\{111\}$ spinel twins.

In hypereutectic alloys this same T.P.R.E. growth mechanism for the silicon phase produced a steady state complex regular structure with a $\langle 110 \rangle$ Si growth texture in addition to the irregular form already mentioned above.

c) Repeated Nucleation and Growth

No experimental evidence was obtained to show that Al/Si eutectic alloys ever grew by a process of repeated nucleation and growth. The eutectic silicon phase was always found to be interconnected.

Unidirectional solidification experiments with the other F.C.C. metal/silicon eutectic systems (Ag/Si and Au/Si) produced microstructures which showed the same silicon morphology and crystallography as the Al/Si system.

Finally, in the light of the work on the pure Al/Si eutectic system, a series of controlled experiments were carried out on the modification of the alloy by metallic sodium. Results showed that the modified eutectic silicon was fibrous and interconnected and very similar to the rapidly quenched pure eutectic. It was concluded that the addition of sodium to Al/Si alloy must produce the change in microstructure by affecting the growth and not the nucleation of the eutectic silicon. From the experimental results it appeared that the sodium was affecting the growth of the eutectic silicon by preferential poisoning of twin plane reentrant growth sites.

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I N D E XVOLUME IPageFRONTISPIECE

Al/Si Eutectic Alloy - transverse section

($R = 1.54 \times 10^{-5}$ cm/sec., $G = 30^{\circ}\text{C/cm.}$)

This Micrograph is currently being used as
a backcloth design by the British Broadcasting
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VOLUME II

FIGURES, PLATES and TABLES

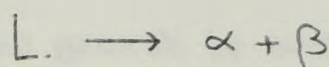
I INTRODUCTION

This thesis describes the information obtained from the detailed investigation of a series of controlled solidification experiments. The unidirectional solidification experiments and the subsequent investigations were designed to discover more about the mode of the eutectic reaction that takes place between metals and non-metals. The eutectic alloy Al/Si was the specific system chosen to find out whether a relationship exists between the mode of the eutectic reaction and the imposed growth variables. Other F.C.C. metal/silicon eutectic systems were investigated to discover whether any similarities exist between these systems and the Al/Si eutectic alloy. It was hoped that the results of this research would have a bearing on metal/non-metal eutectic systems in general.

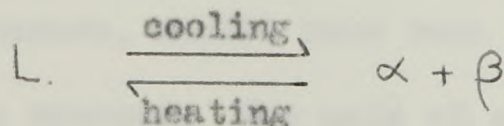
(1) THE EUTECTIC REACTION

Gibbs Phase Rule indicates that the coexistence of three phases in a binary system at constant pressure involves an invariant equilibrium. The three phases can exist at only one temperature and their compositions are fixed. Therefore, an invariant equilibrium in a binary system is represented by a horizontal tie-line; the compositions of two phases coincide with the extremities of the tie-line and the third phase has an intermediate composition.

The eutectic reaction results from such an invariant equilibrium, the three phases involved being two solids α and β and a liquid phase L. The horizontal tie-line representing the invariant equilibrium is called the eutectic isotherm. On cooling a liquid L through the eutectic isotherm a reaction of the following type occurs.



Since the reverse reaction would take place on heating through the eutectic isotherm, the reaction can be written as a reversible one.



This reaction is the eutectic reaction.

Fig. 1 shows how cooling a liquid alloy of composition E through the eutectic isotherm simultaneously deposits solid α of composition a and solid β of composition b until all the liquid has been consumed. As the composition of the liquid and the temperature at which the reaction occurs are invariant, the solidification reaction has to go to completion before the temperature of the system can be further decreased. The reaction occurs isothermally as with a pure metal but with a difference that the process is incongruent, i.e. there is a difference in composition between the liquid and the individual solid phases.

The eutectic reaction proceeds by a normal process involving nucleation and growth, similar to a pure metal, i.e. it requires a certain undercooling ΔT before the reaction takes place, but with added complexity owing to the incongruent nature of the reaction. Nucleation is normally assumed to occur on a heterogeneous nucleation site in the undercooled liquid phase. For eutectic growth to occur nuclei of both phases must be formed. One expects one phase to nucleate first, the second phase nucleating on or near the first because of the solute build-up due to the growth of the initial nucleus. Once the duplex, or two separate, nuclei have been formed, the eutectic solidification can proceed. The rate of growth of the two eutectic phases is controlled by the extraction of heat from the system. If the rate of extraction of heat is controlled externally, then the rate of growth of the eutectic alloy can be made constant.

(2) AN HISTORICAL REVIEW

a) Early Work on the Nature of Eutectic Alloys

The fact that with many pairs of metals it is possible to prepare one alloy which has a minimum freezing point has been known since Roman times; these were the so-called 'fusible metals'. The production of a liquid by mixing a solid salt with solid ice in freezing mixtures was also well known and the analogy of freezing mixtures and fusible metals had been observed by Döbereiner in 1824. In 1864 Rüdorff gave the correct explanation of the production of freezing mixtures showing that the point of minimum temperature thus obtained was the intersection of the curve of separation of ice from salt solutions with that of the solubility of salt in water. However, in spite of the work of Rüdorff, the constancy of composition and freezing point, and the characteristic appearance of the mixture of minimum freezing point led Guthrie (1875) to regard it as a stoichiometric combination of the salt with water stable only below 0°C , to which he gave the name cryohydrate. In his later investigations the complete resemblance between the behaviour of cooled salt solutions, alloys and mixtures of fused salts lead Guthrie to introduce

the word eutectic (1884). Once it was shown that eutectic systems were widely observed and that the deviation from simple molecular ratios was often very marked, the composite nature of eutectic materials was readily admitted. The incongruent nature of the eutectic reaction was not proved until 1895 when Ponsot showed by microscopic examination that freezing mixtures consisted of distinct crystals of ice and salt. However, the idea of stoichiometry for eutectic alloys has continued on (Stockdale 1935, Hume Rothery and Anderson 1960) and as recently as 1965 a review mentioned the possibility of stoichiometric eutectic alloys. (Chadwick 1965)

b) Early Classifications

Once the incongruent nature of the eutectic reaction was proved, classification of the wide range of observed microstructures was begun. These early classifications were from eutectic alloy castings and depended very much on the author's personal preferences on the observed microstructure. (Desch 1910, Vogel 1912, Lamplough and Scott 1914) This fact was noticed as early as 1922 by Brady who remarked that "such classifications all have the serious disadvantage that they fail to account for the structures by a consideration of any physical property of either of the constituent phases, but

merely divide them according to superficial appearance". Brady attempted a classification based on the surface tension of the pure components of the eutectic. This was not successful as the parameter affecting shape would be the surface tension of the phases rather than the pure components. Ironically the 'superficial' classification that this paper produced was adopted, i.e. globular, lamellar, angular and crystalline. Subsequent early classifications still kept to the superficial appearance approach. (Portevin 1923, Green 1925)

c) Later Classifications

In these later classifications further attempts were made to explain the observed microstructure in terms of some physical property. In a series of papers by Scheil (1946, 1949, 1954) and the Koflers (1950, 1954) a new classification was presented based on the form of the phase diagram. The volume fraction was thought to be an important variable as well as the undercooling at which the eutectic alloy solidified. The theory suggests that when the liquidus lines are asymmetrical with respect to the eutectic alloy, the two phases cannot grow simultaneously in a 'coupled' form at large undercoolings in the eutectic ratio. The phases might grow in the coupled form at

large undercoolings, if the composition were not the equilibrium eutectic composition. This work led to the classification of eutectic systems as normal and anomalous. Normal eutectics solidified simultaneously with a common growth front, while anomalous eutectics solidified with less coupling of the phases and did not have a common growth front.

A great improvement in the understanding of the eutectic reaction and the various microstructures formed, came when the effect of impurity on eutectic growth was realised. In 1958 Weart and Mack showed that eutectic colonies were the result of the cellular interface produced by the constitutional supercooling introduced by impurities.

Another major advance was in the unidirectional solidification of eutectic alloys. In this way it was possible to separate the nucleation event of the eutectic reaction from the subsequent growth event and to observe how the structure was orientated to the growth direction.

These major advances led to a new series of classifications. The first was by Tillier (1957b) who used concepts employed in the theory of constitutional supercooling as developed by Rutter and Chalmers (1953) and Tillier et al. (1953) as well as the analysis of eutectoid growth by Zener. (1948) Tillier divided eutectic alloys into two simple classes; the lamellar structure which he predicted could become rodlike and then globular with increasing

growth rates, and the anomalous structure in which the second phase would nucleate in the liquid to give randomly orientated non-interconnected particles of this phase.

Chadwick (1963) classified eutectic alloys as continuous, discontinuous and spiral. Lamellar and rodlike eutectics are classed as continuous; discontinuous eutectics are those in which one phase is thought to exist as discrete random particles in a matrix of the other phase; and spiral eutectics are those in which the phases spiral round each other. This classification is again based only on superficial appearance of the eutectic structure and as such marks a retrograde step. A classification system is required that will enable structures to be predicted.

Sundquist, Bruscatto and Mondolfo (1963) classify eutectics according to the nucleation behaviour of the two phases. Normal eutectics occur when one phase nucleates the other and both grow simultaneously; anomalous eutectics occur when both phases nucleate independently so that there is no definite orientation relationship between the two phases. The third classification is the divorced eutectic in which the second phase only nucleates when the first phase has completely frozen.

Davies (1964) used the classification of normal and anomalous but said that the structure depended on the ratio of a lag/lead distance between phases (d) to the interparticle spacing (λ). When d/λ is less than 1.5, the eutectic

is normal and when greater than 1.5 the eutectic is anomalous.

d/λ was written in terms of the shape of the phase diagram.

The above approach of Davies is very similar to one of Bell and Winegard (1965c) who have recently suggested that the most important factor in eutectic growth is the distribution coefficient, since the distribution coefficients control the undercooling ahead of each phase. The undercooling in turn controls the growth of each phase much as it would do in the single alloy system. These authors draw an analogy between plane interface, cellular, dendritic and equiaxed structures in simple solution alloys and the lamellar, rodlike, crystallographic and anomalous structures in eutectic systems.

All the above systems of classification should have some basis that could be used for prediction but in fact they only represent part of the variables controlling eutectic growth morphology and as such are unreliable. There is at present only one classification system that is powerful enough to allow prediction and that is the one due to Hunt and Jackson (1966). It is this classification system that has been adopted in this thesis. The weaknesses in the other systems will be mentioned at appropriate places in the thesis.

(3) THE ADOPTED EUTECTIC CLASSIFICATION

Jackson, (1957) following Burton, Cabrera and Frank (1951), divided growing single phase materials into two classes depending on a factor α which was almost the entropy of fusion.

$$\alpha = \gamma_f \cdot \frac{\Delta S_f}{R} \quad \text{where} \quad \frac{\Delta S_f}{R} \quad \text{is the entropy}$$

of fusion in dimensionless units and γ_f is a crystallographic factor which is less than and almost one. Most non-metals have high entropies of fusion (α greater than 2) and grow with crystalline facets. Most metals have low entropies of fusion (α less than 2) and grow reasonably isotropically with no facets.

Hunt and Jackson (1966) proposed that eutectics may be classified in a similar manner. There are therefore, three groups of eutectic; those in which both phases have low entropies of fusion, those in which both phases have high entropies of fusion and those in which one phase has a high and the other phase has a low entropy of fusion.

These three groups of eutectics will now be discussed in turn and a review given of the general state of knowledge in each of these groups.

For each of these groups the eutectic reaction can be envisaged to occur by any of three basic growth mechanisms and these are:

- i) Independent, or separate growth of the two phases.
- ii) Co-operative or coupled growth, either steady or non-steady state.
- iii) Repeated nucleation and growth.

The growth mechanism that is observed in a particular eutectic alloy system will depend on the entropy of fusion of the two phases and possibly the variables of growth rate, temperature gradient in the liquid ahead of the growing solid/liquid interface and the alloy composition of the eutectic specimen.

a) Non-faceted/non-faceted Eutectic Growth

As mentioned above, this group of eutectic is formed between phases of low entropy of fusion. Metals fall into this class and by far the greatest amount of recent laboratory work has been carried out on these metal/metal eutectics. (see Chadwick 1963 for review) However, eutectic systems between other materials of low entropy of fusion have been found to exhibit identical eutectic morphologies, e.g. alkali halide eutectics (Cooksey et al. 1964, Penfold and Hellawell 1965) and organic eutectics in which the constituent phases are spherical molecules with rotational degrees of freedom. (Hunt and Jackson 1966)

This group of eutectics appears to grow by only one of the above growth mechanisms, that of steady state co-operative growth. This means that the triple junctions at the growing eutectic alloy interface are stable and that the short range diffusion distance is constant with time and a regular microstructure is produced. The prime requirement in this growth mechanism is solute distribution and the growth of the eutectic alloy is thus diffusion controlled, but a balance is reached between a minimum diffusion distance and a minimum interfacial area, such that growth occurs with a minimum undercooling. This undercooling is smaller than either of the eutectic phases would have if they were to grow independently. The theories developed to explain

this form of eutectic growth contain certain assumptions. These are that both phases grow isotropically with negligible kinetic undercooling and that the eutectic solid/liquid interface is isothermal. To maintain the isothermal interface across each phase it has been proposed that compositional variations in freezing temperature are balanced by curvature variations.

The regular eutectic morphologies that are produced are of two types, either lamellar or rodlike, depending on the volume fraction of the eutectic phases.

Frank and Futtick (1956) showed from a consideration of surface area (and hence surface energy if the material is assumed isotropic) that below a volume fraction of 0.28, rods would be the more stable form for a given interparticle spacing. In practice, lamellar eutectics are found at lower volume fractions than 0.28. This is because the energy of the interface between the eutectic phases depends on its orientation relative to the crystal lattice of the two phases. In the lamellar eutectic, a low energy plane can serve as an interface and thus acts as a stabilising influence. (Cooksey et al. 1964) It has been shown that the phase/phase interface in these eutectics consists of low energy planes or puckered low energy planes and that an orientation relationship exists between the two

phases. (Straumanis and Brakes 1937; Ellwood and Bageley 1949; Kraft 1961, 1962; Lemkey, Hertzberg and Ford 1965) Such an orientation relationship most probably indicates nucleation of the second phase on the first, the subsequent growth maintaining the orientation relationship of the two phases.

Various theories have been put forward to explain the lamellar $\rightarrow$ rod transition sometimes observed in this group of eutectics. Tillier (1957a), Chalmers (1959) and Chadwick (1963) put forward the theory that it was differential short range constitutional supercooling that caused the minor eutectic phase to grow ahead of the other and assume a radial diffusion field and thus a rodlike morphology. The theory was not backed with reliable experimental evidence however, and Hunt and Chilton (1963), Day and Hellawell (1964) and Hunt (1966) have shown that the breakdown from lamellae to rods is caused by the production of a curved solid/liquid interface, either by means of a constriction or by production of a cellular interface. The curved solid/liquid interface causes a loss in preferred orientation between the phases that results in the rodlike eutectic being the more stable form. The observed breakdown upon cell formation of eutectics with volume fractions greater than 0.28 is caused by an increase in interlamellar spacing at cell edges that does not coincide with the increase of solid/liquid

interface of the cell. Thus, the ability of an impurity to modify a lamellar eutectic is determined only by its ability to form impurity cells.

b) Faceted/faceted Eutectic Growth

This group of eutectics is found with non metallic systems, since these materials usually have high entropies of fusion. Eutectic systems that have been investigated have mainly been between organic materials (Boschwar 1934, Penfold 1964 and Hunt and Jackson 1966) but Brady, even as early as 1922, noted the existence of this class of eutectic and mentioned that many igneous rock eutectics belonged to the class.

In these eutectic alloys both phases grow in a faceted manner and the growth mechanism of the eutectic reaction can be either independent growth of the two phases or repeated nucleation and growth.

In the independent growth mechanism the two phases grow fairly near to each other, although they are not necessarily in contact; neither is the solid/liquid interface isothermal. The diffusion distances are large compared with the regular structures above and the microstructures often appear as large

masses of both phases. If these systems are subjected to high growth rates, nucleation can occur ahead of the growing interface and spherulitic growth is observed. (Jackson 1966) Growth is then by a repeated nucleation and growth mechanism.

c) Non-Faceted/faceted Eutectic Growth

This third group of eutectic alloys is found between high and low entropy of fusion materials. The majority of the previous work has been on metal/non-metal systems; especially the systems Fe/C (Wilkinson and Hellawell 1963, 1965; Lakeland 1964, 1965, Hughes 1965 and Brigham, Puffey and Kirkaldy 1966) and Al/Si (see section 1.5) but work has also been carried out on the organic analogues. (Hunt and Jackson 1966) The microstructures of these alloys, which are notoriously sensitive to growth conditions, indicate that different growth mechanisms may be operative in this group. The three basic growth mechanisms postulated above will now be discussed in turn.

i) Independent or Separate Growth of the two phases

This mechanism would be very similar to the faceted/faceted eutectic growth described above with each of the

eutectic phases growing independently as if constitutionally undercooled by the other. The growth process would be non co-operative and diffusion distances would be large. There are no reports, as yet, of non-faceted/faceted eutectic growth occurring by this mechanism.

ii) Co-operative Growth of the two Phases

This mechanism is very similar to the lamellar and rodlike growth discussed above. Growth is by a short range diffusion process, but the growth interface need not be isothermal. Growth is dominated by the crystallographic limitations of the high entropy phase and can be of two types. Either there is a non-steady state diffusion process, in which case an irregular interconnected faceted structure is produced, or there is a steady state diffusion process, in which case a complex regular faceted structure is formed.

The irregular interconnected eutectic has been a matter of much controversy. Fe/C eutectic is now believed to form this structure (Bunin et al. 1953; Oldfield 1960; Lakeland 1965; Brigham, Purdy and Kirkaldy 1966), but the controversy still exists with other metal/non-metal eutectic systems, especially Al/Si, and some of these systems may well grow by mechanism iii mentioned below.

Complex regular structures are sometimes produced in these eutectic systems, particularly when the alloys are slightly rich in the faceted component. These structures with a steady state diffusion field usually comprise small groups of parallel faceted plates which are attached to central spine plates to produce feather and web-shaped particles.

iii) Repeated Nucleation and Growth

This growth mechanism has been the frequently accepted one for metal/non metal eutectics, with nucleation of the non-metallic phase occurring continuously ahead of the growing interface. (Hardy 1951, Tillier 1957b and Chadwick 1963, 1965) This mechanism has been put forward because there appears to be no orientation relationship between the two eutectic phases in metal/non-metal systems. (Straumanis and Brak^us, 1937, Meussner 1959b) The fact that no orientation relationship exists is taken as indication that the two phases nucleate independently. However, this separate nucleation does not mean that repeated nucleation is required for a growth mechanism to operate. Both mechanisms i and ii discussed above are possible with a separate nucleation event for each of the phases followed by subsequent growth of the two phases.

A repeated nucleation and growth mechanism would produce a randomly orientated and non-interconnected faceted phase but, except where careful studies are carried out, it is not possible to tell from a polished surface whether this, or the similar irregular but interconnected faceted phase, has been formed. Spheroidal growth is the only obvious example of this growth mechanism.

The eutectic classification given above is shown in diagrammatic form in fig. 2. The relationship of this classification to other current forms is also shown in the diagram and it can be seen that classifications prior to Hunt and Jackson (1966) were usually based on factors that depended indirectly on the entropy of fusion of the constituent phases.

(4) AREA OF RESEARCH

It has become increasingly apparent that while the non-faceted/non-faceted eutectic systems are now quite well understood and documented, the same is not true for the more complex non-faceted/faceted eutectics. Although a very large amount of literature has been published on some metal/non-metal systems, e.g. Fe/C and Al/Si, the vast majority of this work has been carried out on impure castings and so has contributed little to the understanding of the growth mechanisms of non-faceted/faceted eutectics. It was therefore, decided to carry out a series of controlled solidification experiments on such a metal/non-metal eutectic system in an attempt to discover what the growth mechanism of the eutectic reaction was and whether changes in the variables of growth rate, specimen temperature gradient and alloy composition could change the growth mechanism of the system.

The eutectic system aluminium/silicon was chosen for this investigation as it is the one usually cited as a typical example of a metal/non-metal eutectic alloy.

Further investigations were carried out on other similar eutectic systems such as Ag/Si, Au/Si etc. with the object of producing a better understanding of non-faceted/faceted eutectic growth.

(5) PREVIOUS WORK ON THE EUTECTIC SYSTEM Al/Si

a) The Phase Diagram (fig. 12)

Early work on the eutectic system gave widely varying compositions for the eutectic point. Prior to 1958 the most consistent value quoted in the literature was 11.7 wt.% Si. (Hansen 1958) However, Meussner (1959a) redetermined the eutectic point in this phase diagram. He found that the difficulty in determining the eutectic composition is due primarily to the steep silicon liquidus curve and the ease of nucleation of primary silicon during cooling. This makes thermal analysis of hypereutectic alloys very unreliable. Meussner quotes a eutectic reaction at 12.7 wt.% Si and at 577°C. These values were obtained from thermal data on hypoeutectic alloys and equilibration studies over a wide range of compositions. Zone levelling experiments by Kerr, Bell and Winegard (1965) confirm the eutectic composition at 12.7 wt.% silicon. The range of solid solubility at the eutectic isotherm is very small for both the eutectic phases. The solubility of silicon in aluminium being 1.65 wt.% silicon, and the solubility of aluminium in silicon being quoted at around 0.001 wt.% aluminium. (Elliot 1965)

b) Solidification of Al/Si Eutectic Alloys

Very little early work was carried out on aluminium/silicon eutectic. In 1891 Minet recognised that an abnormal mode of crystallization could occur in the alloys of aluminium and silicon. Interest in the system was revived in 1920 when the commercial potentiality of this alloy was realised. In that year Pacz discovered that the mechanical properties of the aluminium/silicon alloy could be greatly improved by the addition of a small quantity of alkaline fluoride. This process subsequently became known as "modification". Because of the complications and the great amount of confusion that has arisen out of the previous work on modification, this literature will be reviewed in a later chapter reserved entirely for these modification problems. It was felt that modification could only be understood properly if the growth of the pure eutectic was understood. This present literature review will concern itself only with the pure eutectic.

The majority of these early papers are concerned with the modification of the alloy and very little work appears to have been carried out on the pure eutectic.

In 1937 Straumanis and Braks^U unidirectionally solidified the eutectic and showed that the microstructure was still irregular and that the silicon phase appeared to have no preferred orientation. They found a $\langle 100 \rangle$ Al preferred orientation but this is now accepted as being due to α - Al dendrite formation. (see section IV.2.) It appears that, unlike lamellar eutectics, no orientation relationship exists between the two eutectic phases.

Thall and Chalmers (1950) said that the solidification of the eutectic could be represented as in fig 3a. The rate of advance of the interface depending on the balance between the rate of heat flow from the liquid to the solid through the interface, and the magnitude of the latent heat evolved during solidification. Under otherwise similar conditions the interface should advance more rapidly the higher the thermal conductivity and the lower the latent heat of fusion. As the thermal conductivity of aluminium is greater than silicon and the latent heat of fusion less, Thall and Chalmers say that the α -aluminium/liquid interface should advance more rapidly than the silicon/liquid interface.

Thus, during solidification the solid/liquid interface would not be flat and the lead of the aluminium would increase with higher rates of cooling. From this model it is obvious that Thall and Chalmers thought of the eutectic as interconnected at these low growth rates and even refer to the eutectic alloy as lamellar. At high rates of growth the aluminium lead should be such that the aluminium overgrows the silicon and further growth requires repeated nucleation, hence a very fine structure is produced. (This theory was adapted for sodium modification - see section VII 2.b.)

