SOLIDIFICATION OF PERITECTIC ALLOYS

BY

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SOLIDIFICATION OF PERITECTIC ALLOYS
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ABSTRACT

This thesis presents the results of a study of two aspects of peritectic alloy solidification: 1. an experimental and theoretical study of the phenomenon of banding (alternate deposition of layers of primary (α) and peritectic (β) phases) during plane front solidification and 2. a theoretical study of microsegregation during the non-isothermal diffusion controlled peritectic transformation in an alloy system where the solute diffusivities differ greatly, i.e. Fe-C-Mn.

Plane front solidification experiments using Sn-Cd alloys produced specimens which solidified as metastable α phase. The β phase was observed in only those specimens which were purposely disturbed during solidification; the α phase did not re-nucleate at the interface once β phase solidification was established. Banding was observed in one of these specimens, however, the α phase never entirely disappeared from the interface. Mathematical model predictions of the growth transient of the β phase and nucleation considerations showed that the α phase would not be re-nucleated at the β/liquid interface. It is thus expected that when banding occurs in Sn-Cd peritectic alloys, α is never completely removed from the growth front.

The treatment of microsegregation during the non-isothermal diffusion controlled peritectic transformation used in this work exposed several aspects of the problem which are obscured by some of the more sophisticated mathematical treatments of this problem; the transformation was modelled as a series of non-isothermal steps. For the binary Fe-C system, these calculations showed that, while cooling rate and solute diffusivity are important, closure of the δ-ferrite/austenite two phase field ultimately determines the temperature at which the transformation ends and what phases exist at that point. In the ternary case, Fe-C-Mn, the combined influence of constitutional and diffusional solute interactions promotes the following: 1. the concentration gradient of the fast diffusing solute in austenite is minimized with a corresponding greater segregation of the slow diffusing solute in all phases, compared to predictions based on no diffusion in the austenite or complete diffusion in all phases. 2. diffusional solute interaction may increase or decrease the effect of constitutional solute interaction on microsegregation. 3. At the liquid/austenite interface, the possibility of metastable austenite solidification or nucleation of δ-ferrite exists throughout the transformation.
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SOLIDIFICATION OF PERITECTIC ALLOYS

1.0 Introduction

The peritectic reaction is a phase transformation whereby the primary solid, $\alpha$, formed upon solidification of a binary alloy dissolves in the liquid, $L$, around it to form a new phase, $\beta$; i.e. $L + \alpha \rightarrow \beta$, at a fixed temperature. Figures 1 and 2 illustrate respectively, the peritectic corner on a binary phase diagram and a similar monovariant three phase equilibrium, on a ternary isotherm. The term 'peritectic transformation' is used to describe the case where: (a) the peritectic phase forms a layer at the primary phase/liquid interface, in the mushy zone during dendritic solidification and (b) growth of the peritectic phase occurs over the solidification temperature range of the alloy. A peritectic alloy is defined in this thesis, for a binary system, as an alloy with an initial composition which lies within the primary phase/liquid two phase region on the equilibrium phase diagram, at the peritectic temperature. In ternary systems, the three phase reaction described above is a monovariant three phase equilibrium. Although this is neither a true
Figure 1 The Peritectic Corner Of A Phase Diagram For A Binary Alloy.

Figure 2 The Monovariant Three Phase Reaction. "PeritecticReaction" On A Ternary Isotherm.
ternary peritectic nor a quasi-peritectic reaction, for the sake of simplicity the secondary solid phase, \( \beta \), will be referred to as the 'peritectic' phase, when dealing with the ternary system. A 'peritectic' alloy in a ternary system is one which undergoes a monovariant three phase reaction as described above.

Peritectic alloy solidification came under intense research scrutiny during the mid-1970's for two reasons. Firstly, plane front solidification studies of lamellar growth in eutectic alloys encouraged speculation about the possibilities for lamellar growth of the primary and peritectic phases in two phase peritectic alloys. Secondly, the application of continuous casting technology to steels with carbon content in the range 0.1wt% to 0.3wt% carbon was plagued with problems of cracking of the thin ingot shell and "breakout", i.e. the loss of liquid due to catastrophic cracking of the shell, during the early stages of continuous casting. Binary iron-iron-carbon alloys with carbon content in this range lie within the two phase peritectic region of the equilibrium phase diagram. The need to understand the causes for cracking in this instance has provided the impetus for dendritic solidification studies of peritectic alloys, primarily iron-iron-carbon based alloys.

The early work on plane front and dendritic solidification of peritectic alloys was instrumental in
formulating the conceptual models of peritectic alloy solidification that are widely accepted today. However, there are still some questions that the conceptual models are not capable of answering. The research focus in the case of plane front solidification of these alloys was to determine solidification conditions for which lamellar solidification of the two phases could take place. Instead, banding which is the successive alternate growth of layers of primary and peritectic phase, during plane front solidification of a two phase peritectic alloy was usually observed. The question of what thermodynamic and kinetic factors account for the observed strong preference for 'banding' was not investigated.

With respect to dendritic solidification of multicomponent 'peritectic' alloys, the conceptual model cannot reveal how interaction amongst intrinsic factors such as: nucleation kinetics, solute diffusivities, solute constitutional and diffusional interaction, and extrinsic factors such as cooling rate, determine the solidification microstructure observed, as well as peritectic phase composition, concentration gradients and phase growth rate. These questions are addressed in this work in the manner described in the following two paragraphs.

In the literature, a theoretical description of two phase peritectic alloy lamellar co-operative solidification similar to that for eutectics, suggested that this structure
was possible in certain two phase peritectic systems under plane front solidification conditions, at high velocities and temperature gradients. However, 'banding' was consistently observed in plane front solidified two phase peritectic alloys for several different alloy systems. In this thesis, plane front solidification experiments combined with mathematical modelling of the initial transient growth of the peritectic phase sought to answer questions such as: 1. how do banded structures evolve? and 2. what solidification conditions, thermodynamic or kinetic factors promote its evolution? The results of some preliminary plane front solidification experiments on tin-cadmium alloys suggested a re-examination was needed of some of our underlying assumptions about the undercooling necessary for nucleation of the primary and peritectic phases in these systems. The possibility must also be considered that competing processes may be more important in determining solidification microstructure for peritectic alloys than in eutectic or monotectic two phase alloys. An example pertinent to plane front solidification is the possibility that solute enrichment at the primary phase/liquid interface combined with insufficient undercooling for peritectic phase nucleation may lead to cellular growth of the solidifying primary phase.

Dendritic solidification studies of peritectic alloys
combine solidification experiments and mathematical modelling of multicomponent systems in order to quantify microsegregation. The conceptual model currently in use cannot show clearly how the combination of differing solute diffusivities, solute constitutional and diffusional interaction and solidification variables such as cooling rate determines the degree of solute segregation that occurs among the different phases present. This limits one to a "search for trends" approach among experimental data and model predictions in order to say something about the behaviour of certain solutes in a particular system. This approach may reinforce an intuitive knowledge of how certain solutes segregate in one base system; however, this description of solute segregation behaviour may not be transferable to another base system with these same solutes. The conceptual model currently used to describe the diffusion controlled growth of the peritectic phase is further developed in this thesis in order to make more transparent how the factors listed above define the peritectic transformation kinetics and solute partitioning for a given alloy.

The question posed in this thesis with respect to plane front solidification of these alloys was whether or not there exists clearly defined limits to the plane front solidification conditions for which banding was observed in
the tin-cadmium system. Plane front solidification conditions are usually mapped onto a space defined by the variables: the ratio of temperature gradient to interface velocity (G/V) versus initial alloy composition (C). Plane front solidification experiments in conjunction with mathematical model predictions of transient peritectic phase solidification were designed to determine these limits in plane front "space". To minimize convection effects during solidification, thin specimens, less than 0.5mm thick, were horizontally solidified at low furnace temperature gradients (2.5K/mm maximum) and low specimen travel velocities (1.0X10^{-5}mm/sec minimum). Undercooling experiments were done in order to obtain order of magnitude values for the undercooling required to nucleate the peritectic phase in the presence of the primary phase in this system. A theoretical analysis of diffusion controlled peritectic phase growth in multicomponent alloy systems was done with respect to solute microsegregation and peritectic phase transformation kinetics. This portion of the work is proffered as part of a discussion about an important aspect of peritectic alloy solidification in general; it is not supported by an experimental program.
2.0 Literature Review... Plane Front and Dendritic Solidification of Peritectic Alloy Systems

This literature review considers several investigations which were either instrumental in formulating and/or illustrate the use of the models of peritectic alloy solidification that are widely accepted today. In Section 2.1, the work reviewed:

1. describes the microstructure that had been observed in plane front solidification studies of these alloys.
2. offers two conceptual models to describe the evolution of "banded" microstructures.
3. speculates upon the possibilities for steady state lamellar growth of the primary and peritectic phases in these alloys.

The dendritic solidification studies focussed more on developing an understanding of, and mathematically describing solute re-distribution during diffusion controlled growth of the peritectic phase. Section 2.2 is divided into several subsections in order to present clearly ideas on heterogeneous nucleation of the peritectic phase on the primary phase dendrite and the theoretical approaches taken in the development of a mathematical description of the peritectic transformation.
2.1 Plane Front Solidification of Peritectic Systems

Five low temperature peritectic alloy systems were studied during the years from 1974 to 1987: Sn-Cd by Boettinger,\(^1\) Sn-Cd and Pb-Bi by Brody and David,\(^2\) Sn-Sb and Zn-Cu by Titchener and Spittle,\(^3\) Ag-Zn by Ostrowski and Langer,\(^4\) and Pb-Bi by Barker\(^5\) and Hellawell.\(^5,6\) In these solidification studies of two phase peritectic alloys, plane front growth of the primary phase was obtained using furnace temperature gradients ranging from 20.0K/mm to 55.0K/mm and specimen travel velocities ranging from 4x10\(^{-5}\)mm/s to 8.5x10\(^{-3}\)mm/s. Small diameter specimens, 0.78mm, 3mm and 7mm dia, were solidified vertically upward to decrease the probability that convection effects in the liquid would influence the solidification of the alloy. The possibility of convection due to differences in the liquid composition in Zn-Cu and Pb-Bi systems was acknowledged. Successive alternate growth of the primary and peritectic phases, "banding", was consistently observed in plane front solidified two phase peritectic alloys from these five systems.

Boettinger\(^1\) observed banding in plane front solidified tin-cadmium specimens with initial cadmium content within the peritectic two phase range, \(C_a < C_e < C_b\), shown in Figure 1. Interface temperature fluctuations with temporal separations
corresponding to the spacing of the banded microstructure were observed during the solidification of these specimens. Single phase α was observed in those specimens with initial cadmium content less than Cₕ; single phase β was observed in those specimens with initial cadmium contents greater than Cₕ.¹

Brody and David² observed banding in plane front solidified tin-cadmium specimens with a cadmium content of 1.0 to 1.75 wt% Cd, (Cₜ < Cₒ < Cₘ). In plane front solidified lead-bismuth alloys, they observed single phase β solidification in specimens with initial bismuth content within the range Cₜ < Cₒ < Cₘ as indicated in Figure 1. The liquidus temperature measured was consistent with the melting temperature for an alloy of this composition if the β liquidus was extended into the two phase α and liquid region on the phase diagram. This was unexpected because equilibrium solidification of an alloy in this composition range states that the α phase is the first solid formed; solidification of the α phase would continue until the peritectic temperature was reached, at which point the β phase would form.

Titchener and Spittle³ observed alternate bands of

¹ In this section, α and β are used for all alloy systems to denote the primary and peritectic phases respectively.
primary and peritectic phases in plane front solidified tin-antimony specimens, with antimony contents in the range $C_o < C_s < C_g$.

Ostrowski and Langer$^4$ observed banding in zinc-copper two phase peritectic specimens; the solidification structure consisted of successive bands of $\beta$ phase and cellular $\alpha$ phase with peritectic phase in the cell boundaries.

Barker and Hellawell$^5$ obtained banding in two of six plane front solidified specimens, with bismuth contents in the range $C_g < C_o < C_s$, and complete segregation of the primary and peritectic phases in the other four. It was suggested that banding was due to the inevitable small fluctuations in growth rate which correspond to large temperature intervals for the high thermal gradients used.$^{5, 6}$

In the literature the phenomenon of banding has been for the most part ascribed to experimental factors other than fluctuations in furnace temperature gradient and specimen travel velocities. These two factors were ruled out since their influence was not observed in dendritic growth studies for a majority of these alloys using essentially the same equipment. Ostrowski and Langer$^4$ suggested that the differences in thermal expansion between the quartz tube and
specimen may have led to intermittent contact between them. Local undercooling at the interface due to this intermittent contact might have been sufficient to nucleate the peritectic phase.

Titchener and Spittle\(^3\) and Hillert\(^7\) have proffered other explanations of how banded structures could evolve, under plane front solidification conditions. Titchener and Spittle\(^3\) suggested that if mixing in the liquid is assumed to be due only to solute diffusion, then a solute layer would be built up in the liquid at the primary phase/liquid interface. The thickness and solute content of the layer would be determined by the interface velocity. At some temperature below the peritectic temperature, the nucleation and subsequent growth of the peritectic phase would simultaneously deplete and change the shape of the solute layer, in the liquid ahead of the primary phase/liquid interface. The changing solute diffusion profile in the liquid at the interface should lead to peritectic phase solidification with decreasing interface solute concentration and increasing interface temperature, if the solidification conditions permitted plane front growth of the peritectic phase. The change in interface temperature and concentration is described by a progression up the peritectic phase liquidus on the phase diagram as indicated in Figure 3. After some period of
peritectic phase solidification, interface conditions could be conducive to the nucleation and growth of the stable primary phase, thereby creating the conditions for "banding".

Hillert suggested that the peritectic phase diagram indicates that in the absence of the primary phase, steady state solidification of the peritectic phase could occur at a higher temperature $T^8$ than that for the primary phase $T^6$ as shown in Figure 3.\textsuperscript{2} If the nucleation kinetics of the system permit it, the peritectic phase can form a complete layer and grow at the lower concentrations and higher temperatures of the liquid ahead of the primary phase/liquid interface. Since the liquidus temperature for the stable primary phase is higher than that for the liquid/metastable peritectic phase interface, if the primary phase should nucleate ahead of the peritectic phase it may grow along the peritectic/liquid interface, thereby forming a new band. This mechanism could explain the formation of single phase $\beta$ observed in several specimens of two phase solute composition by Brody and David\textsuperscript{2} and the interface temperature fluctuations observed by Boettinger.\textsuperscript{1}

\begin{footnote}
2. Note: steady state solidification is narrowly defined here as the solidification of a solid with a solute concentration equal to that of the bulk liquid: it is possible in situations where mixing in the liquid is due to diffusion alone.
\end{footnote}
Lamellar Growth of the Primary and Peritectic Phases in Two Phase Peritectic Alloys

Further discussion of plane front solidification of two phase peritectic alloys in the literature has been confined to the question of whether or not lamellar co-operative solidification is possible in these alloys. Boettinger proposed the following mathematical treatment of steady state co-operative solidification of two phase
peritectic alloys. This treatment was based on that developed for binary eutectic solidification by Jackson and Hunt. It describes the relationship among the following variables: 1. the difference between the interface and equilibrium transformation temperatures, $\Delta T$, 2. interface velocity, $v$, and 3. lamellar spacing, $\lambda$. This relationship is given by:

$$\frac{\Delta T}{m} = Q^1 \lambda v + \frac{a^1}{\lambda}$$

where the quantity $m$ is a function of the liquidus slope for the primary and peritectic phases; $Q^1$ is a function of the primary ($a$) and peritectic ($\beta$) phase interface concentrations, solute diffusivity and lamellar spacing. The quantity $a^1$ is a function of the ratio of the thickness of the peritectic and primary phases ($\zeta$), heats of fusion and liquid-solid interfacial free energies of the two phases. These quantities are further defined below:

$$\frac{1}{m} = \frac{1}{m_a} - \frac{1}{m_\beta}$$

3. Note: steady state is defined here in terms of a mass balance among solute rejected by one of the solid phases, that absorbed by the other solid phase and that dispersed into the liquid by long range diffusion. The result of this would be constant interface concentrations for the phases present and the maintenance of constant lamellar spacings during unidirectional solidification.
(3) \[ Q^i = \frac{P(1+\zeta)^2}{D} (C_p - C_a) \]

\[ \zeta = \frac{S_b}{S_a}, \quad P = P(\zeta) \]