Hardy (1951) commented that as there was no easy matching plane of good atomic fit in the aluminium and silicon lattices, a mechanism by which one eutectic phase nucleated on the other was not to be expected. Solidification would, therefore, take place by the independent formation of nuclei of aluminium and silicon and should lead, therefore, to an irregular structure. This does not follow as we have already pointed out in section I.3.c.iii

Rhines and Timpe (1957) studied the form of the eutectic silicon by dissolving away the aluminium matrix in HCl, and they noted the faceted nature of the extracted particles.

Obinata and Komatsu (1957) carried out similar work to Rhines and Timpe but also subjected the extracted particles to X-ray and goniometry studies. The eutectic silicon was extracted from a variety of furnace-cooled and sand cast specimens with various impurities added. A wide range of eutectic silicon morphology was observed, the crystals being either prismatic with $\{111\}$ growing in a $\langle 110 \rangle$ direction, or granular with $\{111\}$ and $\{100\}$ faces, or a plate-like form with $\{111\}$ faces in which one pair of faces, which were parallel to each other, were developed.

Tiller (1957b) also took the view that the eutectic reaction in the Al/Si system was because the primary phase was unable to serve as the nucleating agent for the second phase, and that the second phase nucleates heterogeneously in the liquid. The nuclei would of course be randomly orientated and would grow rapidly to reduce the undercooling. Because of the anisotropic growth characteristics of silicon this would lead to needle-like, plate-like or angular particles, but would result in a random orientation of non-interconnected particles. Tiller also added that this mechanism was only inferred from the geometrical shape of the particles as revealed on a polished section and from the fact that no preferred

orientation was obtained from the X-ray work. As mentioned in section I.3.c.iii. this evidence is not enough to determine whether the silicon is interconnected or not.

Plumb and Lewis (1958) also favoured a repeated nucleation and growth process for the eutectic alloy but said that growth was occurring by a cyclic freezing pattern in which the two phases nucleate alternately.

Meussner (1959 b and c), following Rhines and Timpe and Obinata and Komatsu, also conducted some silicon extraction experiments but confined himself mainly to primary silicon, which he noted was heavily twinned. From the similarity between primary and eutectic silicon Meussner inferred that the eutectic silicon was most probably twinned as well. From his extensive research project on the cast eutectic, Meussner stated that the formation of the irregular eutectic structure is the result of the disparity in the nucleation and growth characteristics of the constituent phases. The eutectic silicon phase not only nucleates readily but grows rapidly into a branched plate structure which projects ahead of the eutectic solid into the liquid and the eutectic Al-phase is relegated to the role of forming the matrix around the existing silicon plates. The eutectic Al-grains are, according to Meussner, nucleated on the surfaces of the silicon plates and grow along them. The branching of the eutectic silicon phase effectively restricting

the growth of the eutectic Al-phase. Since the continued growth of the eutectic alloy is said to require renucleation of the Al-phase beyond the obstructing silicon plate and since no preferred orientation relationship appears to exist between the aluminium and the silicon, the eutectic Al-grains of the matrix are small and randomly orientated. Neussner also observed that eutectic silicon grows out from primary silicon. This is an important paper since it states the controlling influence the eutectic silicon has on the eutectic morphology and restates that the eutectic silicon phase is most probably interconnected. The evidence for interconnection is a photograph of the top surface of a solidified ingot which purports to show continuity of the eutectic silicon. The evidence is by no means conclusive. Ghosh, Wilcock and Kondic (1960) also state that the silicon particles appear to be interconnected, but the evidence (silicon particles of similar orientation each side of an α -Al particle) is again not conclusive. (see section III.1.)

Chadwick (1963) in his review, however, reverts to the repeated nucleation model and says that Al/Si eutectic growth is by a non steady state co-operative process, since the eutectic silicon does not grow normal to the solid/liquid interface. When the separation of silicon particles becomes greater than the characteristic of the particles imposed

growth rate, new silicon particles nucleate in the region in between. The growth process is thus a constantly repeating cycle of renucleation of Si particles whenever it is necessary to keep the interparticle spacing at the required value. (see fig. 3b.)

In a later review paper Chadwick (1965) reports some personal experimental work and states that extraction has shown that the eutectic silicon particles are not interconnected and that the individual particles either nucleate separately or originate from the fracture and subsequent growth of a parent particle. This work was on a high purity unidirectionally solidified alloy and represents one of the few papers published that does not base its conclusions on Al/Si growth upon the results of impure sand castings. In these alloys the eutectic silicon particles were found to roughly align themselves with the macroscopic growth direction. Otherwise the eutectic microstructures were the same as impure sand castings. An increase in growth rate was found to lead to a refinement in the eutectic microstructure.

Bell and Winegard (1963) in their unidirectional solidification work on aluminium/silicon eutectic alloys state that the silicon phase of the eutectic alloy is interconnected and that there is no repeated nucleation to give the observed microstructure. The

interconnection was shown by careful extraction of the silicon from the aluminium matrix. The silicon was even interconnected in the rapidly quenched condition. These authors (1965a) also mention a low growth rate form of eutectic silicon which has a rodlike structure with a $\langle 100 \rangle$ Si preferred orientation which is aligned with the growth direction. This structure was reported independently during the course of the work for this thesis.

As previously mentioned, hypereutectic alloys of this group sometimes produce complex regular structures. Al/Si produces a complex regular structure commonly called the spiders web structure. This has been called a form of primary silicon by many workers. (Spengler 1955, Curtler 1953, Scheil and Zimmermann 1957, Meussner 1959b) since its volume fraction is greater than that of the normally observed eutectic. Hunt and Jackson (1966) however, treat it as a special case of faceted/non-faceted eutectic growth, the shape of the structure being determined by the faceted material.

(6) OBJECTS OF RESEARCH

When work on this thesis was initiated, a review of current and previous literature showed that a great deal of confusion and contradiction existed concerning aluminium/silicon eutectic. It was therefore felt that the best way to produce a disinterested research project on this complex system was to assume nothing, and to carry out unidirectional solidification experiments with high purity eutectic alloy over a wide range of carefully controlled and measured conditions of growth. It was then planned to examine the resulting eutectic specimens by variations on the standard techniques of microscopy, extraction, goniometry and X-ray diffraction to discover how the growth conditions affected the structure, and, by inference, the growth mechanism of the eutectic.

Pilot experiments were carried out with the eutectic system Ag/Si and Au/Si to determine whether any similarities existed between them and Al/Si eutectic alloy. In this way it was hoped that answers would be found to the questions provoked by the literature survey, and that a coherent picture would be obtained of metal/non-metal eutectic growth in general.

Finally, controlled modification experiments were carried out in an attempt to explain the reason for the effect of sodium metal on the structure of aluminium/silicon eutectic.

The experimental techniques described in this section were the majority of those used. However, some slight variations were used to produce suitable results. The experimental techniques are described under the appropriate heading in the sections on results. (Sections 3.7, 3.8 and 4)

(1) PREPARATION OF ALLOYS

The alloys used in this work were prepared from high purity elements. The analysis specified with the elements were as follows:-

99.99% Pure Metallurgical Aluminium	Al ^{99.99%} purity, Fe 0.001%, Si 0.001%, Cu 0.001%, Mg 0.001%, Pb 0.001%, Zn 0.001%, Bi 0.001%, Sb 0.001%, Sn 0.001%, Ti 0.001%, V 0.001%, Cr 0.001%, Ni 0.001%, Mn 0.001%, Co 0.001%, As 0.001%, Se 0.001%, Te 0.001%, I 0.001%, Br 0.001%, Cl 0.001%, S 0.001%, P 0.001%, O 0.001%, H 0.001%, N 0.001%, C 0.001%
99.99% Commercial Silicon	Si 99.99% purity, Al 0.001%, Fe 0.001%, Cu 0.001%, Mg 0.001%, Pb 0.001%, Zn 0.001%, Bi 0.001%, Sb 0.001%, Sn 0.001%, Ti 0.001%, V 0.001%, Cr 0.001%, Ni 0.001%, Mn 0.001%, Co 0.001%, As 0.001%, Se 0.001%, Te 0.001%, I 0.001%, Br 0.001%, Cl 0.001%, S 0.001%, P 0.001%, O 0.001%, H 0.001%, N 0.001%, C 0.001%
99.99% Silicon grade	Si 99.99% purity, Al 0.001%, Fe 0.001%, Cu 0.001%, Mg 0.001%, Pb 0.001%, Zn 0.001%, Bi 0.001%, Sb 0.001%, Sn 0.001%, Ti 0.001%, V 0.001%, Cr 0.001%, Ni 0.001%, Mn 0.001%, Co 0.001%, As 0.001%, Se 0.001%, Te 0.001%, I 0.001%, Br 0.001%, Cl 0.001%, S 0.001%, P 0.001%, O 0.001%, H 0.001%, N 0.001%, C 0.001%
99.99% Al-Si grade	Si 99.99% purity, Al 0.001%, Fe 0.001%, Cu 0.001%, Mg 0.001%, Pb 0.001%, Zn 0.001%, Bi 0.001%, Sb 0.001%, Sn 0.001%, Ti 0.001%, V 0.001%, Cr 0.001%, Ni 0.001%, Mn 0.001%, Co 0.001%, As 0.001%, Se 0.001%, Te 0.001%, I 0.001%, Br 0.001%, Cl 0.001%, S 0.001%, P 0.001%, O 0.001%, H 0.001%, N 0.001%, C 0.001%

II EXPERIMENTAL TECHNIQUES

The experimental techniques described in this section cover the majority of those used. However, where slight variations were used to produce specific results, the different techniques are described under the appropriate heading in the sections on results. (sections III, IV and V)

(1) PRODUCTION OF EUTECTIC SPECIMENS

The alloys used in the work were prepared from high purity elements. The analyses supplied with the elements were as follows:-

A.I.A.G. Super Raffinal Aluminium	Si 1 ppm, Fe 2.2 ppm; Cu < 1 ppm
J.M. Czochralski Silicon	Al < 1 ppm; Mg < 1 ppm
J.M. Silver grain	Fe 5 ppm; Cu 3 ppm; Bi < 1 ppm; Cd < 1 ppm; Mg < 1 ppm
J.M. Gold grain	No analysis supplied but assumed ~ 5N

The alloys prepared were usually of eutectic composition but in the course of the work it was found necessary to produce hypo and hypereutectic alloys as well. Work was confined to the three eutectic systems Al/Si, Ag/Si and Au/Si.

Radio frequency induction heating was employed to produce the alloy specimens. Melting up was carried out in a 'bell jar furnace'. (fig. 4) This consisted of a Pyrex cylinder which was closed at both ends by means of large brass plates. The bottom plate contained an exit port for the pumping system which consisted of a 2" oil diffusion pump backed by a large rotary pump. The leads for the induction heating coil entered through O-ring seals in a Tufnol panel which was attached to the bottom plate. The top plate, which was water-cooled, contained a removable portion for specimen access. This removable portion contained a Pyrex glass viewing port and an O-ring seal to allow a thermocouple sheath to be suspended in the melt. The eutectic alloys were prepared in ~ 100 gm. lots in recrystallized alumina crucibles. In order to obtain good coupling with the Radyne 3KW R.F. generator, the alumina crucibles were contained in previously degased graphite susceptors.

The Al/Si alloys were melted up under vacuum ($< 10^{-4}$ torr). The Ag/Si and Au/Si alloys were melted up under argon (30 cm.Hg.) in order to suppress volatilization. The melts were homogenised for one hour at several hundred degrees centigrade above their eutectic isotherms before vacuum casting or furnace cooling.

For vacuum casting, the alumina crucible and the graphite susceptor had a hole bored through them. (fig. 4) This hole was plugged with an alumina sheath which passed through the O-ring seal in the top plate assembly. Casting was achieved by raising the alumina sheath. This caused the melt to run into copper moulds situated beneath the crucible. It was found that vacuum casting was not essential and that remelting and casting in air produced no variation in the properties of the chill cast rods or their subsequent unidirectional growth and so this was sometimes done. The resulting cylindrical chill cast specimens were some 6 cm. long and 0.8 cm. in diameter. The ends of these rods were machined flat so that two could fit neatly together when they were placed into the recrystallized alumina sheath, in which the unidirectional freezing experiments were carried out. The rods were pickled in an appropriate acid to remove any surface impurities introduced by the machining operation.

(2) PILOT EXPERIMENTS

These were of a very simple nature, and were carried out to compare the various eutectic microstructures in the furnace-cooled condition. The eutectic alloys Al/Si, Ag/Si and Au/Si were melted up in small 1" diameter tapered graphite crucibles shielded with alumina. The bell jar furnace was again used. They were homogenised several hundred degrees above their eutectic isotherms for ~ 1 hr. and then allowed to furnace cool in situ. The cooling rate was slow as the primary heat losses by radiation were substantially reduced by the alumina shielding. The resulting small ingots were sectioned vertically and the surfaces prepared for microscopical examination as under section II.4.

(3) UNIDIRECTIONAL FREEZING EXPERIMENTS

It was noted in the section on Previous Work that very little controlled solidification of these eutectic alloys had been carried out. The majority of this work was on small castings in which the growth direction, the growth rate and the imposed liquid temperature gradient ahead of the interface were not known or controlled.

The experiments described below were carried out with high purity chill-cast eutectic alloys under carefully controlled and measured growth conditions. The chill cast specimens were contained in recrystallized alumina tubes 15 cm. long with an internal diameter of 0.8 cm. The alumina tube was supported on a silica rod and placed in a silica tube which was evacuated through a brass end cap using a 1" oil diffusion pump system to produce a vacuum of $< 10^{-4}$ torr. For the Ag/Si and Au/Si eutectic, argon (30 cm.Hg.) was again used to suppress volatilization.

a) Growth Rate Control

The eutectic alloys were unidirectionally grown by pulling the specimens vertically down from a furnace. The specimens were pulled vertically as this tends to minimize effects due to thermal convection currents. (Chandrasekhar 1961, Cole and Winegard 1964, Utech and Flemings 1966, Hurle 1966)

The pulling device consisted of a 1350 r.p.m. electric motor which drove a threaded crosshead via a set of reduction gear boxes. (fig. 5) The first gear box after the motor was a small Kopp Variator. This gear box, with a 1350 r.p.m. input speed, gave an infinitely variable output speed from ~ 500 to ~ 4000 r.p.m. This device enabled the crosshead speed to be varied without stopping its motion. By changing the subsequent gear boxes of the reduction train, a wide range of crosshead speeds could be obtained and a range of 2.5×10^{-6} - 1.5×10^{-3} cm./sec. was used. The silica tube containing the specimen was clamped to the crosshead. The crosshead withdrawal rate was assumed to equal the growth rate of the eutectic alloy at the middle portion of the specimen.

At the beginning of a pull the growth rate is lower than the withdrawal rate and at the end of the pull the growth rate is greater than the withdrawal rate. This is because the specimen acts as a heat sink and the rate of heat extraction is thus dependent on the amount of specimen in the cold zone of the furnace.

b) Temperature Gradient Control

Control and measurement of the temperature gradient in the liquid ahead of a growing eutectic interface is a variable that has not received the attention that it should. For a great deal of unidirectional solidification experiments, the temperature gradient has been taken as the furnace temperature gradient. This is far from being the case. The actual temperature gradient in the specimen depends on such factors as the temperature gradient and geometry of the furnace, the cross-sectional area, the length and the conductivity of the specimen and the shape and thermal conductivity of the specimen container. Results indicated that the specimen and furnace temperature gradient could differ by over an order of magnitude. Previous work (Wilkinson 1965) had shown that temperature gradients above $50^{\circ}\text{C}/\text{cm}$. were almost impossible to achieve using graphite as a container material. This was one of the reasons for choosing alumina tubes. The other reason was that there had been indications that at high temperatures aluminium reacted isothermally with the graphite to form the methanide Al_4C_3 .

The first furnace used was laboratory-built and had Nichrome windings on a 2" i.d. alumina tube $15\frac{1}{2}$ " long. The furnace was well insulated with asbestos wool and asbestolite.

The top end was sealed with an asbestos wool plug to prevent convection cooling. It was found that great care had to be taken to ensure effective sealing as otherwise the incoming cool air would upset the control thermocouple. The bottom end of the furnace tube was fitted with a graphite plug which had a hole bored through it to allow the insertion of the silica sheath containing the specimen. Furnace temperature control was by means of an Ether-Transitrol (Model 991) and associated circuitry. The indicated Ether temperature was calibrated against another Pt/13% Pt.Rh thermocouple using a Cambridge potentiometer. This calibration was checked at regular intervals and although the Ether would control the furnace to $\pm 10^\circ\text{C}$ for many days, it did tend to drift slightly after long periods.

The specimen temperature gradient was measured by an apparatus illustrated in fig. 6. This is developed from a technique used by Wilkinson.(1965) The apparatus consisted of a specimen and container identical to that used for the unidirectional freezing experiments, except that the specimen had a fine (1.2 mm o.d.) thermocouple sheath running up through its centre. A 150 μ chromel alumel thermocouple was free to move up and down this sheath. The thermocouple itself was fused to a glass rod which left the silica vacuum chamber via an

O-ring seal in the brass end cap, and so the position of the thermocouple tip relative to the specimen could be altered by moving the external glass rod. The silica outer sheath was evacuated through a side arm in the brass end cap. By suitable placing of this apparatus in the furnace, it was possible to arrange that the eutectic isotherm was midway along the eutectic specimen. The withdrawal rate equals the growth rate at the midway point along the specimen and so this was the region in which temperature gradient measurements were required.

In both these temperature gradient measurement and unidirectional solidification experiments one hour was allowed for thermal equilibrium to be attained. The gradients were measured at the eutectic isotherm simply by moving the thermocouple relative to the specimen and plotting temperature against distance along the specimen. The tangent to the resultant curve was then drawn at the eutectic temperature. (see fig. 7 for specimen result)

The temperature gradients were shown to vary with the position of solid/liquid interface relative to the specimen itself. They were higher towards the bottom and lower towards the upper end of the specimen. This variation was slight and only became of importance at the very high temperature gradients. The reason for this variation was again the heat sink properties of the specimen and container.

By repeating the above experimental procedure for a wide range of furnace temperatures, calibration curves were produced of specimen temperature gradient against furnace temperatures. (fig. 8a) This meant that unidirectional freezing experiments could now be carried out under known conditions of growth rate R and specimen temperature gradient G . The maximum value of G that was attainable using the above set-up was limited by the furnace maximum temperature. Another factor was that the solid/liquid interface position began to approach the bottom end of the furnace and was, therefore, more affected by changes in room temperature, draughts etc.

c) Production of High Temperature Gradients

The first attempt to produce higher temperature gradients was to place a water-cooled copper lining into the bottom half of the furnace. (fig 9a) This did produce higher temperature gradients but the increase was not as great as required. This was due primarily to the presence of the silica vacuum jacket which did not allow good contact between the specimen and the copper lining. However, calibration readings were taken.

(fig 8a)

Further attempts at producing high G were the replacement of the Nichrome wound furnace with a Johnston Matthey Platinum Furnace (Model K25B). This gave a maximum temperature of $\sim 1500^{\circ}\text{C}$. A water-cooled copper insert was built to fit this furnace and the inner bore reduced so that the vacuum jacket could be discarded. This further increased the range of G values. (fig. 8b)

The highest values of the specimen temperature gradient were obtained by reducing the heat flow down the specimen. This was done by decreasing the specimen diameter from 8 mm. to 2 mm. Good contact with the copper insert was assured by means of a copper cylinder that fitted into the top of the

insert to change the entrance hole so that the smaller sized alumina tubes fitted. (fig. 9b) Again, no vacuum jacket was used. Calibration was carried out by replacing the 2 mm. specimen with a thick thermocouple. At the lower G-values these results could be checked by using the observed microstructure. It was now possible to carry out unidirectional solidification experiments with known temperature gradients over the range $3.5^{\circ}\text{C} - 600^{\circ}\text{C}/\text{cm}$. (see fig 8a and b)

d) Quenched Interfaces

These were obtained by rapidly removing the specimen from the furnace. For the relevant experiments the water-cooled copper insert was used as a quenching pot. The growth rates for which quenched interfaces were produced were very slow and this rather crude quenching method was found to be quite adequate, especially for the silicon phase which was not capable of a rapid kinetic response. (A. Hellawell 1967a)

(4) SPECIMEN PREPARATION

When the eutectic specimens had been unidirectionally solidified under various controlled conditions they were carefully removed from the alumina tube containers and samples were cut from the eutectic rods.

a) Sections

Sections were cut both longitudinal and transverse to the growth direction. These sections were removed from the centre section of the eutectic alloy. Flats were ground with SiC. papers.

It was found that to obtain a reasonable surface worn SiC. papers were best. Fresh papers tended to give a dull deeply scratched surface with SiC. particles embedded in the soft matrix. After grinding on the finest SiC. paper (600 grade), the specimens were polished with diamond paste on a selvyt covered lapping wheel. A good surface finish was obtained with five minutes polishing using light pressure with $6 - 3 \mu$ and then $1 - \frac{1}{2} \mu$ diamond paste on well used lapping wheels slightly lubricated with paraffin. Final removal of polishing compounds from round the slightly proud Si particles

was done with ethanol on a napless cloth. Drying marks were prevented by rapidly evaporating the ethanol with compressed air.

Specimens were viewed under the microscope in the 'as polished' condition. There was no need for etching to show up the two eutectic phases.

Etchants were used however, to show up structures in the eutectic phases themselves. The first was an electrolytic etch developed by Hone and Pearson (1949) for showing up the grain structure in aluminium alloys. This etchant was applied to Al/Si eutectic alloys by Meussner (1959b) to show up the aluminium grain structure.

The etchant was:

350 ccs. 85% orthophosphoric acid

132.5 ccs. diethylene glycolmonoethyl ether

5 ccs. 48% HF

12.5 ccs. distilled water

The specimen was made the anode. Stainless steel was used for the cathode. The solution was stirred magnetically during etching. Five minutes with a potential of 20 V across the cell gave a good anodised film on the aluminium leaving the Si slightly proud of the surface. When viewed under polarized light, the aluminium grain structure was clearly

revealed. Other aluminium grain etchants were tried but severe pitting always occurred at the aluminium/silicon boundaries.

The second etchant used was a modified CP4 etch (Meussner 1959b) to reveal the internal structure of the silicon particles in the eutectic alloy.

The etchant was:

- 1 part 48% HF
- 2 parts concentrated HNO_3
- 15 parts glacial acetic acid

Etching times of ~ 60 seconds were employed. There was no visible attack on either the aluminium or the aluminium/silicon boundaries.

b) Extractions

Further information on the silicon phase of the eutectic alloys was obtained by chemically extracting it from the matrix. The process was first used by Rhines and Timpe (1957) but has been used by other workers in the field. (Neussner 1959b, Bell and Winegard 1965b)

Small sections of the alloys were immersed in suitable chemical mediums. These were:

Al/Si		concentrated HCl and concentrated HCl/water mixtures
Ag/Si		concentrated HNO ₃ /water mixtures

Hydrogen evolution did tend to break up the delicate particles, but this effect could be reduced by 'titrating' the acid against the sample so that the reaction proceeded at a leisurely pace. Extraction was deemed complete when gas evolution had ceased.

It was shown in two ways that the acid had no significant effect on the shape of silicon particles. The first was by leaving the silicon particles in the acids for varying lengths of time and comparing the particles under the microscope. The second was by comparing the extracted particles and the models built up by surface analysis. There appeared to be perfect

correlation, but it is not known if fine surface detail was an etching artefact or not.

When extraction was complete the particles were washed in distilled water and then ethanol. Finally, they were dried by gently warming to evaporate the ethanol.