(4) \[ a^i = 2(1+\zeta) \left( \frac{a_x^i}{m_a} - \frac{a_y^i}{m_b} \right) \]

(5) \[ a^i = (\frac{T_p}{L_i}) \sigma^i \sin \theta^i \]

where the symbols \( m_i \), \( D \) and \( S_i \) denote the slope of the liquidus, the solute diffusivity in the liquid and the thickness of the lamellae of phase \( i \). The symbols \( T_p \), \( L_i \), \( \sigma_i \) and \( \theta \) denote the peritectic temperature, the heat of fusion per unit volume, the solid/liquid interfacial free energy and the angle of the free energy vector with respect to a vertical line, in a vector balance of the interfacial free energies at the three phase junction. On a plot of undercooling, \( \Delta T \), versus lamellar spacing, \( \lambda \), as shown in Figure 4, a negative undercooling implies that the interface is unstable with respect to perturbations; a positive undercooling implies that the interface is stable with respect to perturbations, as is
the case for eutectics. For peritectic systems where \( a^i \) is greater than zero \((a^i_a/m_a > a^i_\beta/m_\beta)\), the theoretical interface undercooling is negative for all possible lamellar spacings; therefore plane front solidification is theoretically unlikely in these systems. The \( \Delta T \) versus \( \lambda \) plot suggests that steady state co-operative growth is theoretically possible in a system where \( a^i \) is less than zero \((a^i_a/m_a < a^i_\beta/m_\beta)\), provided that solidification conditions promote small lamellar spacings, ie. on the left portion of the curve. Steep positive temperature gradients, ie. \( > 25.0 \text{K/mm} \), are required in order to impose plane front solidification conditions at the interface.
velocities necessary in order to obtain small lamellar spacings in some of these systems. However, the undercooling versus interface velocity relationship requires that interface velocity increase as the interface temperature increases. The interface would be unstable with respect to perturbations since protrusions on the interface would be at a higher temperature, especially with the steep positive gradients used in plane front solidification, and would therefore grow faster than the rest of the interface. Therefore, prolonged plane front lamellar solidification is unlikely in these systems.

2.2 Dendritic Solidification of Peritectic Alloys

As stated in the introduction, research concerning dendritic solidification of peritectic alloys focussed on understanding the causes of cracking of steel ingot shells during the early stages of continuous casting, for carbon contents in the range 0.11 to 0.3 wt%, and has provided the impetus for much of the solidification modelling work done on two phase peritectic alloys. The work of Singh and Blazek\(^9\) and Wolf and Kurz\(^10\) illustrate the concerns of researchers interested in the mechanical properties of the thin shell formed during the early stages of the continuous casting of peritectic steels.
Singh and Blazek⁹ did a comprehensive study of the relationship between mould heat transfer rate and the formation of cracks in continuously cast steels, for carbon contents covering the range 0.05 wt% to 2.0 wt%. It is essential that good strand/mould contact be maintained for uniform growth of the thin shell in order to minimize the possibility of "breakout", i.e. loss of liquid due to through-section cracks in the solid ingot shell. Singh and Blazek measured mould temperature variation, calculated the mould heat transfer rate, examined the solid/liquid interface morphology and considered the results with respect to the influence of carbon content. They also studied the effect of additions of Al, S, Ni and Cr on these variables as well as the effect of ferrostatic pressure on the heat transfer rate for these same steels.

Their calculations of the heat transfer rate in the mould showed a minimum in the heat transfer rate versus carbon content curve near 0.1 wt% carbon. This drop in the rate correlated well, for steels with carbon content ranging from 0.1 to 0.4 wt% C, with the following factors: 1. fluctuations in mould temperature which were much higher (100K) for these steels than for steels with carbon content outside of this range, and 2. observed non-uniform variations in shell thickness, which was macroscopically rough inside and outside, in shells obtained by controlled "breakouts". They found that
an elevated reservoir which maintained a constant head of liquid above the top of the liquid pool in the mould improved the heat transfer rate due to better contact between the liquid metal and the mould walls. The percent improvement was similar, 12 to 15%, across the range of carbon contents studied.

Additions of sulphur increased the mould heat transfer rate by as much as twenty five percent; an increase was expected since sulphur is known to change the surface tension of the liquid. The addition of aluminium did not appear to have an effect on the heat transfer rate; like sulphur it was expected to change the surface tension of the liquid by reducing the soluble oxygen content of the liquid steel. Nickel and chromium were added to the steels since they are common alloy additions. The addition of nickel improved the heat transfer rate by as much as eleven percent; the addition of chromium had no apparent effect on the heat transfer rate.

The measured columnar austenite grain size was plotted versus carbon content; the curve had a maximum near 0.1 wt% carbon. This was thought to be due to the variable overall ingot heat transfer rate for these steels. They postulated that the low heat transfer rate was due to a variable air gap due to the influence of the ferrostatic pressure on the thin shell and enhanced solidification shrinkage due to the peritectic transformation.
Wolf and Kurz\textsuperscript{10} argued that the mechanical properties of the as-cast solid shell are more greatly influenced by the solidification structure and microsegregation rather than by solidification shrinkage, during the early stages of the continuous casting process. They suggested that microsegregation of a solute such as phosphorus, which was known to greatly influence the hot strength of steels,\textsuperscript{11} could weaken the integrity of the steel shell. Carbon would play an indirect role in that it controls the phase fraction of delta-ferrite and austenite present during the solidification-peritectic process. They illustrated this point by mathematically modelling the microsegregation of phosphorus within the mushy zone of a solidifying alloy. The phosphorus concentration in the liquid versus fraction solidified was calculated for the following solidification path:

1. Partitioning of phosphorus was described by the binary partition coefficient for delta-ferrite solidification until the fraction of delta-ferrite at which austenite forms as predicted by the Lever Rule, was reached.

2. Phosphorus partitioning is then described by the binary partition co-efficient for austenite solidification until a phase fraction of 0.99 was reached. The final inter-dendritic phosphorus concentrations were used to determine the solidification range for an Fe-C-P alloy.

Strand shell deformation versus carbon content was calculated
by considering the model predictions of the thickness and strength and expected influence of solidification contraction of the steel shell versus a constant ferrostatic pressure exerted by the liquid. Wolf and Kurz's mathematical treatment of ternary solute redistribution is discussed in the subsection entitled 'mathematical modelling of the diffusion controlled peritectic transformation'.

The mathematical modelling showed that given two phase peritectic Fe-C alloys with the same binary equilibrium solidification range (0.1 and 0.25 wt% carbon), for the higher carbon concentration the maximum liquid phosphorus content was higher at a fraction solidified of 0.99 and the addition of phosphorus increased the solidification range. Plots of the calculated bending strain rates due to ferrostatic pressure versus that due to solidification contraction suggested that strain due to ferrostatic pressure would be more important for steels in the range 0.15 to 0.4wt% carbon range. The bend stress of a beam-like element in the shell was used to estimate shell deformation and hence bending strain rates. The results of this analysis suggested that the combined effect of predicted lower shell growth rates due to micro-segregation of phosphorus and larger effect of ferrostatic pressure in this carbon composition range should result in higher heat transfer rates than had been observed in these steels. They suggested that the potential decrease in steel yield strength due to
precipitation, ie. Fe₃P precipitates, could be an important consideration in determining the heat transfer rate.

**Solidification Studies of Peritectic Alloys Concerned With The Nucleation and Growth of the Peritectic Phase**

The work of Nylen¹² and Fredriksson¹²,¹³ and St. John and Hogan¹⁶,¹⁷,¹⁸ provided much needed information about preferred sites for nucleation of the peritectic phase in the mushy zone and the mechanism of peritectic phase growth.

Nylen¹² and Fredriksson¹²,¹³ used controlled unidirectional solidification and differential thermal analysis experiments to study the various mechanisms which operate during the solidification of two phase peritectic alloys of Cu-Sn, Ag-Sn, Al-Mn and stainless steels. Some observations from this work pertinent to the subject of peritectic phase nucleation are described in the next few pages.