(5) MORPHOLOGY DETERMINATION

This was carried out almost exclusively on the silicon phase of the eutectic alloys. The techniques used can be divided into two main groups. The first is section surface analysis of the eutectic alloys and the second is extracted particle analysis.

a) Section Surface Analysis

From the transverse and longitudinal sections of the alloys it was possible to build up models of the various silicon particle shapes. Where angles had to be measured, it was necessary to plot histograms or to carry out three surface analyses. This was usually done under the microscope with a calibrated rotating eyepiece. Distance measurements were normally carried out on photographs taken of the specimen as the irregular structures made simple micrometer eyepiece measurements very tedious. Regular structure distances could be easily measured directly under the microscope using a micrometer eyepiece. These results were compared with those from the extracted particles.

b) Extracted Particles - Optical Microscopy

The particles were studied by breaking the aggregate, if necessary, and scattering them over a glass slide and observing them under the optical microscope. The majority of the work was with reflected mercury illumination. Under low magnification (X50) it was possible to micromanipulate these small particles using a hair mounted on a matchstick. This was an invaluable tool as it was sufficiently greasy to allow the particles to be picked up or moved. It was therefore possible to sort out particles of interest by removing them from entanglements with other particles. It was also possible to orientate them so that plane faces were normal to the incident light beam and true angular measurements could be taken of surface features. The majority of the particles were thin enough to transmit light and information was also obtained by transmission microscopy.

Particles were also subjected to goniometry by picking them up with a 100μ glass fibre; the end of which had been made tacky with a solution of Canada Balsam in xylene. The other end of the glass fibre was cemented onto a nickel pip with Durofix. (fig. 10a) The nickel pip fitted onto the top arc of the three circle goniometer of a Unicam Single Crystal Goniometer. (Model S25) The Unicam was modified by removing

the objective lens of the supplied tele-microscope attachment and replacing it with a Beck half slip illumination train and objective. Fortunately all fitments had the standard R.M.S. threads. By changing the objectives, a range of magnification of 30X to 270X could be used. When a particle plane was normal to the incident light beam, back reflection was observed. This back reflection was fairly sensitive and the angles between the faces of the particles could be measured using the goniometer circles to an accuracy of about ± 30 mins. of arc.

c) Extracted particles - Scanning electron microscopy

Conventional optical microscopy on extracted particles, which has been described above, has two serious limitations. The first is that if the particles are not planar, then the depth of focus of the optical system is often not sufficient to cope with the variation in objective distance. The second limitation is that the resolving power of the optical microscope is not sufficient for the observation of very fine particles. Many of the extracted particles were found to be both non-planar and very fine, and so optical microscopy was not a success. This problem was overcome by the use of scanning electron microscopy.

In the scanning electron microscopy an extremely fine electron probe ($\sim 100\text{\AA}$) is scanned across the surface of the specimen in a minute television type raster using a scanning generator for the line and frame frequencies. (fig. 11) The same waveforms are applied to the scanning coils of a cathode ray oscilloscope which is then scanned in synchronism with the electron beam. The magnification control attenuates the current in the main scanning coils while the cathode ray tube scan is not affected. The magnification is given by the ratio of the two scanned areas. (e.g. a 10 sq. cm. cathode ray tube screen area and a minimum scanning area on the specimen of 1 sq. μ gives a maximum magnification of $\times 100,000$)

The contrast in the recorded scanning electron micrograph comes from the variations in the number of collected electrons. Secondary electrons are produced when the primary electron beam at 20 K.V. strikes the specimen. These secondaries are attracted to a collector by a high positive voltage. The output from the collector is converted into a varying voltage that is used to modulate the brightness of the cathode ray tube. These variations in brightness correspond to variations in the signal from point to point on the specimen surface and are produced by changes in surface topography or chemical composition.

Extracted silicon particles were mounted on aluminium stubs with an electrically conductive adhesive (a mixture of Durofix and graphite) in order to prevent electric charge build-up due to the electron probe. The stub fixed onto a goniometer stage so that the orientation of the particles relative to the electron probe could be altered and the specimen, therefore, observed from different angles. In this way it was possible to obtain a very good indication of the three-dimensional morphology of the extracted particles.

The best results were obtained from heavily etched surfaces of eutectic alloy since handling was avoided and the remaining metal matrix tended to support the fine brittle non-metal particles and so the break-up of the exposed silicon particles was minimized. The morphological relationships of these exposed silicon particles were the same as when the particles were embedded in the metal matrix, and so by using a scanning electron microscope it was possible, because of the instrument's large depth of focus and good resolution, to obtain photographic evidence of these relationships even when the particles were non-planar and very small.

(6) CRYSTALLOGRAPHY DETERMINATION

This work involved the use of standard X-ray techniques modified slightly to deal with the type of specimens used. X-rays were produced on an old Metropolitan Vickers Raymax and a more modern Newton Victor Raymax 60. Both generators were of the continually pumped variety with exchangeable targets. Copper targets were used throughout this work.

The X-ray cameras used were accessories for the Unicam single crystal goniometer. The back reflection Laue camera had a specimen-to-film distance of 30 mm. The rotation camera had an effective radius of 30 mm. The Unicam also had cardioid cams which allowed oscillation photographs to be taken. Exposure times varied from ~ 3 hrs. for a Laue photograph to ~ 6 hrs. for a filtered rotation photograph on Ilford Industrial G film.

The experimental work can be divided under two headings; the eutectic alloys and extracted particles.

a) The Eutectic Alloys

X-ray Laue photographs were taken normal to transverse and longitudinal sections of the eutectic alloy using a 100 μ cobalt glass collimator.

15° back reflection oscillation X-ray photographs were found a useful technique when the preferred orientation of a certain feature of the eutectic alloy was required. The cylindrical camera with a 250 μ collimator was used. The bulk specimen only gave high angle reflections but these were sufficient to enable the identity distance for the two phases to be determined. The phase giving rise to a certain layer line could be found by solving the two superimposed Debye line patterns and finding on which Debye line the layer line fell.

X-ray rotation photographs of small pillars of the eutectic alloys were taken. The rotation axis was the growth direction of the alloy. The small pillars (4 mm. x $\frac{1}{2}$ mm. x $\frac{1}{2}$ mm.) were prepared by grinding and polishing a longitudinal flat and then removing a 1 mm. slice with a jewellers saw. This freshly cut surface was ground and polished to remove saw marks and damage. Finally, the small pillars were cut from this thin slice and were heavily etched to remove this further mechanical damage. The pillar major axis corresponded to the growth direction. The pillars were Durofixed onto the nickel pips

which then fitted onto the top goniometer circle. (fig. 10b)
The layer line in the resulting photograph could be ascribed to the correct phase by solving for the two sets of Debye lines as described above.

b) Extracted particles

Specimen selection and mounting was as for the morphological investigations. The reflected light microscope attachment was used to orientate the crystal. Laue photographs were usually taken normal to a major face of the particle with a prominent surface feature vertical. Rotation photographs were usually taken about a symmetry axis. Large collimators could be used as the particles were smaller than the X-ray beam and so the spot size was determined by specimen size. It also made the lining up of specimens much more easy.

The Unicam was an ideal instrument to use, as goniometry, Laue and rotation photographs could all be carried out on the same specimen without need for remounting.

III PILOT EXPERIMENT RESULTS

These experiments were primarily intended to discover what similarities, if any, exist between the microstructures of the eutectic systems aluminium/silicon, silver/silicon and gold/silicon.

Each of these three systems has a simple eutectic phase diagram between a virtually pure silicon phase and an α -solid solution f.c.c. phase. (see figs. 12, 13, 14) The experimental details of specimen preparation are in section II.2.

(1) Al/Si EUTECTIC ALLOYS

The small furnace-cooled ingots (~ 2 ccs.) were sectioned vertically. The resulting macrostructures showed slight segregation of the primaries. The microstructures of these alloys were consistent with those reported by other workers. (e.g. Meussner 1959b and c)

The silicon phase appeared as an irregular dispersion of plates in an aluminium matrix. (Plate 15a) These plates often appeared in fan-shaped groups (or bursts), which sometimes originated from primary silicon crystals. It was not obvious

from these random sections whether the eutectic silicon was interconnected or not. Evidence such as plate 15b has often been produced as proof of interconnection. (Chosh, Wilcock and Kondic 1960) However, it is not obvious whether the continuation of eutectic silicon each side of a primary α -Al particle proves anything, other than that the individual silicon plates can be large.

When hypereutectic alloys were furnace-cooled, a more regular form of the eutectic was observed. This complex regular eutectic form was only confined to small areas of the eutectic alloy. The majority of the alloy still displayed the irregular form. The complex regular eutectic structure consisted of feather-shaped groupings of silicon plates.

(Plate 16a) In many cases two of these feather-shaped units were observed joined together. (Plate 16b) The appearance of such double feathers gave rise to the name 'spiders web'.

This web structure was usually found attached to a primary silicon particle.

(2) Ag/Si EUTECTIC ALLOYS

This eutectic system showed great similarity to the Al/Si alloy described above. The eutectic structure again consisted of irregularly orientated plates of silicon, this time embedded in a silver matrix. (Plate 17a) However, in addition, the eutectic silicon grew in a filigreed form of what appeared to be twisted fibres. (Plate 17b) Hypereutectic alloys produced a complex regular structure upon furnace cooling. This was similar in general form to the Al/Si structure. (Plates 18)

(3) Au/Si EUTECTIC ALLOYS

These alloys produced microstructures very similar to Ag/Si. The irregular eutectic consisted mainly of a filigreed network of silicon. (Plate 19a) Hypereutectic alloys again produced a complex regular structure with a feather-shaped form. (Plate 19b)

(4) CONCLUSIONS

From the results of these simple experiments one may conclude that many similarities exist between the three systems, and that controlled experiments on one system may well relate to similar experiments with the other two. Therefore, if the growth variables of growth rate, temperature gradient in the liquid ahead of the growing interface, and the composition of the alloy are found to affect the morphology and crystallography of one of the eutectic alloys, then it would be hoped that similar effects would be produced in the other two systems.

IV Al/Si RESULTS

This section describes the results of unidirectional solidification experiments carried out under various controlled and measured conditions of growth with high purity Al/Si eutectic alloy specimens. After controlled solidification, the resultant specimens were analysed by adaptations of standard techniques of microscopy, goniometry and X-ray diffraction. The resulting microstructures were classified in terms of the various growth variables and from these it was possible to infer what growth mechanisms might have been operating in the system.

(1) CLASSIFICATION OF RESULTS

In the introductory section of this thesis it was stated that various growth mechanisms could be envisaged for a eutectic reaction. (section 1.3) These are:

- i) Separate growth of the two eutectic phases
- ii) Co-operative growth, either steady or non-steady state
- iii) Repeated nucleation and growth

Various kinetic mechanisms are possible under each of the above headings. It was felt that the type of growth mechanism that operated would depend on the values of the growth variables, that is supposing that it altered at all.

There are three growth variables that could possibly affect the growth mechanism, and hence the resulting microstructure of the eutectic alloy. These are:

R - the growth rate of the alloy specimen

G - the temperature gradient in the liquid ahead of the specimen's growing solid/liquid interface

C - the composition of the alloy

The information obtained from the experimental work was, therefore, classified in terms of these growth variables, and a relationship was soon discovered between these growth variables and the eutectic microstructure. (Tables 20 and 21) This relationship was most easily shown by two graphs of specimen temperature gradient G, against growth rate R; one for eutectic alloys, the other for hypereutectic alloys. (Figs. 27) Regions could then be identified on these graphs in terms of the observed microstructure of the eutectic. Names were given to the various eutectic forms from their appearance as observed in sections taken transverse to the

growth direction. The various types such as massive, rodlike, angular, irregular and complex regular are shown in plates 22 to 26 and the relationship between these structures and the growth variables of G, R and C is shown in the G/R plots of figures 27a and 27b.

Subsequent work on the eutectic system showed that the G/R plots could be better divided into only three regions depending on the mechanism of the eutectic growth, and that all the information could be placed onto one graph. (fig. 28) The three regions of this G/R plot were as follows:

Region A - separate growth of the aluminium and silicon eutectic phases by a long range diffusion process. This lead to the formation of the massive eutectic alloy. (Plate 22)

Region B - Co-operative growth of the two eutectic phases. The silicon phase showing a $\langle 100 \rangle$ Si preferred growth texture. Short range diffusion was implied by the eutectic microstructure which showed a rodlike or angular form. (Plates 23 and 24)

Region C - this was again co-operative growth of the two eutectic phases, but in this region the silicon particles were related to each other by $\{111\}$ spinel twins. The

microstructure implied a short range diffusion process, which led to the formation of irregular and complex regular forms of the eutectic alloy; (Plates 25 and 26) the complex regular form only being found in hypereutectic alloys. (see figs. 27)

(2) THE ALUMINIUM MATRIX GROWTH TEXTURE

In all the observed forms of this eutectic alloy, it was found that the aluminium phase never exhibited any growth texture. The eutectic alloy microstructure was very much dominated by the growth mechanism of the eutectic silicon. (It will have been noted that the eutectic form names are based on the form of the eutectic silicon) This thesis is, therefore, primarily concerned with growth forms of eutectic silicon. But the experimental results pertinent to the aluminium matrix will be given before dealing with the topic of these eutectic silicon growth forms.

The absence of a growth direction texture was shown by a series of rotation photographs taken of small pillars of eutectic alloy; the rotation axis being parallel to the growth direction. (fig. 10b) The results for each form of the eutectic microstructure gave the same indication of no preferred orientation for the aluminium phase. (see plates 29, 46 and 103) The Debye lines were usually spotty and incomplete but these irregularities varied widely from one specimen to another. A large number of such rotation photographs taken of many specimens, removed from the same unidirectionally grown alloy, showed that the spots present

on the Debye lines were always due to the existence of the relatively small number of aluminium grains in each pillar of eutectic alloy and not because there was any preferred orientation.

In hypoeutectic alloys grown at the higher growth rates, α -Al dendrites were present in the microstructure. Rotation photographs were taken of small eutectic alloy pillars containing these α -Al dendrites and a slight

$\langle 100 \rangle$ Al growth texture was obtained. (Plate 29)

As no growth texture was shown to exist in the pure eutectic alloy, the α -Al dendrites must have the usual $\langle 100 \rangle$ texture. Since the chemical extraction of silicon particles from the aluminium matrix proceeded mainly by attack at the aluminium/silicon phase boundaries, α -Al dendrites could be extracted from the eutectic simply by removing the sample from the acid at an appropriate stage. The extracted dendrites were of the usual orthogonal nature (Plate and Fig. 30) and Laue and Rotation X-ray photographs confirmed the usual $\langle 100 \rangle$ primary, secondary and tertiary arms. This result agrees well with that of Meussner (1959b) and undoubtedly accounts for Straumanis and Brakke's results of a $\langle 100 \rangle$ preferred growth texture for the aluminium phase in the irregular aluminium/silicon eutectic alloy.

(3) G/R PLOTS - PRELIMINARY GUIDE (FIG. 28)

The results on the eutectic system aluminium/silicon were rather involved, and a preliminary guide to these results is, therefore, desirable. It has already been mentioned that it is the growth kinetics of the eutectic silicon phase that essentially determine the structure, and that the aluminium phase just fills up the interstices between the silicon particles and does not appear to influence the eutectic microstructure very much.

Region A

This region was delineated by a parameter of high specimen temperature gradients and low growth rates.

(i.e. $G/R \gg 10^7 \text{ sec. } ^\circ\text{C cm}^{-2}$) The eutectic silicon consisted of large faceted crystals roughly aligned with the growth direction and the aluminium phase grew with a planar interface. The diffusion distances between the two eutectic phases were large and the growth mechanism was, therefore, described as separate or independent.

(Plate 22)

Region B

On decreasing the specimen temperature gradient (still keeping the growth rate low) the planar aluminium phase interface became unstable and formed cells. The eutectic silicon occurred as rods which were aligned in the growth direction and had a $\langle 100 \rangle$ Si growth texture. Diffusion distances were substantially reduced and growth was co-operative. These rods had a hexagonal array as if they grew at aluminium cell triple boundaries. (Plate 23) As the gradient was further decreased, these silicon rods developed side plates, the size of which increased with decreasing temperature gradient. The side plates lay in the growth direction and made regular angles with each other. The eutectic then appeared 'angular' on a transverse section. (Plate 24)

Region C

An increase in the growth rate led to the second co-operative growth region. The growth kinetics of the eutectic silicon were different to that of the rodlike and angular forms and so the resultant microstructure was changed. This kinetic mechanism was associated with the $\{111\}$ spinel twins in the eutectic silicon, and was either a non-steady state type, in which case the resulting microstructure was described as irregular, (plate 25) or a steady state type in which case the complex regular growth form was produced. (plate 26)

The growth conditions found in castings fall in this region of the G/R plot and so the irregular type of eutectic is the one normally observed. The complex regular form is only observed in hypereutectic alloys. (see section III.1.)

The following sections deal with these three regions of the G/R plots in greater detail.

(4) G/R PLOTS - REGION A

This massive form of eutectic silicon was restricted to high G/R values (see fig. 28) and the necessary very high temperature gradients were produced by using specimens only 2 mm. in diameter. (see section II.3.c.)

a) Morphology

Plates 31 show transverse and longitudinal sections of the alloy. The silicon particles were large and etching in modified C.P.4. solution (section II.4.a.) showed that they contained many twin boundaries and solute inhomogeneities. (plates 32) The form of the eutectic silicon appeared to be large crystals elongated in and roughly aligned with the growth direction. The distance between the silicon crystals in this eutectic form appeared very large by comparison with the other eutectic structures of this alloy and with eutectic alloy dimensions in general, and indicated that growth was by long range diffusion.

Extraction of these silicon particles confirmed the general shape of the eutectic phase. The crystals were interconnected, elongated and roughly aligned with the growth direction. (plates 33 and 34) The silicon crystals were

heavily faceted, the facet faces containing many peculiar markings. Some of the extracted crystals were observed to form into two crystals, the axes of which were 30° and 60° apart. Other silicon particles contained 30° and 60° kinks. These angles were measured normal to a faceted face. The similarity of these crystals with "pseudo dendrites" obtained by growth from silicon melts was noted. (Albon and Owen 1963) This is discussed later. (section VI.1.)

b) Crystallography

X-ray rotation photographs were taken about the extracted crystals major axis. Two preferred growth directions were observed, either $\langle 110 \rangle$ or $\langle 211 \rangle$. (see plate 91 and plate 35) The observed angles between the portions of bifurcated and kinked crystals were, therefore, explainable. The facet faces were shown by goniometry to be $\{111\}$ planes and to lie in the growth direction. The measured angles between bifurcated and kinked crystals were always taken normal to a faceted face, and so the preferred growth directions lie in a $\{111\}$ plane. Both $\langle 211 \rangle$ and $\langle 110 \rangle$ directions lie in such a plane and make the observed angles between themselves (60°) and each other (30°).

X-ray rotation photographs of small pillars of the eutectic alloy taken about the imposed growth direction showed that the silicon phase did not have an overall preferred orientation. Each silicon crystal grew with a preferred orientation but the local and the imposed growth directions were not common.

c) Quenched interfaces

The quenched solid/liquid interfaces of these alloys were most successful. This was primarily due to the experimental set-up that was required to produce these very high gradients. (II.3.c.) Good thermal contact existed between the specimen and the water-cooled copper insert, and quenching, which involved rapidly pulling the fine specimen into the cold area, was therefore most efficient. This can be seen by the fineness of the resultant quenched eutectic alloy and the clear delineation of the interface. (Plate 36a) See section IV.6.e. for further details on the rapidly quenched eutectic alloy.

The quenched interfaces showed that the α -aluminium eutectic phase interface was very flat, except for the occasional cusp that was presumably due to the existence of grain boundaries in the solid aluminium. (The cusps may have been due to instabilities in the interface introduced during quenching) (Plate 36b) The silicon phase, however, presented a faceted growth front to the quenched liquid. The silicon crystal profile position appeared to vary greatly relative to that of the aluminium phase. (Plates 37) This fact further indicates the non co-operative nature of this form of eutectic growth.

(5) G/R PLOTS - REGION B ($\langle 100 \rangle$ Si GROWTH TEXTURE)

a) Growth Mechanism Change

The rodlike and angular types of eutectic silicon were found to be the stable form when the eutectic alloy was grown under certain values of G , the gradient and R , the growth rate. (see fig. 28) When the temperature gradient was reduced below a certain critical value ($< 300^\circ\text{C/cm. at } R = 2.78 \times 10^{-5} \text{ cm/sec.}$) the silicon morphology changed from being massive to being the $\langle 100 \rangle$ Si growth texture form. First the rodlike type was produced and on further reduction of temperature gradient the angular silicon form was produced.

This change was actually observed along the length of some specimens. It has been previously noted that the temperature gradient varied along a specimen, being highest at that end first to solidify. (see section II.3.b.) Thus, if the range of gradient values straddled the critical value, a growth mechanism change would be observed.

The rodlike eutectic silicon was the basic form for the phase in this region of the G/R plot. However, the simple rodlike structure was only observed towards high G and low R in the region, (see fig. 28) and the more common form in this

region of the plot was the angular eutectic silicon which was formed when the rods became unstable and produced side plates. The variation of angular eutectic silicon morphology with G and R will be discussed later in section IV.5. In both these forms of the eutectic alloy, the diffusion distances were much shorter than for the massive eutectic (compare plates 22 and 23) and the eutectic growth mechanism was assumed co-operative. Justification of this assumption will be given in the following sections.

b) Rodlike Eutectic Silicon

This form of the eutectic silicon was the simplest and as such represents the basic form for this region of the G/R plot, but as already mentioned it was only observed towards high G and low R.

i) Morphology

Plates 38 show a rodlike specimen produced by unidirectionally growing the eutectic alloy under the following conditions:

$$R = 2.78 \times 10^{-5} \text{ cm/sec.}$$

$$G = 200^{\circ}\text{C/cm.}$$

Other rodlike specimens were produced (see tables 20 and 21) but the morphological and crystallographic analyses were confined to this specimen.

The rods of silicon were of irregular cross section and were some 10μ across, and were arranged on a hexagonal network indicating an attempt at close packing to minimize the diffusion distance. The rods grew parallel to and were continuous in the growth direction. All this indicated that

the eutectic growth was by a co-operative steady state process, very similar to non faceted/non faceted eutectic rodlike growth.

At these very high temperature gradients, slight variations in the growth rate corresponded to large temperature changes at the solid/liquid interface. These changes tended to produce silicon bands across the interface and were caused by the high Si solute build-up ahead of the aluminium phase.

(Plates 39)

Extraction of the silicon rods from the aluminium matrix confirmed the general shape of these particles and showed that the silicon was continuous in the growth direction. (Plates 40) Bifurcated rods were observed indicating that the structure had a branching mechanism. (Plate 41a) However, the growth conditions were not perfectly stable and the rods often developed side plates. (see plate 41b)

ii) Crystallography

X-ray rotation photographs were taken of extracted eutectic silicon rods, about the particles growth axis. The silicon fibres showed a $\langle 100 \rangle$ Si preferred growth texture.

(Plate 42)

c) Angular Eutectic Silicon - General Structure

Although the rodlike eutectic silicon was the simplest form in region A of the G/R plot, the majority of the eutectic silicon produced in this region was of the angular variety.

This angular eutectic silicon, as already described, was essentially a fine silicon rod or spine aligned with the growth direction onto which silicon plates were attached by an edge. (see fig. 43) Transverse sections through this structure thus gave rise to the characteristic angular form.

Longitudinal sections of this type of eutectic alloy showed that it developed from irregular silicon particles. Three centimetres growth was required to form the preferred growth texture.

1) Morphology

Representative samples of eutectic alloy removed from the middle portion of unidirectionally grown specimens showed microstructures as in Plates 44. From such photographs the simple model of the angular eutectic silicon shape was constructed. (fig 43) The angular particles normally had

three or four side plates that appeared to make regular angles with each other. (see later section IV.5.)