Some dissolution of the primary phase was noted at the three phase, (α, β and liquid), interface in the Cu-Sn, Ag-Sn and Al-Mn systems. The peritectic phase completely surrounded the primary phase dendrites in both the Cu-Sn and Ag-Sn systems. The thickness of the primary phase first decreased and then remained constant for the Cu-70Sn alloy; at the lowest velocity at which the specimen was moved through the
furnace, the thickness of the peritectic layer increased continuously with time. At faster velocities, peritectic phase growth appears to be due to solidification directly from the liquid. The eutectic reaction forces the end of peritectic layer growth. In Cu-Sn and Ag-Sn specimens, the peritectic phase forms a thick layer around the primary phase dendrites. Completion of the transformation is much faster in the Ag-Sn alloy than for the Cu-70Sn alloy. The growth of the peritectic phase was over within 10K of the peritectic temperature for these alloys.

Mathematical descriptions were developed to describe the growth of the peritectic layer with and without diffusion of solute in the layer. In the case of no diffusion in the peritectic layer, the Scheil interface solute balance was used to calculate the volume fraction of peritectic phase versus the difference between the peritectic and interface temperature. For the case of solute diffusion in the peritectic layer, the two interface solute balances were simultaneously solved numerically to provide values of peritectic phase fraction versus the difference between the peritectic and interface temperatures, for different values of the diffusion coefficient. Comparison of the measured and calculated values of peritectic layer thickness indicated that the mode of peritectic phase growth in Cu-Sn and Ag-Sn alloys is the result of diffusion of solute through the layer.
In the Al-Mn system, for the most part the peritectic phase covered the primary phase in patches; it showed a weak but increasing tendency to completely cover the primary phase when the temperature gradient in the liquid and/or the cooling rate was increased. To further explore the issue of nucleation difficulties of the peritectic phase in the Al-Mn system, a mathematical description was developed to calculate the growth rate of the peritectic layer around the primary phase dendrite, for the peritectic reaction.

Some of the assumptions for this analysis are: 1. The nucleation of the peritectic phase is described by a minimum undercooling law. 2. Growth of the peritectic phase, \( \beta \), around the primary phase, \( \alpha \), is assumed to be continuous and diffusion of solute in the solid is neglected. The growth rate of the \( \beta \) phase around the \( \alpha \) phase is described by the growth laws for a plate derived by Bosze and Trivedi. The following is the expression for growth velocity, \( v \): 

\[
X = \frac{X_\beta^{1/2} - X_\beta^{1/3}}{X_\beta^{1/3} - X_\beta^{2/3}}
\]

\[
(6a)
\]

\[
v = \frac{9}{8\pi} \frac{D_1}{S_\beta} X \left[ 1 - \frac{2X}{\pi} - \frac{2X^3}{2\pi} \right]^{-2}
\]

\[
(6b)
\]

\[
S_\beta = \frac{32}{3} \frac{S^*}{X} \left[ 1 - 2\pi X - \frac{1}{2\pi} X^3 \right]^2
\]

(7)
(8) \[ S^* = \frac{V_m}{-\Delta G_m} [\sigma^{1/\beta} + \sigma^{\alpha/\beta} - \sigma^{1/\alpha}] \]

(9) \[ \Delta G_m = RT[k_A^{5/1} - k_B^{5/1}] [x_A^{1/\alpha} - x_B^{1/\beta}] \]

In these equations the symbols, \( D_t\), \( X_l^i \), denote the quantities: the liquid diffusion coefficient, solute mole fraction at the solid (i)/liquid interface. The symbols, \( S^i \) and \( S^* \), denote the measured thickness of the \( \beta \) layer obtained from experiment and the critical thickness of the \( \beta \) phase at the moment it is nucleated, respectively. The symbols, \( \sigma \), \( V_m \), \( \Delta G_m \), \( K \) and \( R \) denote the quantities: interfacial free energy, molar volume, Gibbs free energy for a phase transformation, the partition coefficient and the absolute gas constant, respectively. The thickness of the \( \beta \) layer was calculate as a function of the interfacial energy formula, \( \sigma^{1/\beta} + \sigma^{\alpha/\beta} - \sigma^{1/\alpha} \), by setting \( v \) equal to the velocity at which the specimen travelled through the furnace.

The thickness of the \( \beta \) layer at the three phase interface decreased as the solidification rate increased and the value of the surface energy formula decreased. If the interfacial free energy of the \( \beta \)/liquid interface is assumed equal to that for the \( \alpha \)/liquid, then the \( \beta \) layer thickness is a function of the surface energy between the \( \alpha \) and \( \beta \) phases.
The measured and calculated values of β phase thickness for the Cu-Sn and Ag-Sn alloys were compared for different values of the surface energy function. They agreed fairly well given that the following were not accounted for: the temperature gradient of the mushy zone, solute diffusion in the peritectic layer and the accuracy of the phase diagram data. With respect to heterogeneous β phase nucleation on the α phase dendrite, the analysis suggested that the interfacial free energy balance is an important factor. The tendency for the β phase to completely cover the α phase dendrite at faster cooling rates may be due to more favourable conditions for nucleation at lower temperatures, since α phase existed at the lower temperatures, in these specimens.

In the case of stainless steels, peritectic phase completely covered the primary phase/liquid interface in systems containing high concentrations of peritectic phase stabilizers (ie. austenite stabilizers such as Ni, Cr, Si). (Phase stabilizers are alloy elements that expand the single phase region of a given phase on an equilibrium phase diagram). In systems containing high concentrations of primary phase stabilizers (ie. delta-ferrite stabilizers such as Mo, S, P) the peritectic phase did not always completely cover the primary phase/liquid interface and the primary phase existed at lower temperatures than that for systems containing elements which stabilize the peritectic phase. In one case, (a
system containing sulphur) the primary phase was enriched so much in solute during the transformation that a new liquid was formed at the primary/peritectic phase interface by a metatetic reaction, (sometimes called a "catastetic" reaction). In the final structure two regions of quenched liquid were observed in this alloy, the center of the original primary phase dendrite and the interdendritic regions. 4

Fredriksson's' mathematical treatment of ternary solute redistribution is discussed in the subsection entitled 'mathematical modelling of the diffusion controlled peritectic transformation'.

St. John and Hogan' did controlled uni-directional dendritic solidification studies of alloys in two low temperature systems, Al-Ti and Cd-Ag. Three observations made in this work are of direct relevance to the subject of peritectic phase growth and solute partitioning. These are: 1. The peritectic phase was found to nucleate and grow along the existing primary solid/liquid interface in both the Al-Ti and Cd-Ag systems. Calculations of peritectic phase growth rate, based on a mathematical treatment for diffusion controlled growth of the peritectic phase suggested that: (i) in the Cd-

4. Uni-directionally solidified specimens are usually quenched in order to retain details of the interface microstructure.
Ag system, completion of the transformation during solidification is dependant upon solute diffusion through the peritectic phase, and (ii) in the Al-Ti system, growth of the peritectic phase depends upon solidification of the peritectic phase directly from the interdendritic liquid, aided by the existence of the peritectic phase further back in the interdendritic region. 2. The relative values of solute concentrations measured on either side of the $\alpha/\beta$ and $\beta$/quenched liquid interfaces suggested that local equilibrium existed at the interfaces throughout the non-isothermal transformation, although, equilibrium solidification requires that one or two of the phases present disappear directly below the peritectic temperature. 3. The solute concentration gradient across the peritectic phase was small when diffusion through the shell was the dominating method for peritectic phase growth of the phase relative to that measured across the peritectic phase when direct precipitation of the peritectic from the melt dominated.

**Mathematical Modelling of the Diffusion Controlled Peritectic Transformation**

The phrase "diffusion controlled peritectic transformation" describes the case where growth of the peritectic phase is due to the diffusion of solute through the
β phase, from the β/liquid interface to the α/β interface. The four articles reviewed in this sub-section illustrate the approaches taken to solve the mathematical problem posed by diffusion controlled phase growth and mathematically describe solute re-distribution during the peritectic transformation in multicomponent alloys.