Longitudinal sections of the eutectic alloy showed that sections through some of these silicon side plates gave rise to wavy lines. (Plate 44b) Wavy lines were not observed in the transverse section of the alloy, and from multi-surface analysis it was concluded that they were due to sections through corrugated plates; the corrugation direction being at right angles to the growth direction. Side plates, therefore, appeared to be of two basic types - either smooth or corrugated.

Extraction of the silicon particles from the aluminium matrix confirmed the general model of angular particles. After extraction the silicon phase of the eutectic alloy remained as a coherent mass, indicating interconnection of the particles. Individual particles were easily broken from the mass, as the particles were extremely brittle. The silicon particles were found to be continuous in the growth direction and, unless broken, were as long as the eutectic specimen. The morphology of the extracted particles was as expected and was shown to consist of smooth and corrugated plates attached together to give the characteristic transverse section. (plates 45)

ii) Crystallography

X-ray rotation photographs were taken about the growth direction of single extracted angular particles and also of small pillars of the angular eutectic alloy. Both sets of experiments showed that the silicon phase had the same $\langle 100 \rangle$ Si growth texture as the rods. (plates 42 and 46)

iii) Growth Mechanism

From the above general description it can be seen that the growth mechanism is essentially the same as that for the rodlike form. Diffusion distances are short and the silicon phase is continuous in the growth direction. Growth is therefore by a co-operative process, and with only smooth side plates present one can say that growth of the angular eutectic alloy is a steady state process. However, the corrugated side plates must be growing by some oscillatory diffusion process, and as such must be described as non-steady state growth - perhaps the phrase periodic growth would be the best description. These two forms of silicon side plates will now be described in more detail.

d) Angular Eutectic Silicon - Smooth side Plates

Reflected light microscopy provided information on the detailed shape of the individual side plates. These plates could be removed, with care, from the angular silicon particles and subjected to X-ray diffraction analysis.

i) Morphology

The majority of the silicon side plates were of this first basic type and were flat and usually smooth. The plates were either triangular or trapeziform (plate 47 and 49a) and were joined to the central spine of the angular particles by their longest edge. The angles that the edges of the plates made with each other, when viewed normal to the plate's surface, were

$$45^{\circ} \ 90^{\circ} \text{ and } 135^{\circ} \text{ (fig. 47)}$$

Not all the plates were completely smooth, and some of them had slight surface markings at 45° to the growth direction, (plate 48a) otherwise they appeared identical. The silicon plates were thin and with transmitted tungsten illumination appeared yellow, red or brown according to thickness. (plate 48b) The edges of the plates often appeared to be surrounded with a beading that was thicker than the plate itself. (plates 49)

ii) Crystallography (see fig. 47)

X-ray Laue photographs taken normal to these extracted smooth silicon side plates showed them to be single crystal $\{100\}$ plates, with the edge parallel to the growth direction being $\langle 100 \rangle$, and the two edges at 45° to the growth direction being $\langle 110 \rangle$. (Plate 50) Surface markings were also in $\langle 110 \rangle$ type directions. These crystallographic directions were checked by taking rotation photographs about the particle edges.

e) Angular Eutectic Silicon - Corrugated Side Plates

As mentioned above in section IV.5.c.iii. it appears that corrugated side plates are growing by a slightly different mechanism to the smooth plates and that the local growth direction of the plates varies periodically with time.

i) Morphology

This form of silicon side plate was not so common as the smooth plate. Extracted corrugated plates attached to angular particles showed that the corrugation direction was at right angles to the growth direction. (plate 45a) The corrugations, unlike the slight surface markings on some of the smooth plates, were very marked and it was often not possible to focus on the whole extracted plate at once. (plate 51) Goniometry on such extracted plates showed that the faces consisted of alternate steps, the planes of which made an angle of 109° to each other. (fig. 51)

ii) Crystallography (see fig. 51)

X-ray Laue photographs taken normal to one of the sets of planes which comprise the corrugated plate, showed that the plate was made up of two sets of $\{111\}$ planes inclined at 109° . (plate 52) The corrugated plate was a single crystal, the overall growth direction was $\langle 100 \rangle$ as expected and the corrugation direction was $\langle 110 \rangle$. These later results were checked by rotation photographs about the growth and the corrugation direction. The plane of the corrugated plate is, therefore, a $\{110\}$, (see plate 53) which is actually composed of two alternating $\{111\}$ inclined at 109° to each other.

f) Angular Eutectic Silicon - Nodal Angles and Types

It has been mentioned above that on transverse sections through the angular eutectic alloy, the silicon side plates appear to make regular angles with each other. This section will deal with these so-called nodal angles and will attempt a crystallographic explanation of the observed results. The various nodal types that can then be formed will also be classified.

i) Morphology

The angles between the silicon side plates as seen in transverse sections of the alloy were measured using a calibrated rotating eyepiece. Histograms were plotted for these nodal angles. Resulting histograms (fig 54) showed peaks at the following angles:

53° , 82° , 90° , 108° , 127° , 135° , 143°

Further information on these nodal angles was provided by goniometry studies on a wide range of extracted angular silicon particles. This work had the advantage over the histogram plots mentioned above, in that it was possible to tell the nature of the side plates giving rise to specific nodal angles.

The observed nodal angles were the same as those produced by the histogram but it was now possible to divide them up into groups depending on the nature of the silicon side plates giving rise to the angle, i.e.

Smooth/smooth	53° , 90° , 127° , 143°
Smooth/corrugated	82° , 98° , 135°
Corrugated/corrugated	53° , 90° , 127° , 143°

These various nodal angles could give rise to a very large number of different angular eutectic silicon particles, or more simply nodal types. Some of the observed nodal types are shown in fig. 55. However, angular particles were not as simple as indicated in fig. 55 as the particles often used to be joined together and many of the side plates appeared to have anchor endings. (see plate 24) These anchor shaped endings were again either smooth or corrugated plates when the eutectic was completely angular. However, in the transition zone - region B + C (fig. 28) the anchor plates were often sections through inclined irregular plates attached to the angular plates. (see fig. 104 and plates 106a to 107b)

11) Crystallography

From the crystallographic results already mentioned above, we know that since the silicon growth texture was $\langle 100 \rangle$ then a transverse section of the alloy can be represented by a standard $\langle 100 \rangle$ projection for the silicon phase. We also know that the side plate directions can be represented on this projection by $\langle 100 \rangle$ for the smooth plates and $\langle 110 \rangle$ for the corrugated plates. (fig. 56) This will explain some of the observed nodal angles. Two smooth plates, or for that matter two corrugated plates, would be joined together at an angle of 90° and a corrugated plate and a smooth plate could make an angle of 135° , when viewed along this $\langle 100 \rangle$ growth direction.

This does still leave certain of the nodal angles unexplained. A closer look at these unexplained nodal angles shows that they all have a certain angle in common, namely 53°

$$\text{thus } 82^\circ = 180^\circ - (45^\circ + 53^\circ)$$

$$98^\circ = 45^\circ + 53^\circ$$

$$127^\circ = 180^\circ - 53^\circ$$

$$143^\circ = 90^\circ + 53^\circ$$

X-ray Laue photographs were taken of extracted angular eutectic silicon particles containing smooth plates 53° apart. These X-ray photographs (plate 50) showed that both plates were $\{100\}$ planes and that their common growth direction was still $\langle 100 \rangle$.

The Laue photographs showed that the two plates had a common $\{210\}$. The angle between $\{100\}$ and $\{210\} = 26^\circ 34'$. Therefore, the angle between the $\langle 100 \rangle$ of the side plates, when observed in transverse section, would be $2 \times 26^\circ 34' = 53^\circ 8'$. The two smooth plates can be said to be twinned with respect to each other by means of a $\{210\}$ spinel twin. This spinel twin allows us to explain these remaining nodal angles.

53° , 127° and 143° are therefore the angles between $\langle 100 \rangle$ directions for twinned and non-twinned smooth plates of the angular particles. (or similarly they are the angles between $\langle 110 \rangle$ direction for twinned and non-twinned corrugated plates - see plate 53)

82° and 98° are the angles between the $\langle 100 \rangle$ direction of a smooth plate and the $\langle 110 \rangle$ direction of a twinned corrugated plate.

It was possible using the Unicam single crystal goniometer to prove conclusively that the above crystallographic interpretation was correct.

The orientation relationship between the side plates of angular eutectic silicon is summarised by the stereographic projection of fig. 57.

g) Angular Eutectic Silicon - Quenched Growth Front

Quenched interfaces of the angular eutectic alloy showed that, although the interface was macroscopically fairly flat, the silicon phase appeared to be leading the aluminium during growth. (plate 58) The smooth $\{100\}$ silicon side plates were seen to be growing on their leading $\langle 110 \rangle$ edges. This fitted the general picture of the smooth plate, since they were always found to be closed at the leading edge by a $\langle 110 \rangle$ direction, and this shape would be expected if growth on a $\{100\}$ plate was suddenly stopped for any reason. For lateral growth of the silicon particle to occur, it must be in contact with the liquid phase, and as the growing edge was at 45° to the growth direction, a measure of this free edge distance could be obtained from the average length of the side plates as observed in the transverse sections of the eutectic alloy. This length was called the projected free edgedistance, d . (see fig. 58) d -values obtained from quenched interfaces were in very good agreement with those obtained by the above method.

h) Effect of Temperature Gradient, G

The effect of specimen temperature gradient on the microstructure of the $\langle 100 \rangle$ Si growth textured eutectic alloys was found to be considerable. This effect has already been briefly mentioned (section IV.3.) Plates 59a to 60b show a series of transverse section micrographs, all taken at the same magnification, of unidirectional solidification experiments carried out at a constant growth rate $R = 2.78 \times 10^{-5}$ cm/sec. and with a widely varied temperature gradient G . (see also fig 28) The rodlike eutectic silicon was formed at the very high temperature gradients, and as the gradient was reduced, this form became unstable and started to produce side plates. At first a great number of side plates were produced; up to eight per rod, see plate 59b. The angles between the side plates in these eight side arm particles were 53° and 35° and so they could be explained in terms of the $\{210\}$ spinel twin model. (see section IV.5.f.ii.) As the gradient was reduced still further, the general angular form with three or four side plates per particle was observed and the size of these side plates was seen to increase with decreasing gradient. (plates 59b to 60b) Once these four side plate particles were produced, corrugations were observed.

The incidence of the three plate particles increased with decreasing gradient. As the size of the side plates increased, the nature of the centre of each particle, as observed in a transverse section, varied. The centre of the particle changed from being a fibre with side plates on at high G to become just an intersection of side plates at low G values. (plates 59b and 60a)

i) Particle size

The projected free edge distance d (see section IV.5.g. and fig. 58) was measured for each of the separate experiments from the transverse section of the alloy. The following relationship between d and G was found.

$$d = AG^{-1} \quad (\text{see table 61 and fig. 62})$$

ii) Particle separation

λ , the interparticle spacing was a difficult distance to measure, as the particles tended to interweave at low G values. However, as the angular silicon particle node appeared to be the growth centre of this silicon structure, the internodal distance was taken as a measure of λ .

Internodal distance was taken as

$$\lambda = \frac{1}{\sqrt{N_A}} \quad \text{where } N_A = \text{number of nodes/unit area}$$

The above equation assumes that the nodes were arranged on a square lattice. Since the angular particles were derived from the hexagonally arranged silicon rods, a hexagonal lattice would appear more relevant. λ hex. was calculated and shown to be:

$$\lambda_{\text{hex.}} = \left(\frac{2}{\sqrt{3} N_A} \right)^{\frac{1}{2}} \quad \text{or} \quad \lambda_{\text{hex.}} = 1.074 \lambda_{\text{sq.}}$$

The difference is thus small and was neglected. All values quoted for $\langle 100 \rangle$ growth texture silicon are in terms of λ sq.

λ , the internodal separation increased less rapidly with decrease of temperature gradient than did d , the projected free edge distance.

The relationship was found to be:

$$\lambda = AC^{-0.6} \quad (\text{see table 61 and fig. 62})$$

The results obtained from the very low temperature gradient experiments did not entirely agree with the rest of the results. This was because the silicon morphology was not completely angular. The regions between the angular

particles contained further eutectic silicon particles of a different type and these tended to affect the relationships between d , λ and G . d for instance was only proportional to G^{-1} when the bulk of the eutectic alloy grew in the angular form. This other type of silicon which was shown to be irregular silicon is described in section IV.6 and 8.

j) Effect of Growth Rate R

The effect of growth rate on $\langle 100 \rangle$ growth texture eutectic silicon was for the most part involved in the observed change-over from this $\langle 100 \rangle$ Si growth texture form to the $\{111\}$ Si spinel twin form. As we have seen in the above section, the formation of irregular silicon upsets the growth of angular silicon.

However, the change of rodlike $\rightarrow$ angular eutectic could also be produced by an increase in growth rate.

(see fig. 28) Once the general angular silicon form with three or four side plates was produced, very little change in nodal types was observed and corrugations always seemed to be present. With the onset of irregular silicon growth, the incidence of three plate nodal types increased.

(plates 63a to 64b)

When the growth rate was slow and no irregular eutectic silicon was formed between the angular particles, both d and λ decreased very slightly with increasing growth rate. At the onset of the irregular silicon form concomitant with the angular form, these two parameters decreased more rapidly with increasing growth rate. (see table 65 and fig. 66) The methods used for obtaining these values for d and λ were the same as for the completely angular eutectic and the presence of irregular eutectic silicon was not taken into consideration.

(6) G/R PLOT REGION C - IRREGULAR SILICON EUTECTIC

This form of the eutectic was produced over a wide range of specimen temperature gradients and when the growth rate was greater than that required for angular eutectic silicon. (see fig. 28) The majority of the previous unidirectional solidification work on this eutectic alloy has been carried out under growth conditions that fall in this region of the G/R plot. Normal casting methods also produce growth conditions in this region of the G/R plot.

a) General Microstructure

The microstructure of the irregular eutectic appeared to consist of discrete silicon particles embedded randomly in an aluminium matrix. (plate 25) Closer investigation showed that the eutectic silicon was trying to align itself with the growth direction. Bursts were observed fanning out in the growth direction between roughly aligned elongated spikes of silicon. (plate 67a)

Quenched interfaces of the growing irregular eutectic have shown (Chadwick 1965) that these spikes tend to lead the very irregular growth front, with the silicon plate bursts filling in the space between and behind them. (plate 67b)

The work described below shows that the silicon particles were interconnected and continuous. As the diffusion distances were small, the growth mechanism was a short range one, but because of the irregularity of the structure, growth must have been into a non-steady state diffusion field.

b) Morphology

Because of the irregularity of the eutectic, the majority of the information on the morphology of the silicon particles was obtained from extracted particles. The extracted irregular silicon particles appeared as a pile of loose plates and particles. This did not mean that the silicon was not interconnected. The interconnections, if present, could have been very brittle and were thus easily broken by the evolution of hydrogen during extraction.

There were two types of extracted silicon particles; plates and a knotted fibrous form. The knotted form was often attached to the plate silicon and several plates could often be found attached together via these particles. Knotted particles could be taken as the main interconnections between plates. As they were very fragile, the extraction process tended to break the eutectic up. (plates 68 and 49a)

The plates were of two major sorts. The first was the idiomorphic plate. This, as the name suggests, was of no definite shape and a wonderful array of this type of particle was observed. (plates 69) The plates were found to be quite flat and often contained holes. The surface irregularities were accentuated by the lighting train.

The second type was more geometrical in outline. There were triangular plates; the edges of which were 60° apart. These plates were either smooth or had surface markings. (plates 70) Other plates were lath shaped and were often very long. (plate 71a) The lath plates sometimes had equilateral triangular plates attached. (plate 71b)

c) Crystallography

X-ray Laue photographs were taken normal to the faces of extracted silicon plates and showed that they were all $\{111\}$ plates which were twinned by a $\{111\}$ spinel twin; the twin plane lying in the plane of the plate, i.e. the Laue photographs showed sixfold symmetry - see plate 72. In the case of the idiomorphic plates the

$\langle 110 \rangle$ directions in the plane of the plate often coincided with a surface feature. The geometrically shaped plates had edges bound by $\langle 110 \rangle$ and the triangular plates had three $\langle 110 \rangle$ edges 60° apart. The long edges of the lath form were likewise $\langle 110 \rangle$ and this was checked by taking rotation photographs about the particles major axes. As the lath form plates were elongated in the $\langle 110 \rangle$ direction, it appeared reasonable to accept this as the local growth direction of these plates. It was confirmed that this elongation direction was in the local growth direction and that lath and spike crystals were one and the same, by taking back reflection oscillation photographs of those particles which appeared as spikes in longitudinal sections of the eutectic. These particles were observed to lie approximately parallel to the major growth direction and to show a $\langle 110 \rangle$ growth direction. (plate 73)

Rotation photographs taken of small pillars of the eutectic about the major growth direction showed that the silicon phase had no preferred orientation. (plate 29) Although individual silicon spikes grew in a $\langle 110 \rangle$ direction, particles growing in this fashion had local growth directions which did not lie parallel to either the imposed growth direction or each other. There were also the inter spike bursts to be considered. These particles also did not lie in the macroscopic growth direction and it was not surprising to find that no macroscopic preferred orientation existed in the aggregate.

d) Twins

Laue photographs had shown that these plate-like particles were twinned by a $\{111\}$ spinel twin but it was not possible to tell from these photographs how many times the particles were twinned. Goniometry carried out on the edges of the geometrically shaped plates showed them to consist of planes $\sim 70^\circ$ to the major planes of the plate. (figs. 74) As the plate's major plane was $\{111\}$ these edge planes would be likewise $\{111\}$.

By observing the number of $\{111\}$ planes present in the edge of the plate, it should be possible to obtain the number of lamellar twin boundaries present in each geometrical particle. (see figs. 74) In the triangular plates, the $\langle 110 \rangle$ edges were found to consist of two $\{111\}$ inclined mutually at 219° and so these plates were only twinned once. (see fig. 74a) The lath plates were found to contain more than one twin. (fig. 74b)

Silicon cleaves along $\{111\}$ and so it was possible to show up the lamellar twins by fracturing the extracted crystal and plate 75b shows a resulting fractograph. This was a better method than observing edges by goniometry as edges were often not clearly defined in the extracted particles.

A modified C.P.4. etchant was used to show up the twin boundaries in the silicon plates of the irregular eutectic alloy and in this way it was possible to show that the majority of the irregular silicon plates possessed lamellar twin boundaries. In some particles as many as ten twin boundaries were observed. (plates 76)

The twin boundaries usually ran in the plane of the particle and were parallel with each other. However, other twin boundaries which were not in the plane of the particle were also observed. (plates 77)

e) Silicon Interconnection

Indirect proof of silicon particle interconnection has been mentioned above. Direct proof was obtained in two ways.

The first way was utilising the twin boundary traces shown up by the modified C.P.4. etchant. By selecting a given set of parallel twin boundary traces as a reference, histograms were plotted of the angles that other twin traces in this and neighbouring particles made with the reference twin trace. Peaks were observed on the histogram. If the particles were discontinuous, the angles between twin traces would produce a random scatter of results. The fact that peaks were observed indicates that there was an angular relationship between particles and that the particles were, therefore, interconnected. Longitudinal sections of the alloy were used for these analyses and the best histogram peaks were obtained by moving away from the reference particle along the growth direction. This was presumably because the principle interconnections lay along the growth direction and as there was more than one silicon grain, a trace along the growth direction would tend to stay in one grain.

Because of the relationship between twin traces in neighbouring particles, it follows that the particles are most probably related to each other via complex multiple twinning. If one considers only up to third order multiple twins, these would produce on any random cross section up to 160 different twin boundary directions; more than enough to explain the apparent randomness of the irregular silicon form.

The second way of proving the interconnection of irregular silicon plates was by scanning electron microscopy. This was carried out on heavily etched surfaces of the eutectic. The scanning electron microscope proved a most useful tool, since its large depth of focus and higher resolution allowed photographic evidence of interconnections to be obtained. (plates 78a to 79b)

Heavy etching, as opposed to complete extraction, was a more reliable technique for showing interconnection. This was presumably because the evolved hydrogen was more easily released from near the surface and, therefore, particles were less likely to be broken. Also since the silicon particles were well supported by the aluminium matrix, damage by handling was minimized.

f) Effect of G and R

The difference in the microstructure of the irregular eutectic on changing the specimen temperature gradient G was very small and only became at all noticeable at very slow growth rates. (c.f. section IV.5.h.)

The effect of changing the growth rate R was more marked and the microstructure became finer as the growth rate was increased. Plates 80a to 81b show a series of transverse section micrographs all taken at the same magnification, in which R was varied and G was kept constant.

Interparticle measurements were obtained for various growth rates, at constant G. Micrometer eyepiece readings were taken from the transverse section of the alloy in areas where the silicon plates were approximately parallel - i.e. in the bursts. The results are set out in table 82 and represent averages obtained from a large number of observational readings. The dependence of λ , the interparticle spacing, on growth rate R was found to be

$$\lambda = AR^{-0.56} \quad (\text{see fig. 83})$$

The morphology of the eutectic silicon changed as the growth rate was increased. Apart from the irregular silicon plates becoming smaller, the lamellar twin separation and the proportion of these irregular plates decreased as the growth rate was increased. It has been noted (section IV.6.b.) that the irregular silicon morphology is of two basic types; plates and a knotted or twisted fibrous form. When the irregular eutectic alloy was grown at relatively slow growth rates, the majority of the eutectic silicon was in the form of plates. (plate 78a) However, as the growth rate was increased this proportion of silicon plates decreased until at very high growth rates the eutectic silicon was entirely in the twisted fibrous form. These very high growth rates were produced by rapid quenching of the eutectic alloy. (see section IV.4.) The resulting microstructures were very fine and random sections showed small rounded areas of silicon produced by sections through the fibres. (plate 84a) This is the so-called quench modified structure. (see section VII for further details and discussion) Scanning electron microscopy of heavily etched surfaces was used to prove that this rapidly quenched eutectic alloy contained the silicon phase in the form of these twisted and interconnected fibres. (plates 84b to 85b) The large globular particles in these photographs are α -Al dendrites produced by the rapid quench, which have been exposed during the heavy etching process.

(7) C/R PLOTS - REGION C - COMPLEX REGULAR EUTECTIC SILICON

Complex regular eutectic silicon (plate 26) was formed over a different range of growth conditions to the irregular silicon particles described in the section above. (section IV.6.) The range of the growth variables of growth rate and imposed temperature gradient was the same as for the irregular eutectic, but the variable of the composition of the alloy had to be changed in order to produce the complex regular structure. (see fig. 27b)

As mentioned in section III.1., the complex regular structure was only observed in hypereutectic alloy castings and the same observation was made with unidirectionally grown eutectic alloys. The regular silicon form only represented a portion of the total eutectic silicon and in most specimens the majority of the silicon was still irregular. The complex regular structure was only observed concomitant with the irregular silicon form and it therefore appears that the kinetic mechanism leading to this form must be the same as, or very similar to, that of the irregular eutectic silicon. The growth mechanism of complex regular eutectic silicon appears to be a steady state form of that which normally produces irregular silicon growth.

a) General Morphology

It was from transverse sections of this structure that it received its colloquial name. The word spiders web is rather misleading as a completely web-like structure cannot be obtained, and the observed microstructure is always a portion of a web. However, the term has become generally accepted and so is used in this thesis. A range of transverse sections of web forms are shown in plates 86a to 87b. The webs appeared as parallel platelets of silicon attached to a central spine plate to give a regular feather-shaped complex particle upon transverse section. Two such feather-shaped units were often found joined together forming the major portion of a web. The silicon webs were usually attached to primary silicon or large eutectic silicon particles. Histograms were plotted of the angle between spine and platelets as observed in transverse sections (fig. 88) and peaks were observed at 55° , 62.5° and 70° .