Chuang and Schwerdtfeger\textsuperscript{19} treated the non-isothermal diffusion controlled peritectic transformation, in binary two phase iron-carbon alloys primarily as a diffusion problem; the Green's Function method was used to solve the problem of moving boundaries with unknown interface velocity-time laws and changing boundary conditions. The conceptual model of diffusion controlled peritectic phase growth use by Chuang and Schwerdtfeger\textsuperscript{19} is based upon a simple physical model of dendritic solidification originally elaborated by Brody and Flemings\textsuperscript{20} which incorporates the information on peritectic alloy solidification from studies such as those of Nylen\textsuperscript{12} and Fredriksson\textsuperscript{12,13} and St. John and Hogan.\textsuperscript{16,17,18} The following set of assumptions define the physical, thermodynamic and kinetic limits of the one dimensional problem:

1. The heat of transformation is assumed to be instantly dissipated.

2. Dendrites are growing into the melt as parallel sided plates rather than paraboloids.

3. Negligible undercooling due to interface curvature or
kinetic effects occurs before the peritectic phase precipitates; therefore, the peritectic phase nucleates at the peritectic temperature as shown in Figure 5.

4. Local equilibrium exists at the phase interfaces; the solute concentrations at each interface are given by the ends of a tie-line on the phase diagram, as shown in Figure 6.

5. No axial diffusion of mass takes place within the liquid and solid.

6. The progress of the peritectic transformation in the small volume element inside the mushy zone, shown in Figure 5, describes the phase transformation elsewhere in the melt.

7. No volume diffusion of mass takes place into or out of the volume element.

8. Diffusion of solute in the delta-ferrite and liquid phases is always complete.

9. The concentration gradient of a diffusing solute in the austenite phase is assumed to be linear.

Their model predictions of phase fractions versus time were verified by the results of some solidification experiments on 0.39wt% C steels. The experimental results showed that:

1. Under normal casting conditions little micro-segregation of carbon exists at the end of solidification.

2. The peritectic transformation is over within 2 to 10K below the peritectic temperature.
Figure 5 A Schematic Of The Mushy Zone During Dendritic Solidification Of A Peritectic Alloy.

Figure 6 A Schematic Showing The Solute Concentration Profile Across The Volume Element Shown In Figure 5.
Wolf and Kurz\textsuperscript{10} treat the Fe-C-P ternary alloys in this work as "pseudo-binaries", where the re-distribution of solutes is calculated from binary phase diagram data. Ternary solute constitutional and diffusional interaction are not considered. The solidification sequence described by Wolf and Kurz\textsuperscript{10} for a peritectic alloy in the volume element shown in Figure 5 is based upon the conceptual model outlined in the work by Chuang and Schwerdtfeger\textsuperscript{19}. Wolf and Kurz's work assumes that there is no diffusion of phosphorus in the delta-ferrite and austenite phases; carbon diffusion is complete in all three phases. The solidification sequence is as follows: 1. The delta-ferrite phase solidifies until the delta-ferrite and liquid peritectic compositions are reached at the interface.

2. Peritectic phase solidification would then begin. It would continue until either of the following conditions occur: the total fraction solidified of the volume element is 0.99 or the solute concentrations for an intervening reaction, such as the eutectic reaction, are reached.

Since carbon diffusion is faster than most solutes in the delta-ferrite, austenite and liquid:

1. The carbon concentration for each phase is given by the equilibrium Fe-C phase diagram.

2. The carbon concentration alone is assumed to control the ratio of delta-ferrite to austenite.
3. The phase fraction of delta-ferrite at which austenite appears is obtained by applying the Lever Rule to the binary Fe-C phase diagram.

Phosphorus re-distribution amongst the phases during solidification is described by the binary Fe-P partition coefficients and the modified Scheil interface solute balance, which accounts for diffusion of a solute in the solid. The solidus temperature for the ternary alloy is estimated using a simple relationship between initial carbon content and liquid phosphorus concentration at a fraction solid of 0.99; it is based upon the average decrease of the liquidus temperature with phosphorus and carbon determined from their respective binary phase diagrams.

Fredriksson\textsuperscript{13} built his quantitative treatment of the peritectic transformation in a ternary Fe-C-X alloy upon a similar conceptual model as that outlined in the work by Chuang and Schwerdtfeger\textsuperscript{19}. Some of the assumptions in this work that are different from those outlined in reference 19 are:

1. Austenite grows into the liquid and delta-ferrite phases by solidification and a solid state reaction, respectively, due to decreasing temperature in the mushy zone.
2. Diffusion of carbon in the delta-ferrite, austenite and
liquid phases is always complete.  

3. Diffusion of solute X is always complete in the delta-ferrite and liquid phases.

4. No diffusion of solute X takes place in the austenite; the solute X balance at both interfaces is given by the Scheil equation. The Scheil-Chipman interface solute balance describes the solidification of an alloy under conditions such that complete mixing of solute occurs in the liquid and no solute diffusion takes place in the solid.

5. The alloy Fe-C-X is a dilute solution; solute partition coefficients are those given by the respective binary phase diagrams. The solute composition at each interface is given by the ends of a tie-line on the ternary isotherm, at any given temperature.

6. The influence of ternary diffusional interaction is neglected.

The solidification sequence in the volume element described in Figure 5 is as follows:

1. Delta-ferrite solidifies until the peritectic temperature for the ternary alloy is reached.

2. The austenite phase nucleates at the peritectic temperature and upon further cooling grows into the delta-ferrite and

5. Note: In this thesis, carbon diffusion is assumed to be complete only in the delta-ferrite and liquid phases.
liquid phases.

3. This continues until either the delta-ferrite phase disappears or the liquid phase disappears, due to the formation of a eutectic solid.

4. Austenite phase growth continues until the other phase present, either liquid or delta-ferrite disappears.

There is only one solute balance to consider at each interface, that is the "Scheil" solute balance for solute X. The solute X balances at each interface are coupled by the material balance for carbon due to assumptions 2 and 5, across the volume element. Model predictions of solute composition at the interfaces and phase fraction of delta-ferrite, austenite and liquid are obtained by simultaneously solving the solute X mass balances.⁶

Ueshima et al.²¹ developed a mathematical model to predict how manganese and phosphorus would re-distribute during the peritectic transformation, as part of a solidification study of plain carbon peritectic steels, 0.11< wt% C <0.2. Disparate solute diffusivities (on-diagonal diffusivities in the diffusion coefficient matrix) were

⁶ Note: In this thesis, solution of the mathematical problem of diffusion controlled phase growth required that the solute balances for both carbon and solute X be solved simultaneously, in order to obtain predictions of solute composition at the interface and phase fractions of delta-ferrite, austenite and liquid.
accounted for in the solution of a two dimensional diffusion problem. The conceptual model of diffusion controlled austenite phase growth differs slightly from that elaborated by Chuang and Schwerdtfeger\textsuperscript{19} as follows:

1. Two dimensional solute diffusion in the austenite was considered by modelling of the dendrites as regular hexagons.
2. Since the calculation of the peritectic temperature range for ternary and higher order systems is an onerous affair; the peritectic temperature for the alloy was obtained by adjusting the binary peritectic temperature using weighted factors based on alloy composition.
3. They considered only dilute solutions, therefore the dilute solution model was applicable and solute constitutional interaction was described by Wagner interaction parameters.
4. Diffusional solute interaction was assumed to be negligible, the off-diagonal diffusion coefficients are small or zero in value.

The model predictions of solute concentration (iso-manganese concentration lines) versus area fraction (2-D problem) for steels with carbon, manganese and phosphorus contents ranging from 0.05 to 0.2 wt\%C, 1.41, 1.42 and 1.52 wt\%Mn and 0.016, 0.017, 0.018 wt\% P respectively, agreed reasonably well with the experimental data for manganese but not for phosphorus, when the fraction area was less than 0.5.
2.3 Summary of Previous Studies of Peritectic Alloy Solidification

The purpose of this section is to summarize the work that has been done in the field of peritectic alloy solidification, in order to state clearly what the important questions are that remain unanswered. It is to these questions that the work in this thesis was addressed.