Measurements of the volume fraction of silicon in the webs indicated that the silicon concentration in the webs was greater than that of the eutectic alloy and that the volume fraction of the webs varied from the spine outwards, being highest near the spine. Values of up to

0.24 were observed at the spine whereas a value of 0.13 is expected from the phase diagram. (see fig. 12) These high values have led to the view that the complex regular eutectic forms are primary silicon dendrites (sic.). This matter will be further discussed in section VI.5.a.

Longitudinal sections (plates 89) showed that the webs were quite well aligned to the growth direction and that some of them were of considerable length. These sections were misleading as to the actual morphology of the webs as some of the platelets did not appear to lie in the macroscopic growth direction of the web and so the angle between spine and platelet could vary from 0° to 90° depending on the section. True angles could only be determined by three surface analyses or extraction.

Extraction proved rather difficult. This was because the structure was so fine that the evolved hydrogen tended to fracture the platelets of the web. (plates 90) A very slow extraction technique involving 'titrating' the acid against the specimen was more successful (see section II.4.b.) and the extracted webs were subjected to goniometry and X-ray diffraction analysis in the usual way. (sections II.5b and 6b)

b) General Crystallography

X-ray rotation photographs taken about the growth axis of extracted silicon webs showed them all to have a $\langle 110 \rangle$ preferred growth texture. (plate 91) Back reflection oscillation photographs on the eutectic alloy webs produced the same result for the silicon phase. Laue photographs of portions of extracted webs showed that they were heavily $\{111\}$ spinel twinned, but that individual platelets, although $\{111\}$, did not appear to be twinned. The spines appeared to be $\{100\}$. The primary or lath-like silicon particles to which webs were attached were also heavily twinned and showed the same $\langle 110 \rangle$ preferred growth texture. The similarity between the irregular and complex regular forms of eutectic silicon is thus substantiated by this X-ray evidence. Models of the various web forms observed were constructed using the X-ray analysis together with goniometry and three surface analysis.

Webs can be arranged into three groups, of increasing complexity, which depend on the crystallographic relationship between $\{111\}$ platelets, a $\{100\}$ spine and a $\langle 110 \rangle$ growth direction.

c) Single Crystal Webs

A standard $[011]$ stereographic projection (fig. 92) shows that the simplest web structure that can be constructed consists of a (100) spine which lies in the $[011]$ growth direction with $(\bar{1}11)$ platelets attached at $54^{\circ} 44'$ to this spine. The platelets also lie in the growth direction and, therefore, make an angle of $54^{\circ} 44'$ with the spine when the web is viewed in transverse section. (see fig. 93a) This orientation relationship between the web spine and the attached platelets was observed in a number of cases. (see fig. 88) It was, however, unusual to find a web with only this relationship present. As has already been mentioned, webs are very similar to the irregular eutectic silicon and it appears that $\{111\}$ spinel twins are required in the structure for the kinetic growth mechanism to operate.

d) First Order $\{111\}$ spinel Twinned Webs

X-ray photographs have shown that although the webs appear heavily twinned the web platelets themselves appear to be single crystals. This fact can be explained by assuming the twinning event takes place where the $\{111\}$ platelet joins the spine.

From the standard $[011]$ stereographic projection (fig. 92) it can be seen that of the four $\{111\}$ planes, two are axial and the other two are non-axial to the $[011]$ growth direction. The spinel twin can take place about any of these $\{111\}$ planes.

Twinning about an axial $(11\bar{1})$ produces a twinned crystal which still retains the $[011]$ growth direction and has two axial $\{111\}$ and two non-axial $\{111\}$ like the untwinned crystal. The twinning event is geometrically equivalent to a $70^{\circ} 32'$ rotation about the $[011]$ growth axis. (see fig. 94)

Twinning about the non-axial (111) produced a twinned crystal that does not retain the original $[011]$ growth direction and has all of its four $\{111\}$ non-axial with the growth direction. (see fig. 95)

From the above it can be seen that there are various possible orientation relationships between an axial spine and its attached platelets. However, of these various possibilities only one is observed and this is when the platelet is a non-axial $(\bar{1}11)$ plate produced by carrying out an axial $(11\bar{1})$ twinning event on an originally non-axial $(\bar{1}11)$ plate. (see fig. 94) Such platelets make an angle of $70^{\circ} 32'$ with the spine when the web is observed in transverse section and also make an angle of $54^{\circ} 44'$ with the $[011]$ growth direction. (see fig. 93b)

By consideration of the single crystal and this first order twin orientation relationship, a great variety of web-shaped particles can be produced, especially when it is realised that webs can have their two axial $\{100\}$ spines related by an axial $\{111\}$ spinel twin. (see fig. 94) The angle between two twinned axial spines is $109^{\circ} 22'$ and this was confirmed experimentally. Fig. 96 shows some of the web morphology possibilities. All these forms have a simple $\langle 110 \rangle$ texture and are constructed from $\{111\}$ faceted platelets.

e) Complex Webs

Data from the histograms and goniometry on the extracted particles showed that the above web types (fig. 96) were not inclusive. Webs were observed in which the platelets made an angle of 62.5° with the spine when observed in transverse section. (see histogram fig. 88) Such web platelets made an angle of 22° with the growth direction if the spine was axial, or the spine made an angle of 14° with the growth direction if the platelets were axial. (fig. 97a) Other webs were observed in which the platelets were inclined 14° to the growth direction; the spine being axial and the web having a transverse section platelet/spine angle of $70\frac{1}{2}^\circ$. (fig. 97b) The growth axes of all these webs were shown to be $[011]$ by means of X-ray rotation photographs.

The explanation of these complex webs is not complete, but it appears that the spines and platelets are related to each other via second order twin relationships; one or both twinning operations involving a non-axial $\{111\}$.

The 62.5° transverse section platelet/spine angle can be explained if the relationship either involves keeping the (100) spine axial and twinning one of the original axial $(11\bar{1})$ platelets using two consecutive non-axial twinning operations,

(see fig. 98) or keeping the platelets axial and carrying out an axial twinning operation followed by a non-axial twinning operation on an originally non-axial $\{100\}$ plane. (see fig. 99)

The 70° platelet/spine angle webs, with the platelets 14° off the $[011]$ growth direction, can be explained if the spine is kept axial and one of the originally non-axial $(\bar{1}11)$ is first axially and then non-axially twinned. (see fig. 100)

All the above complex webs involve non-axial twins and so a portion of the resultant crystal has lost its $[011]$ growth direction and one would, therefore, expect all complex webs to show multiple textures. The growth textures, apart from $[011]$, that one should observe are of low symmetry, e.g. $[411]$ for first order non-axial twins (see fig. 95) and so layer lines as such would not be expected, but extra spots should appear on all the Debye lines and these do not make themselves apparent in the X-ray rotation photographs. (see plate 91) The reason for this is not at all obvious, unless the outer layer of heavily twinned lath silicon, that is found around all webs, is sufficient to mask the inner growth texture of the platelets or spines.

f) Effect of G and R

The interplatelet distance λ was measured on transverse sections of the alloys, using a micrometer eyepiece and averages were taken from a large number of readings. It was found that the specimen temperature gradient G had no effect on the λ -value for the webs. The size of the webs, however, increased with decreasing gradient, that is except at very low G-values where no webs were produced at all, but this was presumably because the hypereutectic silicon was not taken up into solution and growth was, therefore, not from hypereutectic liquid. The number of webs appeared to increase with increasing gradient and at high G-values the specimen contained a high proportion of webs. (plates 101)

The effect of growth rate R upon the interplatelet distance λ was, that as the growth rate was increased so the value for λ decreased. (table 82) Measurements from a series of unidirectionally grown specimens showed that the relationship between λ and R was

$$\lambda = AR^{-0.46} \quad (\text{see fig. 83})$$

It will be noted that the value for A in the above equation is much lower than that for the irregular {111} spinel type eutectic.

As the growth rate was increased, the size and number of webs decreased. (see plates 80a to 81b)

(8) G/R PLOTS - REGION B + C - THE TRANSITION ZONE

As the title of the section implies, this region occurred between regions B and C on the G/R plot and eutectic alloys grown under these conditions produced microstructures in which both $\langle 100 \rangle$ Si textured eutectic and $\{111\}$ Si spinel forms were to be found. (see fig. 28)

The low growth rate boundary of the region occurred at a constant G/R value, i.e. the beginning of the formation of $\{111\}$ spinel twinned silicon crystals concomitant with the $\langle 100 \rangle$ Si form occurred at lower growth rates with lower temperature gradients, or, in other words, as the angular particles increased in size so the irregular eutectic silicon formed more easily in the regions between the angular particles.

As the growth rate was increased, the proportion and size of the angular particles decreased until above a certain critical growth rate ($R_c = 3 \times 10^{-4}$ cm/sec.), the eutectic silicon was completely of the $\{111\}$ spinel type.

a) General Morphology and Crystallography

Transverse sections of specimens grown under these conditions are shown in plates 63a to 64b and 102a. The angular silicon particles in the eutectic alloy were well aligned with the growth direction and nodal angles were found to be the same as the previously described angular silicon (section IV.5.f.), and longitudinal sections (plate 102b) and extracted particles showed that corrugated side plates were present. The angular eutectic silicon appeared to be the first to form, the irregular silicon growing in the spaces in between the angular plates.

The irregular silicon was shown by extraction to be the same as the irregular silicon already described (section IV.6.) and to consist of $\{111\}$ spinel twinned plates or twisted fibres. Occasionally in hypereutectic alloys the web form of $\{111\}$ spinel twinned silicon was observed. X-ray evidence of the formation of the two eutectic silicon forms was obtained by taking a series of rotation photographs of small pillars of the eutectic alloy. (see section II.6.a.) These experiments showed that as the proportion of $\{111\}$ spinel twinned silicon was increased, so the rotation photographs changed from showing a $\langle 100 \rangle$ Si texture to showing complete Debye lines only. (compare plate 103 with plates 29 and 46)

b) Silicon Interconnection

It was shown that the two forms of eutectic silicon present in this region of the G/R plot were interconnected. Extracted silicon particles from this region showed irregular plates attached to the angular silicon side plates. Some of the $\{111\}$ irregular plates were found by goniometry to make an angle of 55° with $\{100\}$ smooth side plates, both particles having a common $\langle 110 \rangle$ edge. (fig. 104) Optical photographic evidence of the interconnection of irregular and angular silicon particles was difficult to show because of the poor depth of focus available. Scanning electron microscopy on extracted silicon particles showed the interconnection far more conclusively. (see plates 105) Further scanning electron microscopy on heavily etched surfaces of eutectic alloy also showed that the irregular silicon was connected to the angular particles, but showed in addition that the irregular eutectic itself was interconnected as in the completely irregular eutectic alloy. (section IV.6.d.) (see plates 106a to 107b)

The modified C.P.4. etchant showed that the interangular silicon was twinned in the same manner as the irregular silicon (plates 108) and that like irregular silicon, the particles were interconnected, since histograms plotted of the angles between twin traces were found to be non-random. (see section IV.6.e.)

c) Effect of G and R

The effect of both these variables on the microstructure of these eutectic alloys was most noticeable in the change in the size of the angular silicon particles. This change in angular particle size was similar to that of the completely angular eutectic silicon, except that the presence of irregular silicon caused an increase in d , the projected free edge distance (see section IV.5.h.) with decrease of G that was less rapid than the $d \propto G^{-1}$ relationship found for the angular eutectic silicon on its own. Similarly, as the growth rate was increased, the proportion of irregular eutectic increased and this caused the angular particles to decrease more rapidly in size than was observed in the completely angular eutectic alloys. (see section IV.5.j and fig. 66)

d) Morphological Stability

Unidirectional solidification experiments were carried out in which the growth rate was altered during growth. (section II.3.a.) The growth rate was increased so that a complete gradation of microstructure from angular through to irregular was produced in the one specimen. G was assumed constant for the experiment. ($G = 29.5^{\circ} \text{C/cm}$) The microstructures that were produced at the various rates corresponded exactly to those from specimens grown only at this same growth rate. This experiment showed that the observed microstructures were stable for a given set of growth conditions and that they were not dependent on previous growth history.

(9) ALUMINIUM/SILICON EPITAXIAL RELATIONSHIP

It has been mentioned in section IV.2. that no α -Al preferred orientation was found in any of the eutectic forms described above. Even in forms of the eutectic in which the silicon phase was well aligned with the growth direction, no α -Al growth texture was observed. This was taken as an indication that no epitaxial relationship existed between the silicon and the aluminium phases, i.e. if the silicon phase had a growth texture and an epitaxial relationship existed between the aluminium and the silicon phase, then one would expect the aluminium to have a growth texture as well.

Further experimental evidence substantiating this view of the absence of an epitaxial relationship between the eutectic phases was provided by polarised light microscopy on eutectic alloy specimens anodised to show up the α -Al grains. (see section II.4.a.) The results showed that the eutectic silicon grains were usually larger than the α -Al grains and that eutectic silicon particles crossed α -Al grain boundaries.

Transverse sections of the angular eutectic alloy were anodised and attempts made to determine whether any orientation relationship existed between the silicon particles and the α -Al matrix. This was one of the few forms of

eutectic on which this analysis could be carried out, since the silicon phase was aligned with the macroscopic growth direction. However, identically orientated angular silicon particles were found in adjacent α -Al grains (plates 109) and the angles between such α -Al grains were shown to vary randomly, indicating that no epitaxial relationship existed even in this most ordered of the eutectic forms.

Another indication of the absence of any constant orientation relationship between silicon and its aluminium matrix was obtained by goniometry on incompletely extracted eutectic silicon. It has been mentioned previously (section IV.2.) that extraction proceeds mainly by chemical attack at the aluminium/silicon boundaries; nevertheless silicon particles removed from the acid before hydrogen evolution had finished often showed small heavily etched aluminium particles attached to the silicon. (see plates 78 and 106) These aluminium particles had exposed cubic facets and previous work on α -Al dendrites had shown that these cube facet faces were $\{100\}$. (see section IV.2.) It was therefore possible, knowing the crystallography of both phases, to determine the orientation relationship between the two phases. This experimental procedure was carried out for both the $\langle 100 \rangle$ growth texture and the $\{111\}$ spinel twinned eutectic silicon forms, and in neither case was any recurring orientation relationship found.

V Ag/Si AND Au/Si RESULTS

It has been shown (see section III) that similarities exist between the microstructures of furnace-cooled alloys of the eutectic systems Ag/Si, Au/Si and Al/Si. In the above section (section IV) it was shown that the microstructure of the eutectic system aluminium/silicon depended primarily upon the growth of the silicon phase, and that the form of the eutectic silicon could be altered by changing the growth variables. This being the case, one would expect further similarities to exist between these three eutectic systems. This section deals with the results obtained from unidirectionally growing the two eutectic alloys silver/silicon and gold/silicon.

(1) Ag/Si MORPHOLOGY

A specimen of the eutectic alloy was unidirectionally grown under the following conditions:

$$R = 2.78 \times 10^{-5} \text{ cm/sec.}$$

$$G \approx 30^{\circ}\text{C/cm.}$$

a) Sections

The sections cut transverse and longitudinal to the growth direction are shown in plates 110. The similarity between the Ag/Si alloy and an Al/Si alloy grown under similar controlled conditions is striking. (see plate 63a)

The majority of the eutectic silicon in this Ag/Si alloy is in the angular form, but the spaces between the angular particles appear to contain more irregular eutectic silicon than Al/Si eutectic grown under similar conditions. A histogram plotted of the various inter-angular side plate angles produced the same result as that for the aluminium/silicon angular eutectic, namely 53° , 82° , 90° , 98° , 127° , 135° and 143° . The longitudinal section(plate 110b) shows that both smooth and corrugated silicon side plates exist. One may therefore assume that the angular silicon morphologies in the two systems are the same.

b) Extraction

Further confirmation of the similarity in silicon morphology was shown by extracting the eutectic silicon from its silver matrix. In the case of the angular silicon plates, all the forms were observed, (see plates 111a to 112b and compare with plates 45a, 47 and 51) i.e. smooth, corrugated and surface-marked.

Extraction also proved that the inter-angular eutectic silicon particles were irregular silicon particles. (plate 112b) There were fewer irregular silicon plates than in the Al/Si eutectic alloy and a far greater percentage of this irregular eutectic phase was in the twisted fibrous form. (c.f. similar form produced in Al/Si system - plates 68)

Extraction and low power micrographs of extracted particles confirmed the crystalline nature of this eutectic form to be the same as the angular eutectic silicon in the Al/Si system. That is, the angular particles were plates were made up of (100) smooth silicon plates of corrugated plates composed of (111) plates. These silicon plates were often related by means of a (111) crystal axis. (see section IV.5 for more complete details)

(2) Ag/Si CRYSTALLOGRAPHY

a) The Silver Matrix

X-ray rotation photographs taken about the growth axes of small pillars of the eutectic alloy showed that the silver matrix had no preferred orientation. (plate 113) This was to be expected considering the great similarities between the systems Al/Si and Ag/Si.

b) Eutectic Silicon

The same rotation photograph of a small eutectic alloy pillar also showed that the silicon phase of the eutectic had the expected $\langle 100 \rangle$ Si preferred orientation.

Rotation and Laue X-ray photographs of extracted Si-particles confirmed the crystallography of this angular form to be the same as the angular eutectic silicon in the Al/Si system. That is, the angular particles side plates were made up of $\{100\}$ smooth silicon plates or corrugated plates composed of $\{111\}$ planes. These silicon side plates were often related by means of a $\{210\}$ spinel twin. (see section IV.5 for more complete details)

The irregular silicon particles were shown to be $\{111\}$ spinel twinned, and some of the few $\{111\}$ platelike irregular particles showed $\langle 110 \rangle$ preferred growth directions. (c.f. section IV.6)

(3) EFFECT OF G AND R ON Ag/Si EUTECTIC ALLOY

The effects of the imposed growth rate R and the specimen temperature gradient G upon the angular eutectic silicon morphology were exactly the same as in the Al/Si eutectic system. An increase in temperature gradient G led to a decrease in angular particle size and an increase in growth rate R also led to a decrease in particle size. (see plates 114)

However, in this eutectic system the irregular eutectic silicon appears to be stable to lower growth rates and the angular silicon stable to higher growth rates than in the aluminium/silicon alloy. The development of large irregular silicon plates did not take place and the majority of the irregular eutectic silicon was in the form of the irregular twisted fibrous type.

Further mention of this observation will be made in the discussions on both pure eutectic and modified alloys. There was very little evidence of silicon web formation.

(4) Au/Si EUTECTIC ALLOY

A specimen of this eutectic alloy was unidirectionally grown under the following conditions:

$$R = 2.78 \times 10^{-5} \text{ cm/sec.}$$

$$G \approx 30^{\circ}\text{C/cm.}$$

Sections transverse and longitudinal to the growth direction are shown in plates 115. Vestiges of the angular silicon form still remain and these were again found to conform with the angular silicon particles found in the Al/Si eutectic system. Longitudinal sections indicated that both smooth and corrugated side plates exist.

The majority of the eutectic silicon exists as the irregular form, however, and as in the case of the Ag/Si eutectic described above, the greater proportion of these irregular particles appear as twisted fibres of eutectic silicon.

VI DISCUSSION

In the introduction (section I.3.) three basic growth mechanisms are postulated for the eutectic reaction and these are:

- i) Independent, or separate growth of the two eutectic phases by relatively long range diffusion.
- ii) Co-operative growth of the two eutectic phases by short range diffusion.
- iii) Repeated nucleation and growth

The experimental results (sections III, IV and V) show that the eutectic systems between F.C.C. metals and silicon can grow by the first two of these three basic growth mechanisms. The growth mechanism, and hence the resulting morphology and crystallography of the eutectic alloy, depends on the imposed variables of growth rate (R), specimen temperature gradient (G) and alloy composition (C).

In sections VI.1 to VI.4 the effect of growth rate and temperature gradient on the two observed growth mechanisms will be discussed. Section VI.5. will deal with the effect of alloy composition on the eutectic microstructure produced at the various G and R-values investigated, and section VI.6. will discuss the possible mechanism of repeated nucleation and growth.

It has already been mentioned (section I.3.) that the two phases in metal/non-metal eutectic alloys grow in a different manner. The F.C.C. metal phase has a low entropy of fusion and grows essentially isotropically with an atomically rough interface. The silicon phase, however, has a high entropy of fusion and usually grows with a smooth faceted solid/liquid interface; growth occurring by the successive passage of layers of atoms across the smooth interface. The growth of silicon requires a fairly large undercooling to drive this process of initiating growth layers, whereas the aluminium with its rough interface requires a negligibly small kinetic undercooling. One might have expected that the metal would lead the silicon during growth since it needs a smaller undercooling, but in this event the isotropic growth of the metal would cause it to envelop the silicon, resulting in renucleation and the

production of discontinuous particles but the experimental results have shown this not to be the case. (section IV.6.d.) Growth can proceed at a lower total undercooling if the silicon grows ahead of the metal phase; since the large kinetic undercooling of the silicon can be balanced by the large solute undercooling of the metal matrix. (Hellawell and Tiller 1967)

In this way overgrowth of the silicon by the metal is reduced and in some cases almost completely prevented. The later sections in this discussion will show how the three growth variables can affect the ease of metal overgrowth and thus alter the eutectic morphology.

The eutectic alloy attempts to grow by a short range diffusion process but is prevented from doing so at G/R values above $10^7 \text{ sec. } ^\circ\text{C cm}^{-2}$ by metal overgrowth of the silicon. (see section VI.1.a.) Below this value of G/R , growth is by a short range diffusion process and the form of the eutectic alloy depends on the amount of undercooling at the growing solid/liquid interface. There are two kinetic growth mechanisms for the eutectic silicon and at low undercoolings the kinetic growth mechanism of the silicon phase produces a $\langle 100 \rangle$ Si preferred growth texture whilst at higher undercoolings a different mechanism produces silicon particles related by $\{111\}$ spinel twins. As the silicon tends to lead during growth, the form of the eutectic depends very much

on the kinetic growth mechanism of the faceted phase.

Models are proposed for the various growth mechanisms encountered in preparing the G/R plot and an attempt is made to explain the observed change-over from one mechanism to another. The discussion will centre around the Al/Si eutectic alloy but, except where especially mentioned, the conclusions and models adopted are applicable to the other two F.C.C. metal/silicon eutectics as well.

(1) SEPARATE GROWTH OF THE TWO EUTECTIC PHASES

This was postulated as one of the possible growth mechanisms for a eutectic reaction (section I.3.) but has so far only been observed in faceted/faceted eutectic systems in which the two phases sometimes tend to grow independently with large diffusion distances at the growing interface.

The production of a separate growth form of the eutectic alloy aluminium/silicon is the first time any mention has been made of a non-faceted/faceted eutectic system growing by this mechanism. (see section IV.4.)

Recent experiments on Al/Ce, another non-faceted/faceted eutectic alloy, have shown that separate growth of the two phases occurs in this system as well, if sufficiently high G/R values are used. (Hellawell 1967b)

a) Constitutional Undercooling

The proposed explanation of this growth form of the eutectic alloy is that during growth the aluminium phase presents a planar solid/liquid interface because of the very high G/R values that are imposed upon it. Nucleation of silicon on the aluminium phase has to occur at a greater

undercooling as the easy nucleation sites, which are usually present on a non-isothermal growth front, have been removed. Once formed, these silicon particles are easily overgrown by the aluminium phase, since any lead the silicon may have is drastically reduced by the high temperature gradient. Because of these two factors, the number of silicon particles is small and growth occurs by long range diffusion between the planar aluminium and this small number of large silicon particles.

A few simple calculations can be carried out to test whether the above hypothesis is reasonable, i.e. whether the constitutional undercooling produced by a 13 wt.% concentration of silicon can be suppressed by the observed values of G and R .

The simplest calculation is to assume that the eutectic alloy grows out of eutectic liquid as two single phase materials and that there is no lateral diffusion at the interface.

If we assume that there is no solid state diffusion and that there is no thermal convection in the liquid phase, we may use the following well known formula:

$$G/R = \frac{mC_0}{Dk_0} (1 - k_0) \quad (\text{Tiller et al. 1953})$$

where G = temperature gradient in liquid at the interface

R = growth rate

m = slope of the liquidus

C_0 = solute concentration

D = diffusion coefficient of solute in the liquid

k_0 = equilibrium distribution coefficient

If we consider the aluminium phase, then all the above parameters are accurately known, except D the diffusion coefficient which is only known very roughly, and so the above equation could be used to calculate a value for D .

The breakdown of the planar aluminium interface was found to occur at $G = 300^\circ\text{C}/\text{cm}$. and $R = 2.78 \times 10^{-5} \text{ cm/sec}$. and as $m.C_0 = 83$ and $k_0 = 0.125$

$$D = 5.4 \times 10^{-5} \text{ cm}^2/\text{sec}.$$

This gives a reasonable value for D , although indications are that it may be rather high. (Lommel and Chalmers 1959)

The model is, however, unreasonable in that the composition C_0/k_0 that builds up at the interface, in order that solid of the same composition as the liquid can be put down, has an equilibrium liquidus temperature some 600°C below the eutectic isotherm! (fig. 116a)

It appears that a correction must be added to the above equation because of lateral diffusion of solute across the interface. If we assume that this effect is similar to that of thermal convection in a single phase material, we can use the Burton Primm and Slichter equation (1953) for the observed distribution coefficient k_e . k_e is defined as the ratio of the solute concentration in the solid phase to that of the average solute concentration in the liquid phase. In the above case where we assume no mixing in the liquid phase $k_e = 1$ since the composition of the solid being deposited is the same as that in the bulk of the liquid but with perfect mixing in the liquid phase k_e will equal k_0 .

If the concept of k_e is applied to the derivation of the above G/R formula, the following formula is obtained:

$$G/R = \frac{mC_0}{D} \left[\frac{k_e}{k_0} - k_e \right]$$

In this formula we can substitute the Burton, Primm and Slichter (1953) equation for k_e in terms of k_0 .

$$k_e = \frac{k_0}{k_0 + (1 - k_0) \exp. \left(\frac{-Rx}{D} \right)}$$

where X is the thickness of the diffusion layer built up ahead of the growing interface. When $X = \infty$ then $k_e = 1$, and when $X = 0$ then $k_e = k_o$. We thus obtain the formula:

$$C/R = \frac{mC_o}{D} \left[\frac{1 - k_o}{k_o + (1 - k_o) \exp. \left(- \frac{Rx}{D} \right)} \right]$$

Taking the value of X to be the same order as the observed separation of the silicon particles, i.e. 0.1 cms., we find that the observed C/R breakdown gives a value of $D = 5 \times 10^{-6} \text{ cm}^2/\text{sec.}$ which appears more reasonable. (see Lommel and Chalmers 1959) This then gives a value of $k_e = 0.2$ and so the silicon concentration C_i in the built up layer at the growing interface = $\frac{C_i k_e}{k_o} = 20 \text{ wt.\% Si}$ (fig. 116b) This has an equilibrium liquidus temperature of 47° below the eutectic isotherm. This model of separate growth appears to give a far more reasonable result in that the ΔT at the interface, although very large, is not ridiculous. The model will now be elaborated upon.

At the beginning of a specimen unidirectionally solidified at this high G/R value (i.e. $G/R > 10^7 \text{ sec.}^\circ\text{C cm}^{-2}$), aluminium is most probably the first phase to nucleate. (Sundquist and Mondolfo 1961) Subsequent growth of the aluminium phase occurs

with a planar interface and silicon builds up at the interface until the equilibrium liquidus temperature is sufficiently below the silicon liquidus for nucleation of silicon to occur on, or near, to the aluminium solid/liquid interface. Alternatively, silicon may build up until the aluminium interface begins to form cells allowing nucleation of the silicon to occur at smaller undercoolings in the cell triple junctions. Once the silicon has nucleated, lateral diffusion of silicon occurs across the interface decreasing the silicon build-up ahead of the aluminium and thereby stabilising the aluminium front.

The aluminium, because of its non-faceted growth, has a mechanism by which it can overgrow the silicon. In order to support a steady short range diffusion process, the faceted material must project sufficiently for these facet faces to be stable to overgrowth. If, however, the gradient is very high then this projection of the faceted phase can be reduced to such a small value that the isotropic matrix phase can overgrow the silicon and either terminate its growth, or cause the silicon to constantly have to change its growth direction. This overgrowth is also assisted by growth perturbations since the metallic phase is kinetically more capable of a rapid response to changes in growth rate.

A balance is reached between the silicon particle termination process and the nucleation of new particles due to solute build-up. Once the structure has been formed, the silicon, although not a stable growth form, does not appear to have to renucleate often for growth to continue.

The silicon particles are interconnected and capable of branching by twinning and so when one particle is overgrown by the aluminium, the increased silicon build-up can be absorbed by one of the remaining silicon particles increasing locally in size or branching. If this cannot occur too readily, then the build-up of silicon will cause local loss of the planar aluminium growth front and subsequent renucleation will occur.

Although the aluminium interface is planar, the temperature gradient is not sufficient to overcome the effect of constitutional undercooling of the silicon phase, and so the silicon grows as if into an undercooled melt. The form of these silicon particles, as we have seen in section IV.4., is that of elongated faceted crystals. When observed in longitudinal section (plate 31b) these crystals indicate the unstable nature of the aluminium (S) / silicon (S) interface which is brought about by overgrowth of silicon by

aluminium and accentuated by the unavoidable fluctuations in growth conditions. The growth form of this eutectic silicon is very similar to that produced when twinned silicon is grown from a supercooled silicon melt. Results show that the eutectic silicon is heavily $\{111\}$ spinel twinned and has either a $\langle 211 \rangle$ or a $\langle 110 \rangle$ local growth direction; a result identical to twinned silicon crystals grown from undercooled Si melts.

b) Twin Plane Reentrant Edge Growth Mechanism

The growth of silicon and germanium crystals from supercooled melts is now well understood and we shall show how this work is relevant to eutectic silicon in some of its growth forms.

This growth mechanism is based upon $\{111\}$ spinel twins that are observed in both silicon and germanium crystals. Ellis and Treuting (1951) and Ellis and Pangeant (1954) have shown that in germanium ingots the grains are related via multiple $\{111\}$ spinel twins. Billig (1955) found a $\langle 211 \rangle$ preferred growth direction in Czochralski grown silicon crystals. Subsequent work (Bennett and Longini 1959; Wagner 1960; Hamilton and Seidensticker 1960, 1963 a, b and c; and Albon and Owen 1963) showed that both $\langle 211 \rangle$ and $\langle 110 \rangle$ preferred growth directions could be observed in Czochralski grown diamond cubic materials so long as at least two parallel $\{111\}$ spinel twins were present. From these results a twin plane reentrant edge growth mechanism was postulated and convincingly proven.

The twin plane reentrant edge (T.P.R.E.) growth mechanism is most readily understood by considering a $\{111\}$ silicon plate which is octahedral in shape. The plate contains a single $\{111\}$ twin plane lying in the plane of the plate and the edges of the particle are again built up from $\{111\}$, i.e. the crystal contains only $\{111\}$ facets. (see fig. 117a) The edges of the octahedral particle consist of pairs of $\{111\}$ inclined at either 141° or 219° to each other, i.e. there are three reentrant grooves and three ridges on the six edges of the silicon particle. If the crystal is placed in a supercooled melt, growth will occur most readily using the twin plane reentrant edge sites and the crystal will grow rapidly into a triangular shape, when growth will essentially stop. This effect has been observed (Wagner 1960) and will be used later in this discussion to explain the triangular form of some of the irregular eutectic silicon plates. (section VI.4.a.)

If the silicon particle contains more than one twin plane lying in the plane of the plate, (see fig. 117b) then the reentrant edges cannot grow themselves out, since growth in a 141° twin plane reentrant groove produces another 109° groove with the other twin of the crystal. Further growth can thus occur on this new groove (see fig. 117b) preventing the growing out of the 141° groove. The growth direction must lie in the $\{111\}$ twin plane and $\langle 211 \rangle$ growth occurs when silicon atom addition is preferentially onto one set of twin plane reentrant edges and a $\langle 110 \rangle$ growth texture is produced when growth is on two sets of twin plane reentrant edges simultaneously. (fig. 117b)

From the experimental results on these eutectic silicon particles, twin traces were observed parallel with the growth direction and this, together with the observation of $\langle 110 \rangle$ and $\langle 211 \rangle$ growth textures, must indicate that a T.P.R.E. mechanism is operative. The majority of the crystals had $\langle 110 \rangle$ growth textures and this may be because overgrowth on the two inclined growth faces occurs less easily than with a flat $\langle 211 \rangle$ growth front. (see fig. 117b)

(2) CO-OPERATIVE GROWTH - $\langle 100 \rangle$ Si GROWTH TEXTURE

a) Cell Formation

When the G/R values for a unidirectionally grown Al/Si eutectic alloy fall below $10^7 \text{ sec.}^\circ\text{C cm}^{-2}$ the solid/liquid interface of the aluminium phase becomes unstable and develops a cellular form. The silicon phase can nucleate easily in the cell triple boundaries and produces a hexagonal array of fibrous particles dispersed in an Al matrix. The gradients are now sufficiently low so that the silicon leads the aluminium by an amount large enough to prevent the possibility of aluminium overgrowth. At these higher gradients, however, the lead is still small enough to prevent the silicon fibres from producing side facets. (plate 23) The silicon in this fibrous form of the eutectic is growing in a co-operative manner and the diffusion distances across the growing interface have been drastically reduced by comparison with the massive form of the eutectic. (see plates 22 and 23) However, growth fluctuations produce silicon growth bands indicating that there is still a great deal of silicon build-up at the growing interface. Growth of the eutectic silicon now takes place at

a smaller undercooling and as this undercooling is not sufficient to produce $\{111\}$ spinel growth twins (Bolling, Tiller and Rutter 1956) a different mechanism is operative, which produces a $\langle 100 \rangle$ Si growth texture. The reason that this mechanism of eutectic silicon growth is not found at very high G/R values is probably because the silicon does not possess twins so that it can change its growth direction. Thus, when aluminium overgrowth occurs, the silicon growth is terminated and subsequent eutectic growth has to proceed by means of a different mechanism. (see section VI.1.b. above)

When cells are produced in impure single phase materials, the cell size at constant growth rate depends inversely on the temperature gradient in the liquid at the interface. (Coulter and Elliot 1967) Therefore, as the specimen temperature gradient is decreased, in these eutectic alloys, one would expect the spacing of the cell triple boundaries, and hence that of the $\langle 100 \rangle$ Si fibres, to increase. This is observed, and the relationship between the internodal distance λ and the temperature gradient was found to be $\lambda = AG^{-0.6}$. The discrepancy between the inverse relationship and that observed was probably caused by a change in the mode of solidification of the eutectic silicon, i.e. the fact that towards low G values it is a

co-operative eutectic reaction that is being dealt with rather than an impure single phase material with precipitation at cell triple junctions. It is very difficult, however, to state where one model finishes and the other begins. If one considers just the cell formation model, then one would have expected that the aluminium lead would have increased with decreasing gradient but in fact the opposite was observed and the silicon lead increased.

As the temperature gradient is reduced, the silicon grows further ahead into the liquid and is able to produce side facets that give rise to the angular silicon particles. (plates 59a to 60b)

A growth mechanism has to be postulated to explain the observed morphology and crystallography of these $\langle 100 \rangle$ Si growth textured particles.

b) Screw Dislocation Growth

Diamond cubic materials have a shortest lattice vector of $\frac{1}{2}a \langle 110 \rangle$ and so a pure screw dislocation in such a material will have a Burgers vector $\frac{1}{2}a \langle 110 \rangle$. (Hornstra 1958)

This screw dislocation is of low energy and can be produced in a diamond cubic material without the occurrence of broken bonds at the dislocation core. (see fig. 118a) If the line of such a screw dislocation extends to the crystal surface, the face on which it ends will now contain a step which runs from the point where the dislocation emerges to the edge of the face. Growth of the face can occur by continual deposition of material onto this self perpetuating step.

(Frank 1949)

The experimental work on the $\langle 100 \rangle$ Si growth texture form of the eutectic silicon showed that no $\{111\}$ spinel twins existed in the structure; the undercooling at the interface was not apparently large enough to provide the energy necessary to produce the growth twins. Screw dislocation growth has been observed to occur at very low undercoolings in many systems and so it was felt that this was a very likely alternative kinetic mechanism.

c) Steady State $\langle 100 \rangle$ Si Growth

The simplest nodal type for this $\langle 100 \rangle$ Si form is shown in fig. 118b, and consists of four $\{100\}$ joined together at right angles along a common $\langle 100 \rangle$ direction. In this case a $\langle 100 \rangle$ Si growth texture could occur by making use of four $\frac{1}{2}$ a $\langle 110 \rangle$ screw dislocation sources which are mutually inclined at 45° to the growth direction, each side plate producing one operative screw source. The growth layers from each of the $\frac{1}{2}$ a $\langle 110 \rangle$ screw dislocations spill down the leading $\{111\}$ facet faces of the $\{100\}$ side plates and so growth is rather similar to that of non-faceted dendrite growth, i.e. growth is simultaneously on four $\{111\}$ close packed planes to give a $\langle 100 \rangle$ growth texture. (Tiller 1957, Hellawell and Herbert 1962) The complication of smooth side plates related to each other via $\{210\}$ spinel twins does not appear to affect the growth mechanism of the silicon crystals and it is not believed that these twins are the cause of the growth kinetics. The reason for their formation remains obscure but they may well be an attempt by the growing crystal to obtain more effective removal of solute during growth. $\{111\}$ spinel twins do not lie in the growth direction and would, therefore, tend to grow out and so a form of twin is produced

which lies in the $\langle 100 \rangle$ growth direction. If their number was small, as appears to be the case, very little extra undercooling would be required for their formation.

d) Non-Steady State $\langle 100 \rangle$ Si Growth

The mechanism described above gives rise to a steady state co-operative growth process, since all triple junctions at the growing interface are stable. The experimental results showed that there was also a corrugated side plate which must have grown by a non-steady state co-operative growth process.

Corrugated side plate growth is not so much non-steady state as a periodic growth mechanism. The experimental results showed that the side plates were single crystals and that they were found whenever angular particles with three or four side plates were observed. (section IV.5.e.) From fig.51 it can be seen that the form of the corrugated plate is such that it cannot grow by itself using a screw dislocation source ($b = \frac{1}{2} a \langle 110 \rangle$). However, this type of angular particle side plate was found under the same growth conditions as the smooth plate, and so one must infer that the same kinetic mechanism is operative.

Corrugated plates are found attached to smooth plates and the relationship is such that the corrugated plates can be supplied with growth layers from the screw dislocation sources on the smooth plates. (see fig. 119) Two sources take it in turns to supply the corrugated plate; the periodicity of the structure is produced because the

corrugated plates local growth direction is not $\langle 100 \rangle$ but $\langle 211 \rangle$ (see fig. 51) and so the growing plate is soon affected by the diffusion field of a neighbouring angular particle and alters its growth direction by utilizing another screw source until the same effect happens again. (see fig. 119) Calculations show that for a diamond cubic material (as with F.C.C. materials) the $\{111\}$ is the plane with the lowest surface energy, with the $\{110\}$ and $\{100\}$ planes having successively higher energies. Therefore, the reason for corrugated plate formation is presumably because of the lower energy of $\{111\}$ planes compared with a $\{110\}$ plate which could form by simultaneous growth utilizing two screw sources from adjoining $\{100\}$ smooth plates.

Not all plates are corrugated since smooth $\{100\}$ type side plates are required to supply the growth layers for these corrugated plates. The formation of the relatively high energy $\{100\}$ plates is thus a direct result of the screw dislocation growth mechanism. When the angular particles can produce the low energy $\{111\}$ they do so by alternate growth using the screw dislocation sources from adjoining smooth particles.

The periodic surface markings at 45° to the growth direction on some $\{100\}$ plates are presumably due to sympathetic fluctuations of growth when a $\langle 110 \rangle$ screw dislocation in the $\{100\}$ plate is acting as one of the sources for corrugated plate growth. This can be seen by looking at the model in fig. 119.

e) Effect of G

It appears that the $\langle 100 \rangle$ growth textured eutectic silicon grows by a screw dislocation mechanism and it is now possible to produce a model to explain the change in size of the angular particles with temperature gradient. It was found experimentally that the projected free edge distance varied inversely with the temperature gradient G. (see section IV.5.h.)

$$d = AG^{-1} \text{ (table 61 and fig. 62)}$$

If one assumes that for a given rate of growth a certain extra undercooling ΔT_K is required to operate the screw dislocation source, then one would expect this source to be at the base of the silicon particle free edge, i.e. the relevant screw dislocations would be those with the greatest undercoolings. If ΔT_K is independent of the temperature gradient at the interface, then the distance corresponding to ΔT_K increases as the temperature gradient is reduced. If ΔT_K is assumed zero at the apex of the growing angular particle then since the growing edge is at 45° to the growth direction, the projected free edge distance

will be equivalent to a temperature difference of ΔT_K

$$\text{thus } d = \frac{\Delta T_K}{G}$$

This is the same relationship that was found experimentally and at $R = 2.78 \times 10^{-5}$ cm/sec. $\Delta T_K = 0.24^\circ\text{C}$ ΔT_K would appear to be made up almost entirely from a kinetic undercooling term. (Cooksey, Day and Hellawell 1966)

(3) CO-OPERATIVE GROWTH - THE CHANGE-OVER FROM $\langle 100 \rangle$ Si $\rightarrow$ $\{111\}$ TWINNED Si

It appears that a certain critical undercooling has to be exceeded before silicon can form $\{111\}$ spinel twins. (Bolling, Tiller and Rutter 1956) This fact can be used to explain the experimentally observed change-over from the $\langle 100 \rangle$ growth textured silicon to the $\{111\}$ spinel type in the G/R plot. (fig. 28) It was observed that above a certain critical growth rate R_c , all the eutectic silicon occurs in the $\{111\}$ spinel form. In this case the undercooling at all parts of the interface is sufficient to produce the necessary twins. At growth rates below R_c , irregular silicon is still formed together with the angular variety; the irregular form being stable to lower R-values, the lower the specimen temperature gradient. (see figs. 27a and 28) This transition region is produced because, at any constant R-value, the angular particle size and separation increases with decreasing temperature gradient. When the angular particles are very large, a solute problem exists for the matrix in the areas between the angular particles and there is a local high solute undercooling which can be reduced if the $\{111\}$ spinel silicon form is produced.

At higher temperature gradients the inter angular particle distance is smaller and the extra solute undercooling in the spaces in between is far less and not sufficient to produce irregular particles. However, as the growth rate is increased, the extra solute undercooling required to produce $\{111\}$ spinel twins is less and so irregular particles can form in eutectics with smaller internodal separations. This in itself would lead to a triangular transition region on the G/R plots but there is also the effect that growth rate has on the internodal separation and as the growth rate is increased, the diffusion path $\sqrt{Dt}$ becomes shorter and the separation of the angular particles is, therefore, less, and so the range of R values over which the transition structure is found decreases rapidly with increase of temperature gradient G . (see figs. 27a and 28)

In the eutectic systems Ag/Si and Au/Si the amount of solid solubility of silicon in the metal matrix is less and the volume fraction is not significantly greater than Al/Si so that the local pockets of high solute undercooling occur more readily in inter angular particle regions and irregular silicon is thus found at lower growth rates. (see results section V.3.)

The undercooling needed to drive a screw dislocation depends on R according to the following relationship:

(Burton, Cabrera and Frank 1951)

$$R \propto \Delta T^2$$

The undercooling required to operate the twin based growth mechanism is most probably based on the energy required to form the twin boundaries at the necessary rate, since the continual overgrowth of the silicon by the metallic matrix necessitates the reproduction of T.P.R.E. sites. If reproduction of T.P.R.E. sites need not occur, as in the case of growth from a silicon melt, the necessary undercooling ΔT is proportional to the imposed growth rate. (Hamilton and Seidensticker 1963a)

As it is $R = \text{nucleation rate} \times \text{subsequent growth rate}$

$$\text{and so } R = \text{const. } \Delta T \exp. \left(\frac{-\Delta F - \Delta S \Delta T}{kT} \right)$$

where ΔF is the activation energy for twin formation which is assumed independent of undercooling.

The two curves for the dependence of R upon undercooling cross at a critical value R_c . (see fig. 120) At growth rates less than R_c , the screw dislocation mechanism can operate at a lower ΔT , whereas above R_c , the twin based mechanism can operate at the lower ΔT . The above argument assumes that ΔT is constant across an interface but it has been observed that the twin based mechanism can operate at growth rates lower than R_c , when there are local increases in solute undercooling.

(4) CO-OPERATIVE GROWTH - $\{111\}$ SPINEL TWIN TYPE -
NON-STEADY STATE GROWTH

When aluminium/silicon eutectic alloy was unidirectionally solidified above a certain critical growth rate, ($R_c = 3 \times 10^{-4}$ cm/sec.) the eutectic silicon all grew by a mechanism that appeared to entail the use of $\{111\}$ spinel twins.

The experimental results (sections IV.6 and 7) showed that eutectic silicon growth was still the controlling influence upon the eutectic morphology, and that the silicon could grow by either a non-steady state or a steady state co-operative growth process. Both processes produced faceted crystals but in the non-steady state growth process the faceted silicon crystals did not have a common growth direction. The steady state form had faceted silicon platelets which were parallel to each other and the local growth direction. This form of the eutectic alloy was only produced in hypereutectic alloys and so will be discussed under section VI.5 on the alloy composition growth variable.

The non-steady state growth of these alloys produces an irregular microstructure. (plate 25) Sections through this form of eutectic alloy show the silicon plates to be apparently randomly distributed in the metal matrix. The experimental results showed that these silicon plates were interconnected and related to each other via multiple twinning operations. (section IV.6.e.) The $\{111\}$ spinel twins also appeared to be relevant to the kinetic growth process.

a) T.P.R.E. Growth

The eutectic silicon consisted of two basic types; the irregular fibre and the so-called irregular plates. Irregular plates were shown to be $\{111\}$ plates containing $\{111\}$ spinel twins; the twin boundary lying in the plane of the plate. These irregular silicon plates grew by the T.P.R.E. growth mechanism as described above. (section VI.1.b.) The triangular plates (plates 70) contained only one twin plane and so this triangular shape was produced by the T.P.R.E. sites growing themselves out. (see fig. 117a) The lath form (plates 71 and 75) on the other hand was shown to always contain more than one twin plane and we saw above (section VI.1.b.) that in such a crystal the T.P.R.E. sites do not grow themselves out. T.P.R.E. growth can occur in any direction lying in the $\{111\}$ and so the observed $\langle 110 \rangle$ is fully explained. T.P.R.E. growth takes place simultaneously on two sets of T.P.R.E. sites to give a $\langle 110 \rangle$ growth direction and this mechanism appears to have been favoured over a single T.P.R.E. mechanism on one set of reentrant edges because of the greater difficulty of aluminium overgrowth at the solid/liquid interface, (see fig. 117b) i.e. the $\langle 110 \rangle$ form was more stable.