Plane Front Solidification

In the literature on plane front solidification of two phase peritectic alloys, the discussion focussed on whether or not lamellar co-operative solidification was possible in these alloys. The objective of these previous solidification studies was to determine plane front solidification conditions for which lamellar co-operative growth would be an inherent two phase peritectic system response. However, the apparent ease of formation of banded microstructures in many plane front solidified peritectic alloys suggested rather that banding may be an inherent system response to plane front solidification conditions and it appears that the ideas on the origin of banding put forward by Titchener and Spittle\(^3\) are reasonable possibilities for these systems. The explanation implicitly assumes that there is little or no barrier to nucleation of
the peritectic phase either heterogeneously on the primary phase, and vice versa, or by some other process in the liquid. Nowhere in the literature is there mention of studies undertaken to determine what the limits are, if any, to the banding regime defined by the solidification variables of temperature gradient and velocity. The question of whether or not banding is an inherent peritectic system response to plane front solidification conditions has not been addressed in the literature.

The work of Barker and Hellawell, who obtained complete segregation rather than banding in four of six plane front solidified two phase peritectic lead-bismuth specimens showed that banding does not always occur: this fact is supported by the results of plane front solidification work on tin-cadmium alloys to be reported in this thesis. Thus, the question of what is an inherent peritectic system response to plane front solidification requires:

1. a re-examination of the common assumptions on the thermodynamics of phase nucleation in these alloys and the implications with respect to solidification microstructure and
2. a recognition of the possibility that competing processes may be important either in certain types of systems or under particular solidification conditions.
Dendritic Solidification

The difficulties of continuously casting low carbon peritectic steels, 0.11< wt% C<0.3, provided the impetus for much of the work on dendritic solidification of peritectic alloys. The focus of industrial research concerned with the casting of these steels has usually been on determining the following factors:
1. The point in the process at which deleterious cracks form.
2. The correlation among the variables: frequency of cracking, steel composition, and operational variables such as casting speed and cooling rates.
3. Operational procedures and methods of controlling steel chemistry to alleviate the problem.

The influence of steel chemistry on hot strength observed in these studies set the stage for a continuing exploration of the link between solute microsegregation and the integrity of the thin steel shell in the early stages of continuous casting.

Dendritic solidification studies most often have had as a goal the development of a mathematical treatment of the peritectic transformation which would quantify microsegregation and the type and scale of solidification microstructures in terms of solidification variables, such as cooling rate, and including wherever possible the effects of
phase transformations and precipitation. Chuang and Schwerdtfeger's work showed that analytical solutions to the problem in diffusion controlled peritectic phase growth of binary systems can be obtained with the use of advanced mathematical treatments. This is facilitated for binary systems by the fact that interface concentrations are completely determined at any temperature.

Calculations are more difficult for multicomponent systems for the following two reasons. Firstly, there exists a range of equilibrium interface tie-line possibilities from which the system will choose one in some non-transparent manner, at any given temperature. The tie-line chosen is determined by the following factors: constitutional and diffusional solute interaction, disparate solute diffusivities and solidification variables such as cooling rate. Secondly, solute diffusional interaction may be very important in determining phase compositions and growth kinetics, especially in the later stages of solidification. The degree of diffusional interaction changes constantly throughout the transformation because the influence of one solute on the diffusivity of another is a function of local concentrations. This may be a factor worthy of consideration in describing the partitioning of some solutes, eg. P. Often diffusional interaction cannot be exactly described mathematically since the data required are difficult to obtain experimentally. As
a result, multi-component systems are most often treated as pseudo-binaries because a description of constitutional solute interaction is more difficult to calculate as the number of components increases, and the binary phase diagram is the simplest to visualize and from which to do calculations. This may lead to unrealistic predictions of the degree of micro-segregation in the solidified alloy due to the assumption that partitioning of a solute in solution is independent of the presence of other solutes and uniquely determined at any temperature.

Incorporation of a pseudo-binary treatment of multicomponent alloys in a mathematical treatment of peritectic alloy solidification does not take into account the influence of those considerations outlined above. All of these considerations make the arithmetic onerous in the development of a mathematical description of the peritectic transformation in multicomponent systems. The basic conceptual model cannot make clear the role of solute constitutional and diffusional interaction, disparate solute diffusivities and solidification variables in determining the degree of microsegregation obtainable due to the peritectic transformation. Therefore, when faced with a lack of agreement between model predictions and experimental results, one cannot judge which of the assumptions in the conceptual model leads to unreasonable predictions. Herein lies the difficulty encountered by Ueshima
et al.\textsuperscript{21} with the phosphorus model predictions. The basic conceptual model needs to be further developed in order to provide a clear picture of the contribution of each of these factors to the total microsegregation obtained during the transformation. Knowledge of how they interact provides a sound basis for the "search for trends" stage in building a description of the solidification of a multicomponent peritectic alloy of a specified composition.
3.0 Plane Front Solidification of Peritectic Tin-Cadmium Alloys

In describing the mode of solidification of binary alloys, the boundaries of regions corresponding to plane front, cellular and dendritic solidification are usually mapped onto a 'space' in a plot of the ratio of temperature gradient to interface velocity (G/V) versus initial alloy composition (C). The question posed in this thesis with respect to plane front solidification of these alloys was whether or not banding occurs within clearly defined limits in the 'plane front space' of such a plot for two phase peritectic tin-cadmium alloys. Two phase peritectic tin-cadmium alloys have initial compositions, C, that lie in the range \( C_a < C < C_g \), as shown on the tin-cadmium phase diagram in Figure 7. Accordingly, plane front solidification experiments as well as mathematical model predictions, of transient peritectic phase solidification were designed to determine the plane front solidification conditions that might produce banding. The plane front solidification experiments and the mathematical modelling study are described in the Sections 3.1 and 3.3, respectively. In addition, undercooling experiments and a calculation of values for several thermodynamic factors
important to peritectic phase nucleation at the primary phase/liquid interface were done in order to obtain a measure of the undercooling required to nucleate the primary and peritectic phases in the alloys used. The details of the undercooling experiment and the thermodynamic calculations for nucleation of the peritectic phase are presented in Sections 3.1 and 3.2 of this chapter.
3.1 Description of Experimental Methods for Plane Front Solidification of Peritectic Tin-Cadmium Alloys

3.1.1 Specimen Preparation

Tin and cadmium of purity 99.98 and 99.999% respectively were used to prepare tin-cadmium alloys, containing 1.21 and 2.58 weight percent cadmium, by the following procedure. The oxide on the tin metal was removed by grinding on a silicon carbide 120 grit belt grinder; oxide on the cadmium metal was removed by scraping it with the edge of a microscope slide. After the appropriate amounts of tin and cadmium needed to make up an alloy were weighed, they were encapsulated in a pyrex tube, under vacuum. The metal was melted, mixed by shaking the tube and solidified by plunging the tube into an ice/water bath. The master alloy so produced was subsequently cut into slices for use in the preparation of thin specimens for plane front solidification, using a slow speed saw; a few samples weighing less than 1gm each were sent for chemical analysis.

Pieces of the master alloy were placed in two shallow depressions each, 47.5mm x 16.0mm x 1.0mm, cut into the surface of a circular graphite slab. A graphite mould cover was placed over the specimens and the whole assembly placed in the center of an induction heater coil. The melting and
solidification of the metal was done in an argon atmosphere. The resulting ingots were rolled into sheet less than 0.5mm thick. Specimens were cut from the tin-cadmium sheet to fit snugly inside a boron nitride cell having an inner cavity measuring, 47.25mm x 12.5mm x 0.78mm. Oxide on the specimens was scraped off using the edge of a microscope slide before the specimen was used. Once the specimen was placed inside the boron nitride cell, the two halves of the cell were sealed using a ceramic bonding agent called Ceramabond 569. This alumina cement was allowed to dry at room temperature before the crucible was handled and allowed to cure in the furnace during the experiment.

3.1.2 Procedure for Plane Front Solidification

The plane front solidification experiments were done in the laboratory of Dr. J. Rutter at the University of Toronto, on a furnace designed by one of his former graduate students. The details of this apparatus are described elsewhere. The furnace consists of two stainless steel bars separated by a soapstone insert and powered by heaters of the thermal valve type at each end. It is designed to maintain a stable, low temperature gradient (2.5K/mm max) across the soapstone insert, permitting stable growth at very low speeds (10nm/s) for periods of several weeks. The heaters at either
end of the furnace were set to 533K and 453K respectively in order that the temperatures measured at the 5mm positions either side of the center of the furnace (507± 2.2K and 489± 2.2K) would encompass the peritectic temperature for this system (496K). The cell was inserted into the center of the furnace from the cold end, a distance of 163mm, to ensure that at least 30mm of the sample would be melted at the start of solidification. The ends of the furnace were covered with Fibrefax and the specimen cell was set in motion. The specimens were pushed through a channel in the furnace, from the hot to the cold end, at speeds as low as 1.0X10⁻⁵ mm/sec, by means of a pushrod driven by a micrometer screw arrangement. The velocities were low enough, 1mm per day, that the specimen did not have to be allowed time to partially melt before the experiment began. The cell was allowed to travel 20mm to 25 mm before the specimen was quenched to reveal the solid-liquid interface contour. The specimens were quenched using helium gas introduced into the furnace from a nozzle located over the center of the furnace. The crucible was removed from the cold end of the furnace and the specimen was allowed to cool in the crucible before it was removed. The entire assembly is enclosed in a glove box and kept under an argon atmosphere to prevent oxidation.
3.1.3 Undercooling Experiments

To prepare specimens for undercooling experiments approximately 5 grams of alloy were melted in a beaker on a hot plate, under a flux consisting of a 60/40 mixture of tin chloride and zinc chloride. The metal was rapidly frozen by pouring it onto a pyrex dish. The flux was broken off and the metal rinsed in water to remove any residue. The metal was then cut into small pieces with scissors and these pieces were put into a 3mm ID quartz crucible; flux was placed on the metal to protect it from oxidation. A small cylindrical furnace with an inconel block in the center was used for the undercooling experiments. The quartz crucibles were placed in holes, 5mm in diameter, that were equally spaced about the center of the block. Chromel-alumel thermocouples were used for temperature measurement; contact between the melt and the thermocouples was prevented by shielding the thermocouples with thin quartz tubing. The thermocouples were wired in such a manner that both a cooling curve of a tin-cadmium specimen and the difference in temperature between the tin-cadmium specimen and a solid lead (standard) specimen during cooling could be obtained. The thermocouple was used to stir the melt before solidification took place. The alloy cooling curve and differential thermal curve were recorded using a two pen chart recorder.
3.1.4 Chemical Analysis

**Solution Optical Emission Spectroscopy**

The tin-cadmium specimens used in this work were analyzed using solution optical emission spectroscopy. The essential features of this technique are as follows: 1. the ions in a gas plasma are inductively excited as the gas flows pass a copper coil through which alternating current is flowing. 2. The relaxation of an individual ion of an element results in the emittance of light of several different wavelengths. 3. the intensity of the emitted light, of a particular wavelength is measured by a photometer, for a fixed duration, eg. 10 seconds; this data is collected for several "exposures". 4. The intensity data is converted to a weight percent for the element of interest using the calibration curve prepared for the material to be analyzed.

Light of several different wavelengths will be emitted for a particular element. It is important to ensure that another element does not contribute to the intensity measured for the chosen wavelength of the element of interest. Several cadmium lines that did not 'overlap' with tin lines were available for this method of chemical analysis of tin-cadmium alloys. The wavelengths used for tin and cadmium in the analysis were 0.1899X10^-6 m and 0.22785X10^-6 m, respectively.
Calibration of the Spectrometer

Tin and cadmium standards containing 1000 ppm concentrations of the element, were purchased from Canlab. The tin standard solution was not diluted for calibration purposes because of the relatively small weight percent of cadmium in the tin-cadmium alloys. The cadmium solutions used for calibration purposes contained 1000 ppm and 100 ppm cadmium. The solution containing 1000 ppm tin was used as the 'zero' reference for the measurements of cadmium intensity.

Procedure for Chemical Analysis by Emission Spectroscopy

A sample weighing less than or equal to one gram was dissolved in a known volume of a mixture of hydrochloric and nitric acid. This solution was then diluted to a predetermined concentration of alloy in solution, e.g. 1.0 x 10^-6 g/ml. During the analysis, this solution was aspirated at a constant rate from the container into a flowing argon gas stream, which was then excited in the induction coil. The intensity of light of wavelengths 0.1899 x 10^-6 m and 0.22785 x 10^-6 m, for tin and cadmium respectively, was measured and recorded four times for a duration of ten seconds each time. The test results are expressed as an average value for each wavelength (ie., element) with an accuracy of ± one standard deviation. The reproducibility of the results is indicated by the ratio (expressed as a percent) of the standard deviation
to the average weight percent value.

3.1.5 Methods for Metallography and Microscopy

From the thin sheet and rod specimens produced in the plane front solidification and undercooling experiments, suitable sections were cut with the tip of a scalpel and a slow speed saw, respectively. The resulting samples were mounted in a low curing temperature epoxy (Struers' Brand). The mounted samples were polished from the 600 grit (used paper) stage through the 6 and 1 micron diamond polishing stages. The diamond polishing fluid was either kerosene or a mixture containing soap and a glycerol based polishing liquid. The samples were rinsed with water, petroleum ether and alcohol in between the polishing stages. A quarter micron diamond spray was used for the final polish. The specimens were etched with a mixture of 2% nitric acid in lactic acid and examined in the optical microscope.

**Wavelength Dispersive Spectrometry**

X-ray dot maps of cadmium distribution were used as an aid in identifying the peritectic phase in the plane front solidified specimens. Wavelength dispersive spectrometry was used to produce dot maps because this technique can differentiate between x-rays with an energy difference of 5eV,
versus 150ev for the more routinely used energy dispersive spectrometry technique. This is important for tin-cadmium alloys because the Lα, x-ray energy peaks for these two elements overlap significantly on an energy dispersive spectrum. Wavelength dispersive spectrometry when used to produce element x-ray dot maps is not quantitative.

The essential features of this technique are as follows: 1. The x-rays generated when an electron beam penetrates the surface of a sample are directed towards an analyzing crystal. 2. The crystal diffracts x-rays of a particular wavelength when it is tilted at the appropriate Bragg angle for that x-ray wavelength, with respect to the sample. 3. The diffracted x-rays are focussed onto the detector where they are counted. An advantage of wavelength dispersive spectrometry over energy dispersive spectrometry is that signals as high as 10,000 to 15,000 counts per second can be processed with essentially zero detector deadtime.

The x-ray dot maps were produced using a JEOL-JXA 840 scanning electron microscope at Dofasco Research Division (Dominion Foundries and Steel Company). The x-ray spectrometer attached to this microscope has two channels, each containing two analyzing crystals. Each of these four crystals allows one to collect x-ray information for elements over a range of atomic numbers on the periodic table; between them the four
crystals cover all the elements on the periodic table. The unpolished samples were viewed because the surfaces were clean enough for the purposes of producing element x-ray dot maps. An optical microscope, which could be inserted into the viewing chamber of the electron microscope, was used to bring the surface of the sample into focus for the spectrometer. This is done to ensure that the analyzing crystal, detector, and sample surface are located on a circle, called the Rowland circle, thereby keeping the sample-crystal and crystal-detector distances equal. As the electron beam slowly rastered the area of the sample in view, the cadmium Lα, x-rays of wavelength 3.95635Å and an excitation voltage of 3.133 Kev were counted. The cadmium map was developed line by line in the manner of all scanning electron microscope images. A photograph of the dot map on the microscope view screen was taken as required. Backscattered electron images were used to check the information provided by the element maps; the contrast due to differences in average atomic number for phases enables one to differentiate the shape and location of the different phases present.
3.2 Calculation of Values for Several Thermodynamic Factors Important to Peritectic Phase Nucleation at the Primary Phase/Liquid Interface

Thomson and Spaepen\textsuperscript{26} have published a treatment of crystal nucleation in binary metallic melts which allows one to calculate values for the following as a function of temperature:

. the composition of the solid phase nucleus,
. the molar volume and entropy of fusion of the nucleating \( \beta \) phase,
. the Gibbs volume free energy change for the transformation,
. the Gibbs free energy barrier for nucleation of the critical size nucleus,
. the interfacial free energy for the solid/liquid interface.

The peritectic phase (\( \beta \)) in the tin-cadmium system has simple hexagonal packing (SHP); lattice stabilities (\( \Delta G^\circ \)) and surface energies for this phase are not easily obtainable. Therefore, in this work, values for the thermodynamic factors listed above were calculated for the nucleation of an hexagonal close packed peritectic phase (\( \beta \)HCP), in order to provide an order of magnitude value for the critical \( \beta \) nucleus size and the undercooling required to nucleate the peritectic phase either heterogeneously or homogeneously, at a planar primary (\( \alpha \)) phase/liquid interface in tin-cadmium alloys. Consideration of
the question of banding in peritectic alloys must include some thought on nucleation of the primary and peritectic phases; information on order of magnitude values for the thermodynamic factors listed above is useful in any discussion of nucleation of a phase.