Although the silicon phase tends to lead the aluminium at the growth interface, overgrowth of the silicon by the aluminium occurs fairly easily at these higher growth rates, especially as the silicon particles do not have a common growth direction and this leads to local solute build-up and depletion at the growing non-isothermal interface. Complete overgrowth at the interface is unlikely, however, since the aluminium phase grows by rejection of silicon solute. The growing irregular plates can change their growth direction when partial overgrowth occurs, because of a local increase in solute undercooling which is sufficient to increase the number of twin boundaries and leads to the formation of heavily twinned irregular silicon fibres. Subsequent irregular platelet growth proceeds from the twins contained in this irregular fibrous silicon. Irregular eutectic silicon is, therefore, of a frondose nature and consists of irregular branched fibres with plates attached, dispersed in a metal matrix.

Some of the irregular silicon plates find themselves fairly well aligned with the growth direction and if they contain more than one twin plane they are capable of continued growth in a $\langle 110 \rangle$ direction for quite some distance before overgrowth occurs. (plate 67a) These silicon spikes are also stabilized because they often grow well ahead

of the rest of the non-isothermal interface. (plate 67b)

This is because T.P.R.E. growth occurs at a fairly low undercooling but is usually held back by metal phase overgrowth in these eutectic systems.

Although the kinetic growth mechanism of the irregular silicon plates is well substantiated, that of the irregular fibrous silicon that connects such plates is less well understood, but it seems very reasonable to assume that it involves the formation of growth twins.

At growth rates just above the critical growth rate R_c , the majority of the eutectic silicon is in the form of irregular plates growing by the T.P.R.E. mechanism. As the growth rate is increased, the diffusion distance ($\sqrt{Dt}$) decreases and so the interparticle spacing decreases accordingly. ($\lambda = AR^{-0.46}$, see fig. 83) Aluminium overgrowth of the silicon occurs more readily as the growth rate increases and this causes a decrease in the proportion of irregular plates produced during growth so that at very high growth rates, (i.e. rapid quenches) the eutectic silicon appears entirely in the fibrous form. (see plates 84 and 85)

b) Other Metal/Non-Metal Systems

The irregular form of F.C.C. metal/silicon eutectic alloys is very similar to that produced by many other metal/non-metal systems. It has been shown in only a few cases, however, that the non-metal phase is interconnected and so these observed microstructures could have resulted from a repeated nucleation and growth mechanism.

One group of metal/non-metal eutectic systems in which the interconnection of the non-metal has been proven is that of the metal/graphite eutectic alloys. (Bunin et al. 1953, Oldfield 1960) Growth of graphite flakes would appear to be very similar to that of the silicon in the Al/Si alloys described above, except that the graphite can change its growth direction very easily by sub-boundary faults as well as by twins (Oron and Minkoff 1964a and b) and so the graphite flakes are of a wavy nature. Another difference between F.C.C. metal/silicon and metal/graphite systems is, that at high growth rates nucleation of the graphite occurs ahead of the growing interface, giving rise to the formation of non-metal spherulites. (Morrogh and Williams 1949)

The eutectic system Al/Ge has been investigated recently (Hellowell 1967a) and it was shown that in this system too, the non-metal was interconnected. The twin boundary energy is lower for germanium than for silicon and so twin formation can occur at much lower growth rates than in the F.C.C. metal/silicon systems. (i.e. no $\langle 100 \rangle$ Ge growth texture was observed even at growth rates as low as 2.5×10^{-6} cm/sec.) At these very low growth rates the bulk of the germanium was not being overgrown and a T.P.R.E. mechanism could operate in which all the twin planes were parallel and lying in the growth direction (plate 121a) The irregular plates do not always lie in the growth direction and an increase in the imposed growth rate produces an apparently random structure very similar to Al/Si alloys. Extraction of the germanium from the aluminium matrix indicated that the germanium was interconnected and that its growth mechanism was very similar to that of the irregular Al/Si alloys.

(5) EFFECT OF COMPOSITION ON F.C.C. METAL/Si EUTECTICS

a) Complex Regular Eutectic Alloy Formation

The major effect of composition changes in these eutectic systems was that when the silicon rich hypereutectic alloys were unidirectionally solidified under the same conditions of growth rate and imposed temperature gradient as the irregular eutectic alloy described in the section above, they produced, in addition to the irregular structure, portions of the microstructure in which the eutectic silicon grew by a steady state co-operative process. These complex regular structures have been observed before in Al/Si eutectic alloys, (Spengler 1955; Görtler 1953; Scheil and Zimmermann 1957; Meussner 1959b, and Hunt and Jackson 1966) but no experimentally backed explanation has been attempted as to their reason for formation. An attempt will now be made to explain the formation of the complex regular structure using the results obtained in this present work. (see section IV.7.)

The experimental results on Al/Si alloys show that in these regular structures it is again the faceted phase that dominates the growth process and determines the form of the structure. The faceted material leads the metal phase during

growth sufficiently for a faceted silicon solid/liquid interface to develop; the metal matrix growing slightly behind the silicon and filling up the interstices between the faceted plates so as to maintain a short range diffusion growth front. The growth mechanism differs from the irregular eutectic described above (section VI.4.) in that the faceted plates comprising the regular structure are parallel to each other and lie in the local growth direction, and that all the faceted plates are joined to a common spine. (see plate 26)

For this complex regular structure to be stable the following conditions must be met:

i) A single easy growth site must operate for each regular portion of the structure, since otherwise the growth of each facet by means of its own easy growth site would lead to the plates growing at different rates and this would cause the regular structure to break down.

ii) The regular structure must be stable to growth fluctuations. Various reasons can be put forward for the stability of the web structure.

Firstly, eutectic growth into a hypereutectic liquid will cause a greater solute undercooling ahead of the metallic phase and this increased undercooling will further retard the position of the metallic phase interface thus making overgrowth of the silicon phase more difficult.

Secondly, Al/Si eutectic has a very low volume fraction (0.13) and so if it is to form a lamellar structure that is stable it will have to increase its volume fraction by further incorporation of silicon. This is observed and Si webs have a volume fraction of about 0.23.

Thirdly, the ease of metallic phase overgrowth could depend on the webs volume fraction. (i.e. the thickness of the silicon platelets)

The volume fraction was observed to decrease towards the outside edges of webs and this was presumably because the aluminium, rejected from the growing web tip, caused a decrease in local silicon concentration. At a certain web volume fraction, the aluminium overgrows the silicon and further web development is prevented.

Therefore, for web growth to occur, solidification must take place from a hypereutectic melt and so an indication of ease of web formation could be the ease of suppression of primary silicon growth by the imposed growth conditions.

Mollard and Flewings (1966) grew Sn/Pb eutectic alloys over a range of high G/R values and observed primary incorporation into the matrix when

$$\frac{G}{R} \gg \frac{m(C_e - C_o)}{D}$$

where m = liquidus slope

C_e = eutectic composition

C_o = alloy composition

D = liquid diffusion coefficient

If this factor is relevant, then primary silicon growth will be further suppressed as G/R is increased and so the amount of regular eutectic should increase with G/R. This was experimentally observed (see section IV.7.f.) but numerical calculation indicates that the amount of extra solute incorporation ($C_e - C_o$) into the eutectic by primary suppression is not sufficient to produce the observed amount of complex regular eutectic. The quantitative failure of the above equation may be because the complex regular structure represents a hopped crystal form intermediate between a eutectic and a primary particle and, therefore, does not require such high G/R values as the equation would indicate. The observations made during the work on Al/Si webs, that primary Si crystals act as growth

centres for these complex regular structures and that primary Si particles were extracted which showed rudimentary webs attached, help to substantiate this view.

The m/D value for a given eutectic system gives an indication of the ease of suppression of primary growth and hence in a metal/non-metal eutectic system should give some indication of ease of web formation in hypereutectic alloys, i.e. a system with a high m/D value will only be able to suppress primary formation over a small range of composition whereas a system with a low m/D value will be able to suppress primary formation over a wider composition range and, therefore, produce a large number of webs. In as far as values can be ascribed to m/D for different systems, the above hypothesis appears reasonable and systems such as Al/Ce and Ag/Ce with low m/D values produce large numbers of webs and systems such as Au/Si and Au/Ce with high m/D values produce few or no webs.

In the eutectic system Al/Ce, webs were far more numerous and were even found in hypoeutectic alloys. (Hollawell 1967) The reasons for the increased number of webs, (see plate 121b) apart from the supposedly easier incorporation of faceted component, (see above) is probably due to the high volume fraction (0.36) which would optimize the lamellar form and also prevent such easy overgrowth by the aluminium.

Once complex regular structures are produced they have diffusion distances at the growing interface that are much shorter than in the irregular structure formed under the same growth conditions. (see fig. 83) The web structure therefore grows with a smaller undercooling and will grow in preference to the irregular form if the growth conditions are favourable.

b) Mechanism of Complex Regular Eutectic Growth

The indication from the experimental results are that there are T.P.R.E. sites present in the webs which act as sources for the successive steps that pass over the low energy crystal facets during growth. These T.P.R.E. sites are available where the parallel platelets join the spine, (section IV.7.d.) and from the lath shaped silicon particles to which the webs are usually attached; the lath form of irregular silicon having been shown to grow by a T.P.R.E. mechanism. (section VI.4.a.) Such sources can supply all the growth facets of the parallel platelets on one side of spine, thus ensuring that they all grow at the same rate. The platelets and spines of the Si webs are usually related via $\{111\}$ spinel twins and this means that many of the $\{111\}$ platelets are not lying in the $\langle 110 \rangle$ growth direction. (see figs. 93b and 97) Local growth is on the $\{111\}$ macrofacet face of the platelets that can minimize the diffusion distance at the growing interface, and so as many of the platelets facet faces are inclined to the major $\langle 110 \rangle$ growth direction, the interface is observed to be non-isothermal and macrofaceted. (see fig. 122)

The growth of these silicon macrofacets takes place from the T.P.R.E. sites which have the greatest undercooling. Aluminium overgrowth limits the size of the macrofacets and

hence the size of the webs. But if at a given growth rate the silicon T.P.E. sites can operate only up to a certain ΔT value before overgrowth takes place, then the size of the webs will be affected by temperature gradient ahead of the growing interface in much the same way that gradient affected the size of the angular particles, i.e. an increase in gradient leading to a decrease in web size. The experimental results on web silicon confirm this effect. (see section IV.7.f.)

c) Other Complex Regular Structures

Weblike complex regular structures are observed in other systems besides F.C.C. metal/silicon eutectic alloys, and so it would appear that many of the observations made on Al/Si eutectic alloy should be applicable to metal/non-metal systems in general.

Mention has already been made to the formation of a web form in the system Al/Ge (section VI.5.a.) and experimental results have shown that the morphology and crystallography of these Ge webs is essentially the same as the silicon webs in Al/Si alloy. (Hellawell 1967a)

It would appear, therefore, that all the complex regular structures of diamond cubic/F.C.C. metal eutectic systems are very similar and depend on the ability of the diamond cubic material to form stable macrofacets whilst still retaining a steady state short range diffusion front. The growth layers necessary to cause growth of the macrofacet are supplied either from T.P.R.E. sites in the web structure itself or from T.P.R.E. sites in an attached primary particle. Hypereutectic alloys always tend to favour the formation of this structure.

Another group of metal/non-metal eutectics that produces weblike structures is that of the bismuth alloys. Bi/Sn, Bi/Pb and Bi/Tl all produce a weblike regular growth form apart from an irregular one. (Kerr and Winegard 1966) The formation of these webs is favoured in hypereutectic alloys (Hunt 1963) and again the form of the structure would appear to be dominated by the formation of bismuth growth facets. At present no crystallographic information on the form of the bismuth web is available and so the mechanism of growth is not known, but it would appear that the reasons for complex regular formation are very similar to those applicable to F.C.C. metal/diamond cubic eutectic alloys. (Whelan and Haworth 1967, Kerr 1966)

d) <100> Si Eutectic Alloys

In section VI.5.a. mention was made of Mollard and Flemings' work on Sn/Pb eutectic alloys (1966). This stated that suppression of primary growth could occur in a eutectic system when

$$\frac{G}{R} > \frac{m(C_e - C_o)}{D}$$

When this condition is fulfilled the eutectic system changes its volume fraction to incorporate the increased amount of one of the eutectic phases. This effect was observed in the present work on F.C.C. metal/Si eutectic alloys, and angular eutectic specimens of Al/Si alloys grown from hypoeutectic alloys at high G/R values were found to have 'eutectic' compositions of about 11.5 wt.% Si ($R = 2.78 \times 10^{-5}$ cm/sec. $G = 30^\circ\text{C/cm.}$) If this is assumed to be the maximum value of C_o capable of being incorporated under these conditions and C_e is taken as 12.7 wt. % Si, we obtain a value for $D = 7.9 \times 10^{-5}$ cm²/sec. which is in very good agreement with that obtained in section VI.1.a. Assuming a reasonable value of D of

aluminium in the eutectic liquid of say $D = 10^{-5} \text{ cm}^2/\text{sec.}$, we find that these growth conditions can suppress primary silicon growth in an alloy of 13.8 wt. % Si. Therefore, alloys of silicon concentration from 11.5 to 13.8 wt. % Si all produce angular eutectic without the presence of primary. The only difference being the volume fraction of the alloys.

e) Independent Eutectic Growth

Mollard and Flemings' (1966) equation is not applicable to this form of the eutectic alloy since the interparticle distance is large. However, because of the very high G/R values needed to produce this form one would expect a similar structure to be produced over a wide range of alloy composition but this was not substantiated experimentally.

(6) REPEATED NUCLEATION AND GROWTH

This basic growth mechanism for eutectic growth was amongst those postulated in the introduction. (section I.3.) In this type of eutectic reaction, growth proceeds by repeated nucleation of one of the phases ahead of the growing interface.

Because of the apparently random orientation of the silicon plates in an aluminium matrix, irregular Al/Si eutectic alloy has been mistakenly assumed to grow by this mechanism. (Hardy 1951, Tiller 1957b, Plumb and Lewis 1958, Chadwick 1963 and 1965) The arguments for this mechanism are based mainly upon the experimental evidence that there is no epitaxial relationship between the silicon and the aluminium. (although it had been proved only that the eutectic phases were not single crystals, and that they did not have a preferred growth texture) The present work confirmed this observation. (see section IV.9.) The silicon could therefore have nucleated heterogeneously in the liquid but not epitaxially on the aluminium. It has been mentioned previously (section I.3.c.) that just because there is separate nucleation of the two phases, it does not follow that eutectic growth has to proceed by a process of repeated nucleation and growth. Further experimental results are required before one can state that this is definitely the growth mechanism.

The work for this thesis has shown that the eutectic silicon is always interconnected and that growth does not occur by this mechanism of repeated nucleation and growth, even under extreme conditions of growth rate and temperature gradient. (It is shown later that sodium does not cause the eutectic to grow by this mechanism either - see section VII)

Experimental evidence shows that the eutectic systems between an F.C.C. metal and silicon do not ever grow by this mechanism but this does not invalidate the possibility of some non-faceted/faceted eutectic materials growing in this way. The fact that the group of eutectics Fe/C, Ni/C, Co/C and Au/C all produce graphite spherulites proves the existence of a growth mechanism involving repeated nucleation. (Morrogh and Williams 1949)

Repeated nucleation and growth occurs because the metal phase at a non-steady state growth front may completely overgrow the non-metal phase under certain growth conditions. Once this process occurs subsequent growth must be preceded by renucleation of the non-metal ahead of the growing interface. This change-over in growth mechanism from a co-operative process to a repeated nucleation type is observed in the metal/graphite systems with increase in growth and/or decrease in temperature gradient. (Wilkinson and Hellawell 1963, 1965;

Lakeland 1965; Brigham, Purdy and Kirkaldy 1966) Spherulitic growth is at present the only type of eutectic growth where the growth mechanism can be assumed to be that of repeated nucleation and growth. However, there is no reason to suppose that other metal/non-metal systems do not grow by this mechanism. The growth anisotropy of these faceted materials could produce platelike, needlelike or angular particles. Such particles would appear very similar to the irregular Si particles when observed on random sections and very careful experimental work would be required to show that these were indeed formed by a process of repeated nucleation and growth, and not by non-steady state growth. The indications are that a good many, perhaps the majority, of metal/non-metal eutectics, when observed in an irregular form, have grown by a non-steady state growth process. Certainly the proof that aluminium/silicon eutectic does not grow by a repeated nucleation and growth mechanism means that much of the previous work on this group of eutectics must be reconsidered.

It remains to be shown that the mechanism of repeated nucleation and growth would be very unlikely to produce the observed irregular eutectic microstructures. For the growth mechanism to be feasible it must have a nucleation frequency of silicon particles which is comparable with that needed to

produce the observed number of silicon particles. (Hellowell and Tiller 1967) Let us consider the microstructure of an aluminium/silicon eutectic alloy unidirectionally grown under the following conditions:

$$R = 1.37 \times 10^{-3} \text{ cm/sec.}$$

$$G = 29.5^{\circ} \text{ C/cm.} \quad (\text{see plate 81b})$$

In this eutectic alloy the interparticle distance was found to be 5.8μ . If each of the sectioned particles is assumed to be the result of a separate nucleation event, then the number of nucleation events per cm^3 can approach λ^{-3} and I , the number of silicon nuclei/ $\text{cm}^3/\text{sec.}$ will approach $\lambda^{-3}R$, i.e. 7.5×10^6 nuclei/ $\text{cm}^3/\text{sec.}$

Using the theory of absolute reaction rates and the theories of nucleation processes laid down by Volmer and Weber (1925) and Becker and Döring (1935) we may write:

$$I = \frac{n k T}{h} \exp \left(\frac{-\Delta F^*}{k T} \right)$$

where n = number of atoms per cm^3 in the liquid phase.

$$\text{and } \Delta F^* = \frac{16 \pi \gamma^3}{3 (\Delta F_v)^2}$$

where

γ = solid/liquid interfacial energy

ΔF_v = bulk free energy $\left(\Delta F_v = \frac{\Delta H_v \Delta T}{T_0} \right)$

ΔH_v = latent heat

ΔT = undercooling

T_0 = equilibrium temperature

Assuming $\gamma = 250 \text{ ergs./cm}^2$ and that ΔF_v for nucleation from an alloy melt is the same as from pure liquid silicon for the same undercooling below the melting point, we obtain a value for $\Delta T = 170^\circ\text{C}$. This is obviously too large.

If we consider heterogeneous nucleation then

$$I = \frac{n_s kT}{h} \exp \left(\frac{-\Delta F_s^*}{kT} \right)$$

where n_s = number of atoms of liquid absorbed on 1 cm^2 of solid nucleating surface (a mono-layer is assumed) and

$$\Delta F_s^* = \Delta F^* f(\theta)$$

$$\text{where } f(\theta) = \frac{(2 + \cos \theta)(1 - \cos \theta)^2}{4}$$

and θ = the wetting angle between silicon and the nucleating substrate. If we assume a reasonable undercooling at the interface of $\sim 2^\circ\text{C}$ we obtain a value for $f(\theta) = 8 \times 10^{-5}$

This corresponds to almost perfect wetting and means that at these reasonable undercoolings there are present in the liquid an almost unlimited number of heterogeneous nuclei of ideal character, which is almost as doubtful as the existence of the

incredibly high undercoolings at the growth front. We know that in practice pure alloy liquids cannot be greatly undercooled, and so this model of repeated nucleation and growth does not appear to be able to explain the observed irregular aluminium/silicon eutectic microstructure, and must be considered as further proof that irregular eutectic silicon grows by a non-steady state co-operative growth process that does not require renucleation. That is, if any further proof were needed after the micrographs of plates 76, 79, 84, 85 and 125.

(7) CONCLUSIONS

The major experimental conclusions on F.C.C. metal/silicon eutectic alloys may be summarised as follows:

- i) The growth variables of the growth rate R , the temperature gradient in the liquid ahead of the growing interface G , and the alloy composition can alter the growth mechanism of the eutectic alloy.
- ii) Above certain G/R values, the two eutectic phases grow by a long range diffusion process.
- iii) Below this certain G/R value, eutectic growth is by a short range diffusion process.
- iv) This short range diffusion process (co-operative growth) can be either steady or non-steady state leading to either a regular or an irregular eutectic microstructure.
- v) The form of the eutectic alloy microstructure hinges upon the kinetic growth mechanism of the facet faces of the silicon phase.
- vi) The eutectic silicon can grow by two distinct kinetic mechanisms depending on the undercooling at the growing interface. At low undercoolings, growth is by utilizing a screw dislocation source; above a critical undercooling, growth entails the use of $\{111\}$ spinel twins.

vii) The metallic phase fills up the interstices between the silicon particles and, when C/R is low, helps to maintain a short range diffusion growth front. It does not effect the shape of the eutectic silicon very much except at very high C/R values when the metallic interface becomes planar and leads to the formation of a long range diffusion process.

viii) The repeated nucleation and growth mechanism for a eutectic reaction is not found in this group of eutectics.

The object of this research programme was primarily to obtain a more coherent picture of the mode of solidification of metal/non-metal eutectic alloys in general, and aluminium/silicon eutectic alloy in particular. (section I.6.)

The policy of unidirectionally solidifying eutectic alloys under carefully controlled and measured growth variables has enabled this prime object of the research programme to be partially fulfilled.

It has become increasingly obvious that to fully understand such metal/non-metal eutectic systems, this systematic approach must be applied to other groups of eutectics. One such group is that of metal/graphite eutectics. Basic research on this system is required especially if the commercial process of modification and spheroidal growth is ever to be fully understood. Another group is that of the bismuth based alloys.

The next chapter shows how insight into pure F.C.C. metal/silicon alloys can greatly assist in the understanding of the modification effect of sodium. This research was only of a pilot nature but it does show very clearly how, when one is dealing with a complex phenomenon it pays to reduce the number of variables.

One of the conclusions of this thesis is, that in order to understand the more complex eutectic reactions of metal/non-metal systems, it is necessary to carry out a series of carefully controlled unidirectional solidification experiments. The resulting microstructures must then be analysed by as many techniques as possible and the information thus obtained classified in terms of the various controlled variables. Only in this way will it be possible to understand fully the complications of metal/non-metal eutectic growth.

VII MODIFICATION

(1) INTRODUCTION

The experimental work carried out on the modification of aluminium/silicon eutectic alloys with metallic sodium has been separated from the rest of the thesis for two reasons. Firstly, the experiments were essentially of a pilot nature and did not represent a thorough research programme and secondly, the interpretation of the results depends very much on the mechanism of pure aluminium/silicon eutectic growth described and substantiated in the previous sections.

As already mentioned in the review of the literature on pure Al/Si eutectic growth, a high percentage of the papers published on this eutectic system has been primarily on the modification process. Pacz (1920) found that the microstructure of the eutectic alloy could be drastically altered by the addition of a small quantity of an alkaline fluoride. The microstructure changed from an irregular to a very finely dispersed eutectic silicon form, not unlike

that in the rapidly quenched eutectic alloy. (see section IV.6.f.) This form of the eutectic is of commercial interest because of its good mechanical properties. It was soon found that alkali metals and alkaline earth metals and their oxides also produced modification. Sodium metal modification is, however, the method currently employed.

The literature on the subject of aluminium/silicon eutectic modification is very confusing and some of the papers are almost incomprehensible. A major reason for this confusion is the lack of controlled experiments. The majority of the work has been with low purity sand cast alloys and with this lack of control it is not surprising to find many contradictions and misinterpreted results.

However, from this literature survey certain facts on the modification process can be stated with reasonable certainty. These are, that on modification

- i) There is a marked reduction in the size of the silicon crystals and they appear more rounded.
- ii) The freezing point of the eutectic is lowered whilst the melting point is unchanged.
- iii) The eutectic composition changes with the degree of modification and moves towards high silicon concentration with increasing modification.

- iv) Both primary silicon and α -aluminium can appear in hypereutectic alloys.
- v) The alloy can be overmodified, when bands of larger crystals appear in the modified structure.
- vi) Modification increases the viscosity substantially and lowers the diffusion rate.
- vii) Rapid chilling of sodium free melts also leads to a general refinement of the eutectic structure.

As we have seen from the previous sections, the pure aluminium/silicon eutectic alloy is a complicated system and required controlled unidirectional solidification experiments on high purity materials to enable a reasonable picture of the growth mechanisms to be obtained. The modified eutectic is, likewise, a complicated system and if the mechanism of this process is to be understood it appears that similar controlled experiments will have to be carried out. The work described below was primarily to show along what lines a more rigorous research project could proceed. Because of the promising nature of the results obtained it was felt that these should be included in the thesis.

(2) PREVIOUS WORK

From the accepted facts on modification, three of the earliest theories on the effect of sodium can be readily dismissed.

Guillet (1922) proposed that the modifying agents react chemically in such a way as to remove the impurities alumina and silica by reduction. The increased purity was believed to account for the improvement in mechanical properties. Experiments with high purity alloys soon disproved this so-called 'true flux' theory.

Jeffries (1922) put forward the suggestion that two systems of Al/Si alloys exist, one of which is metastable. X-ray diffraction showed that this theory was untenable also.

The third theory (Hansley and Neufeld, 1950 Mondolfo 1951) was one based on the assumption that the modified eutectic was a ternary Al/Si/AlNaSi₄ eutectic. This was discounted because it did not explain why the melting temperature was the same as that of the binary eutectic. Moreover Scheil (1949) showed that the observed depression in freezing point, some 15°C, was too large to be explained by the simple addition of sodium.

The remaining published work on aluminium/silicon eutectic modification can be split up into two groups. The first group say that sodium addition affects the nucleation of the silicon particles and the second group that it is the growth that is affected.

a) Restricted Nucleation

This group of theories is based on the commonly held view that the normal Al/Si eutectic grows by a process of repeated nucleation and growth. (see section 1.3.c.iii.) If this view is accepted, it is obvious that the nucleation centre can have a determining influence on the resultant microstructure. Therefore, if the nucleation characteristic of the nucleation centre can be altered in any way it is to be expected that the microstructure of the alloys will change. This concept is central to all theories of modification based upon the restricted nucleation of the silicon particle. (Tiller 1957b, Plumb and Lewis 1958, Hardy 1951, Görtler 1953) It is postulated that the sodium becomes adsorbed onto the heterogeneous nucleation centres that exist in the liquid, and that the potency of their catalytic action in nucleating silicon crystals is reduced. It is presumed that they again become effective nucleating agents when the melt is further supercooled. In all these theories of restricted nucleation, the observed undercooling is directly responsible for the modification effect. Most theories imply that silicon growth is completed before they get taken in to the α -Al matrix and that no co-operative growth takes place at all.

Diverse reasons are put forward to explain the refinement of the structure that accompanies the lowering of the eutectic arrest temperature. These are an increase of nucleation frequency with temperature (Spengler 1955) or a decrease in diffusion rate with temperature. (Plumb and Lewis 1958) Tillier (1957b) says that the refinement in the structure is caused directly by the increase in local growth rate of the silicon particles. When the eutectic is solidified at a certain cooling rate, the sodium causes the silicon to nucleate at a lower undercooling. Once nucleation has occurred, growth is rapid and the interface temperature rapidly increases towards that of the liquid when growth stops. This is because the silicon grows in the liquid until its undercooling due to solute build-up equals the imposed ΔT when growth stops. As the growth rate is increased, the undercooling due to solute build-up increases more rapidly than the imposed ΔT and the particle size decreases. Bulk growth is by means of many such nucleation and growth processes. In this way growth occurs at a greater undercooling than for the pure eutectic, and since the silicon phase particles are growing at a greater rate, the particle size will be smaller than for a pure eutectic growing at the same overall rate of cooling.

There is, however, no evidence that growth of the silicon is complete before incorporation into the α -Al matrix and Chadwick (1963) postulates that his repeated nucleation and growth mechanism is still operative. (see section I.5.b.) If the sodium adsorbs onto all the nuclei responsible for nucleating the silicon particles that continue the growth process, then the eutectic reaction can only occur at a lower undercooling than normal. At this lower temperature the rate of growth of the alloy is increased and the time allowed for diffusion of aluminium and silicon atoms across the interface is decreased. The interparticle spacing is, therefore, decreased during the spasmodic growth following each nucleation event.

In a later review Chadwick (1965) reports the result of an experiment in which sodium-doped aluminium/silicon eutectic alloy was unidirectionally solidified in a graphite container. The result showed that the microstructure did not differ from that of the pure eutectic alloy grown under identical conditions. This result was explained by suggesting that the sodium only affects the initial nucleation event and that once the silicon growth is controlled by the motion of a temperature gradient through the liquid, there is no further nucleation problem for the silicon. Growth takes place from small particles produced by fragmentation of the larger leading silicon crystals.

b) Restricted Growth

In this alternate group of theories the mechanism of aluminium/silicon growth has still been taken to be that of repeated nucleation and growth. In this case, however, it is the growth part of the sequence that is affected by the presence of sodium. Although these theories will be reviewed as originally written, it is important to note that all the restricted growth theories can be discussed in terms of a fluctuating short range process at a duplex solid-liquid front.

Edward and Archer (1924) assumed that the sodium formed a "colloidal mist" in the alloy just prior to solidification and that this suspension inhibits the growth of silicon crystals by mechanical obstruction. The alloy must then supercool to nucleate more of the silicon phase.

Archer and Kempf (1926) modified the above theory and said that the sodium could be adsorbed directly onto the silicon crystals, thus preventing further growth. This theory has been elaborated upon by Davies and West (1963) who say that the sodium is surface active and chemisorbs to the interface between the solid silicon and the eutectic liquid.

The sodium deposits on the best growth sites for the silicon and the depositing silicon has to seek less favourable sites. To maintain growth the driving force must be increased and growth occurs at a greater undercooling. The growth of the fast growing faces is slowed down to approach that of the slowest and this results in a considerable change in the size and shape of the eutectic silicon crystals.

Boom (1948) published the experimental observation that in unmodified alloys the leading phase at the reaction interface is the silicon which grows unrestricted into the melt, whereas in sodium modified alloys the leading phase is aluminium which forces the silicon to be restricted into interdendritic regions. Thall and Chalmers (1950) elaborated on this observation and proposed that the sodium in the melt reduces the surface energy of the aluminium/silicon solid boundary such that the aluminium overcomes the silicon particles more easily. Without seed crystals on which growth can continue, the melt has to undercool in order to provide fresh nucleation sites for subsequent growth. The structure is, according to the authors, modified since the growth mechanism has changed from a non-steady state diffusion mechanism to one involving repeated nucleation and growth.

Tsumura (1957) explains the modification effect simply in terms of the retardation of the silicon diffusion in the melt ahead of the growing interface. This means that at a given growth rate the system has to decrease its inter-particle spacing and increase its undercooling.

In these theories of restricted growth, the observed undercooling is not the direct cause of the refinement of the structure. On the contrary, the undercooling is a necessary consequence of the primary modification effect.

(3) SMALL SODIUM DOPED INGOTS

a) Experimental Techniques

Small amounts of metallic sodium were added to melts of the following eutectic systems: Al/Si, Ag/Si and Au/Si. The alloys were prepared in the bell jar furnace in an identical manner to that already described for the pilot experiments. (section II.2.) The only difference being that an atmosphere of argon was used in all cases to suppress the volatilization of the sodium. Early doping attempts by melting up the metallic sodium with the constituent elements proved to be abortive. The sodium was obviously being lost either through volatilization or by absorption into the graphite crucible. Successful retention of sodium in the alloys was achieved by carrying out a laboratory equivalent of the industrial modification process. The requisite amount of metallic sodium was wrapped in a suitable metal foil (i.e. Al, Ag or Au) which was wedged into the bottom of a silica tube free to move through the O-ring seal in the removable portion of the top plate of the bell jar furnace. (see fig. 4)

The two constituent elements of the eutectic were melted up in small tapered 1" diameter graphite moulds; the sodium wrapped in its foil being kept well above the melt. When the melt had homogenised, sodium inoculation was achieved by turning off the R.F. power and rapidly pushing the silica tube with its charge into the alloy melt. It was found that a constriction in the silica tube just above the foil-wrapped sodium was necessary to make sure that all the sodium went into the melt. Without the constriction, the high vapour pressure of the sodium propelled the foil and contents up the silica tube. The resulting furnace-cooled alloy specimens were sectioned vertically and prepared for microscopical examination in the usual way. (see section II.4.a. for details)

b) Results

Sodium retention in the alloy was checked by two methods. Qualitatively in the laboratory by means of a Hilger Watts D.C. arc spectrometer and quantitatively by having the alloys analysed by atomic absorption spectrophotometry at I.M.I. (Kynoch). (These analyses are shown in table 123)

The microstructure of an aluminium/silicon eutectic alloy with 0.011 wt. % sodium present is shown in plate 124a. It can be seen that the microstructure has been considerably modified. (c.f. plate 124b in which a pure Al/Si alloy has been furnace-cooled) The eutectic silicon structure is very fine, and on the polished section appears as separate short rounded areas. From these sections it was not possible to elucidate whether the silicon was occurring as discrete globular particles, or whether the elongated silicon areas represented sections through a more rodlike structure.

By comparing the sodium modified alloy with the rapidly quenched eutectic alloy structures, (plate 124a with 84a) it would appear that silicon morphologies could be very similar. Scanning electron microscopy on heavily etched surfaces of rapidly quenched alloys had shown that the

eutectic silicon was interconnected and exhibited a frondose morphology. (section IV.6.f.) Similar experiments were carried out on etched surfaces of the sodium modified alloy and these showed that it had a eutectic silicon morphology very similar to the rapidly quenched alloy. (plates 125, c.f. plates 84b to 85b)

The eutectic silicon consisted of long interconnected fibres which branched often and were intertwined. Sections through such a structure would obviously give the impression of discrete particles, especially in the case of castings where the growth was not unidirectional. When smaller amounts of sodium were added, the microstructure was not so modified and appeared to be just a finer form of the irregular eutectic, i.e. as the amount of sodium added was decreased, the eutectic began to increase its platelike nature. It would thus appear that the change of microstructure upon successive addition of sodium is the same as that of increasing growth rate on the pure eutectic. (see section IV.6.f.) Bell and Winegard (1965b) came to the same conclusion as this by conducting a series of extractions on quenched and modified eutectics. These results were not conclusive owing to the problems of extraction. (see section II.4.b.)

Sodium had only a very slight modification effect on the eutectic systems Ag/Si and Au/Si, even when added in quite large amounts. The change in microstructure was similar to that of a very small amount of sodium upon the structure of the Al/Si eutectic alloy. The scale of the particles just decreased. (see plates 126 and 127) When large amounts of sodium were added to Au/Si eutectic all that happened was that a third phase appeared. (see plate 127a)

(4) UNIDIRECTIONAL SOLIDIFICATION EXPERIMENTS

a) Experimental Techniques

These experiments were carried out using the same apparatus as already described under section II.3. High purity chill-cast cylindrical specimens identical to those used in the normal unidirectional solidification experiments were doped with metallic sodium. The specimens were doped by drilling a small hole in one of the alloy rods and placing the requisite amount of sodium wrapped in aluminium foil into this hole. The eutectic alloy was then placed in a recrystallized alumina tube as for the normal method. Argon was let into the outer silica sheath in order to suppress volatilization. The specimen was placed in the furnace, homogenised and then unidirectionally grown in the same manner as the pure eutectic. The resultant alloys were sectioned and prepared for microscopical examination in the usual way.

(section II.4.a. for details)

b) Results

Further analysis both in the laboratory and at I.M.I. (Kynoch) showed that the sodium retention in these experiments was good and that the specimens contained sodium in sufficient concentration to produce modification in a furnace-cooled ingot. (see table 123 for analysis)

Doped eutectic alloy grown at very slow growth rates ($R = 2.78 \times 10^{-5}$ cm/sec. $G = 29.5^{\circ}\text{C/cm.}$) showed no change in its angular microstructure from that of pure eutectic alloy grown under identical conditions. (see plate 63a) One pull was removed from the furnace before solidification had finished and the more rapidly grown eutectic was found to be completely modified.

A doped eutectic alloy grown at a higher growth rate ($R = 1.37 \times 10^{-3}$ cm/sec. $G = 29.5^{\circ}\text{C/cm.}$) did show a different microstructure to the pure eutectic grown under identical conditions and the alloy was modified. Optical microscopy on C.P.4. etched specimens showed that the eutectic silicon was very similar to that in the furnace-cooled alloys and it appeared that these silicon particles still contained lamellar twins. The scale of the eutectic

was very much finer. (see plates 128) Analysis had shown that the sodium content of this alloy (0.009 wt. % Na) was such that complete modification was not to be expected. All the indications were that the eutectic silicon was interconnected. As in the case of the small ingots mentioned in the above section, the addition of sodium to the unidirectionally grown specimen produced a microstructure the same as if just the growth rate had been increased.

(5) DISCUSSION

Despite the fact that only a few experiments were carried out, it is possible in the light of the above results to dismiss a great deal of the previous work and theories on the modification of aluminium/silicon eutectic alloys.

a) Restricted Nucleation Theories

It is now possible to state that the addition of sodium affects the growth of the eutectic alloy, and that it is this effect that alters the microstructure of the alloy. In the work on the pure irregular eutectic alloys, (section IV.6.f.) it was proved that this form of the eutectic grows by a non-steady state and short range diffusion growth process and that the eutectic silicon particles are always interconnected. It follows that since the growth process in the pure eutectic alloy is never one of repeated nucleation and growth, then the addition of sodium must affect the growth of the eutectic in order to modify the structure. The sodium may well restrict the nucleation of the eutectic silicon but once the initial nuclei have been formed there is no need for repeated nucleation.

If the sodium only affected the nucleation of eutectic silicon, no change in the eutectic microstructure would be observed in a doped unidirectionally solidified alloy. The above experiment, in which a doped alloy was grown at such a rate so as to produce the irregular eutectic, gave a modified structure. One must, therefore, state that the addition of sodium restricts the growth of the eutectic alloy in order to produce modification.

The result of Chadwick's experiment (1965), which is basically the same as that described above, contradicts the above statement. Chadwick found that no modification of structure occurred upon unidirectional solidification. The answer to this apparent contradiction can be found by an examination of the container materials used. Chadwick grew his doped eutectic alloy in a graphite container. Graphite has been shown to absorb sodium (Bell and Winegard 1966) and so it appears probable that this unidirectionally solidified eutectic alloy soon contained no sodium at all. The resultant alloys do not appear to have been analysed. This would then explain why the pure and the doped alloy specimens gave identical microstructures. One would, therefore, say that Chadwick's model of aluminium/silicon

alloy modification is unlikely since it is based upon the results of this experiment. Two other reasons can also be suggested. Firstly, the fragmentation of the large leading eutectic silicon particles to provide fresh growth sites seems very unlikely, especially in vertically grown specimens where the turbulence due to convection currents is very small. Secondly, although a unidirectional solidification experiment differs from a casting in that the nucleation and growth events are separated, radial growth in a casting is sufficiently similar to unidirectional growth for one to expect the same type of microstructure. Metallographic examination of modified castings has not shown the existence of any coarse eutectic structure except in overmodification bands.

The other piece of evidence from the present work that is of great importance is that the modified structure itself is interconnected and is apparently identical to that produced by rapid growth of the pure alloy. The modified eutectic structure, therefore, also grows by a non-steady state short range diffusion process and not by one of repeated nucleation and growth.

We are therefore left with the restricted growth theories to explain the effect of sodium on aluminium/silicon eutectic alloys. These theories fall into three categories, which are dealt with in the next three sections: (b, c and d)

b) Restricted Growth by Diffusion Control

This theory is based on the reported fact that the diffusion coefficient of silicon in the eutectic liquid is reduced by the addition of sodium. Diffusion coefficients have been measured by Tsumura (1957) and by Davies and West (1963). These results were out by at least two orders of magnitude owing to thermal convection currents in the eutectic liquid. The results, however, purport to show a reduction, although the amount must be a matter for conjecture.

Sodium is not very soluble in either the α -aluminium or the silicon phase, and so at the growing interface one would expect quite a high sodium concentration to be built up. Hence the transport of silicon along the interface from the α -phase to the silicon phase would be made more difficult and the system would tend to grow with a smaller interparticle spacing. This finer spacing would require an increased undercooling to provide for the increased amount of interphase boundary. However, with this model one would expect a refinement in structure to occur whatever the growth mechanism of the eutectic alloy. The fact that no modification was observed in the case of the angular eutectic form must be taken as evidence against this model.

c) Restricted Growth due to Mechanical Obstruction
by Eutectic Aluminium

This model first put forward by Boom (1948) and elaborated upon by Thall and Chalmers (1950) says that the addition of sodium reduces the aluminium (solid)/silicon (solid) interfacial energy. This would allow the aluminium to grow over the silicon more easily. Thall and Chalmers suppose that overgrowth would be complete, meaning that for the eutectic growth reaction to proceed further nucleation will have to take place ahead of the growing interface. The growth mechanism would, therefore, change from a co-operative one to one involving repeated nucleation and growth. The experimental evidence does not substantiate this view. Further, it seems improbable that complete overgrowth by the aluminium can occur since the growth of the aluminium proceeds by silicon rejection and thus the likelihood of sealing off all the eutectic silicon particles is rather remote. The structure would, therefore, refine but would remain interconnected. Again an increase in undercooling is necessary to provide for the extra solid/solid interface that would be formed.

Reasons for not preferring this model are firstly that one would expect a change in interfacial energy to affect the angular particles as well as the irregular, and secondly if this mechanism were operative, one would expect modification to be observed in non faceted/non faceted eutectic systems as well as non faceted/faceted ones. No such effect has ever been observed.

d) Restricted Growth of Eutectic Silicon by Interfacial Poisoning

This model of the modification effect of sodium on Al/Si eutectic alloys does appear to be the most promising. It is possible to explain the majority of the observed experimental results.

First put forward by Archer and Kempf (1926), the theory has recently received support from the published work of Davies and West (1963). Sodium is presumed to adsorb preferentially onto certain eutectic silicon growth sites. Since silicon has a high entropy of fusion, it will grow in an essentially faceted fashion and its growth will, therefore, stem from specific growth sites. These growth sites could be steps formed by emergent screw dislocations or by twin plane reentrant edges.

Modification was only observed when the multiple $\{111\}$ spinel twin kinetic mechanism was operative, i.e. the initial eutectic structure had to be irregular. From this one infers that the sodium only affects specific growth sites. Examination of eutectic silicon morphology showed that the sodium retarded the formation of the platelike silicon particles in the irregular eutectic, and so it appears probable that the sodium adsorbs

preferentially onto T.P.R.E. growth sites. The eutectic silicon, therefore, has to grow in the more fibrous form which normally coexists with the platelike irregular eutectic silicon. This irregular fibrous form grows at a greater undercooling than the irregular plates since extra energy is required for the increased number of twins and aluminium/silicon surfaces. As Davies and West propose in their paper (1963) the easy growth sites for the silicon are removed by the sodium and an increase in undercooling is required to make other growth sites operative. However, this extra undercooling needed to produce the irregular fibrous silicon can be produced in two ways; either by removing the easy T.P.R.E. growth sites that lead to irregular silicon plate growth by the addition of sodium, or by increasing the growth rate. Resulting microstructures are so similar (plates 84b to 85b and 125) that it would appear that an increase in growth rate has a similar effect on the growth of silicon to that of sodium poisoning by making inoperative the T.P.R.E. growth sites that produce irregular plates. (see discussion section VI.4.a.)

The effect of sodium on the other silicon/F.C.C. metal eutectics investigated can likewise be explained using a poisoned growth model. In both Ag/Si and Au/Si eutectics the incidence of platelike irregular eutectic silicon is not nearly so high as in the Al/Si eutectic. The majority of the eutectic silicon is already in the fibrous form. It follows, therefore, that if the sodium produces the same effect on the eutectic silicon in these systems, then the prevention of irregular plate growth will only have a slight effect on the resultant microstructure.

Obviously further unidirectional growth experiments with varying amounts of sodium present, and a very intensive programme of scanning electron microscopy on the resulting microstructures are required before a rigorous proof of the mode of modification can be put forward. But on the work so far carried out, it appears that this poisoning theory of modification is the most promising. Work by Minkoff and Nixon (1966), using a scanning electron microscope, has shown that the effect of lanthanum on Ni/C eutectic alloys is very similar to that of sodium on Al/Si eutectic alloys in that the lanthanum affects the development of graphite plates and that in modified alloys the graphite is in a fibrous form.

e) Concomitant Changes upon Modification

There are still certain of the facts enumerated at the beginning of this section of the thesis that have not been explained. The first of these is the presence of primary α -aluminium in modified castings and the apparent shift of eutectic compositions to higher silicon concentrations. The major problem here is that it is not obvious whether this is due to a nucleation or a growth phenomenon, since no unidirectional growth experiments have been used to study the effect.

From nucleation work of Sundquist and Mondolfo (1961) one expects the aluminium phase to nucleate first on cooling through the eutectic isotherm since it has the lower entropy of fusion. However, the α -aluminium once nucleated appears to be a poor nucleating agent for the silicon phase and so α -Al dendrites can thus form before eutectic growth starts. This could happen in castings but the effect would only occur at the beginning of unidirectional grown specimens.

If one considers just the growth of the eutectic alloy, then one might expect that since the eutectic alloy has a high volume fraction of aluminium, that growth can occur at a lower total undercooling by some of the aluminium phase

growing as primary dendrites and the remaining alloy growing as a eutectic with a shorter diffusion distance.

Both these models can explain the formation of both primaries in hypereutectic alloys. On cooling, primary Si is nucleated because of the steep silicon liquidus slope and when the eutectic composition is reached primary Al will form for the reasons mentioned above.

Further work is again required on unidirectionally grown specimens in order to establish which, if any, of these two models is relevant.

The second fact of modification that requires explanation is the formation of overmodification bands of larger eutectic silicon particles. Scheil and Zimmermann (1957) and Davies and West (1963) explanation of this phenomena appears reasonable. It is, that as the sodium concentration is increased, NaAlSi eventually forms in the built-up layer of high sodium concentration at the growing interface. It is the formation of this compound that produces overmodification bands presumably by depleting the surrounding area of sodium.

f) Conclusions

Experimental evidence has been produced to show that it is the effect of sodium on the growth mechanism of aluminium/silicon eutectic alloys that produces the modified structure. The effect of sodium addition appears to be poisoning of the specific growth sites on the eutectic silicon that normally produce the irregular silicon plates, i.e. T.P.R.E. growth sites and this leads to a more fibrous form of the eutectic silicon which is still interconnected like the pure quenched irregular eutectic alloy. The effect of sodium addition on T.P.R.E. sites appears identical to that of increasing the growth rate of the pure eutectic alloy, and so the eutectic silicon morphology produced by modification is identical to that produced by rapid growth. The good mechanical properties of modified Al/Si eutectic alloys is, therefore, due to silicon fibre reinforcement. (Day and Hellawell 1967)

The modification effect of sodium on other silicon/f.c.c. metal eutectic systems is not so marked. The reason for this observation appears to be that the undoped irregular eutectic alloys already contain less irregular plates than aluminium/silicon eutectic and are mainly in the form of twisted and branched fibres. Sodium, which affects irregular plate formation therefore, does not alter these eutectic morphologies to the same extent.

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