The Thomson and Spaepen analysis assumes the following thermodynamic properties for the liquid and solid phases:
1. Both the liquid and solid phases are regular solutions.
2. The molar excess free energy for the liquid phase is a function of solute concentration; the molar excess free energy for the solid phase is not a function of solute concentration.
3. The molar volume and the entropy change for fusion of the solid phase is a weighted sum of the values of the molar volume and the entropy change for fusion of the pure components.

The variables listed above are calculated using equations (10) to (16), from the Thomson and Spaepen analysis:

\[ X = \frac{x_{Cd, eq}^{Sn} x_{S, eq}^{Cd}}{x_{Cd}^{Sn} x_{S}^{Cd}} \]  

\[ \frac{1}{x_{S}^{Sn}} = 1 + \frac{x_{I}^{Cd}}{x_{I}^{Sn}} \exp\left[ \left( \Delta S_{f}^{Sn} - \Delta S_{f}^{Cd} \right) \left( T - T_{liquidus} \right) + R T_{liquidus} \ln(X) \right] \]

\[ T \ldots is the temperature at the \alpha/liquid interface \]
\( T_{\text{liquidus}} \) is the \( \beta \) liquidus temperature for the liquid at the \( \alpha \)-liquid interface.

\( X_i^l \) is the mole fraction of component \( i \) in the liquid at the \( \alpha \)-liquid interface; \( i = \text{Sn or Cd} \).

\( \Delta S_i^l \) is the entropy of fusion of the pure component \( i \).

\( R \) is the universal gas constant.

\( X_i^s(T) \) is the mole fraction of component \( i \) in a critical size nucleus of the peritectic phase, \( \beta \text{HCP} \), at the \( \alpha \)-liquid interface.

\[ \Delta g_i^{j/l}\beta = \frac{1}{V} \left[ \Delta S_i^l (T_i^{j/l}-T) + RT \ln \left( \frac{X_i^l}{X_i^s(T)} \right) - RT_i^{j/l} \ln \left( \frac{X_i^l}{X_i^s(T_i^{j/l})} \right) \right] \]

\( X_i^s(T_i^{j/l}) \) is the mole fraction of component \( i \) in the peritectic phase, \( \beta \text{HCP} \), at the \( \beta \) liquidus temperature for the liquid, at the \( \alpha \)-liquid interface.

Note: \( X_i^s(T) \) is the mole fraction of component \( i \) in the peritectic phase, \( \beta \text{HCP} \), for a critical nucleus and is not equal to the equilibrium peritectic solid composition \( X_i^s(T_i^{j/l}) \); these two compositions are shown in Figure 7.

\[ \gamma^{j/l}\beta = \frac{\alpha \Delta S_i^{\text{alloy}} T}{(N_A^2)^{1/3}} \]

\( \alpha = 0.86 \) for an H.C.P. system.
(13) \[ r^* = \frac{2\gamma^{1/hcp}}{\Delta g_{\gamma}^{1/hcp}} \]

(14) \[ \Delta G_h^* = \frac{16}{3} \pi \frac{\gamma^3}{\Delta g_\gamma^2} \]

h...homogeneous

(15) \[ \gamma^{\alpha/\beta} = \gamma^\alpha + \gamma^\beta/1 \cos \theta \]

(16) \[ \Delta G_{ht}^* = \Delta G_h^* (2 - \frac{3\cos \theta}{4} + \cos^2 \theta) \]

ht...heterogeneous

. \( \Delta S_f^{alloy} \)...is the entropy of fusion for the BHCP phase at the interface temperature; the BHCP phase is a solution of tin and cadmium.

. \( \Delta g_{\gamma}^{1/hcp} \)...is the Gibbs volume free energy change for the solidification of the BHCP phase from the liquid at the \( \alpha \)/liquid interface.

. \( V \)...is the molar volume of the BHCP phase at the interface temperature.

. \( \gamma^{1/hcp} \)...is the surface free energy of the interface between the liquid and the BHCP phase.

. \( N_a \)...is Avogadro's number.
\( \alpha_n \) ...is a proportionality constant

\( \Delta G^* \) ...is the free energy required for the homogeneous or heterogenous nucleation of a nucleus of BHCP of critical size, at the \( \alpha/\text{liquid} \) interface

\( r^* \) ...is the radius of a critical size nucleus of the BHCP phase at the \( \alpha/\text{liquid} \) interface

\( \gamma^{\alpha/l} \) ...is the surface free energy of the \( \alpha/\text{liquid} \) interface

\( \gamma^{\beta/l} \) ...is the surface free energy of the BHCP/liquid interface

\( \gamma^{\alpha/\beta} \) ...is the surface free energy of the \( \alpha/\beta \)HCP interface

\( \cos \theta \) ...is the cosine of the wetting angle \( \theta \) for the BHCP phase on the \( \alpha/\text{liquid} \) interface

In this work, the value of the \( \alpha/\text{liquid} \) interface temperature was allowed to vary over a temperature range up to 175K below the \( \beta \) liquidus temperature in order to evaluate the undercooling necessary for homogeneous and heterogeneous nucleation of the BHCP phase, for a given value of the cadmium concentration in the liquid at the interface. The cadmium concentration in the \( \alpha \) and liquid phases at the interface was specified; the \( \beta \) liquidus temperature for that cadmium concentration was obtained from the phase diagram data of Hanson and Pell-Walpole.\(^{27}\) The free energy for heterogeneous nucleation of the \( \beta \) phase was calculated for several different values of the surface free energy for the \( \alpha/\beta \)HCP interface, 10 to 100\text{mJ/m}^2. \text{The nucleation rate for formation of BHCP nuclei}
of critical size was calculated using equation (17):  

\[
I_{ss} = \frac{10^{30}}{\eta} \exp \left( \frac{-\Delta G^*}{kT} \right)
\]

- \( I_{ss} \)... is the steady state nucleation frequency  
- \( \eta \)... is the liquid viscosity \( 10^{-3.3} \exp(3.34T_s/(T-T_{glass})) \)  
- \( T_{glass} \)... is the glass transition temperature which is  
- \( 0.25 \times (X^A T_m A + (1-X^A) T_m B) \); \( T_m \) is the melting point  
- \( k \)... is the Boltzmann constant  

The data from these calculations dealing with the subject of homogeneous and heterogeneous nucleation of the βHCP at the α/liquid interface are presented in Section 5.3.

3.3 Modelling of Transient Peritectic Phase Solidification In Plane Front Solidified Binary Peritectic Alloys

As noted earlier, a number of investigators have observed banding, i.e. the alternate deposition of layers of the primary (α) phase and the peritectic (β) phase, during plane front solidification of peritectic alloys having compositions within the limits of the peritectic isotherm. In this section, the assumptions of the conceptual model used to describe the solidification of these alloys will be outlined and a technique used to solve certain mathematical equations to predict conditions at and near the solid-liquid interface.
will be presented. The mathematical model is based on the concept of transient peritectic phase solidification elaborated by Titchener and Spittle. The mathematical model is intended to predict whether or not conditions can be obtained at the peritectic solid/liquid interface leading to re-nucleation of the primary phase, thereby initiating the first in a series of bands of primary and peritectic phase.

**Conceptual Model**

The assumptions of the conceptual model describing the one-dimensional, plane front solidification of a peritectic alloy are as follows:

1. Initially, a long thin sample is completely melted and of uniform composition.
2. The primary phase is nucleated and grows uni-directionally with a plane front.
3. Local equilibrium conditions apply at the solid-liquid interface.
4. No solute diffusion takes place in the solid.
5. Mixing in the liquid is due to diffusion only.
7. The concentration profile and linear temperature gradient in the liquid ahead of the interface are as shown in Figure 8.
8. Nucleation of the peritectic phase (8) occurs after steady
9. Solidification conditions are conducive to plane front solidification of both the primary and peritectic phases.

10. Primary phase re-nucleation will take place when the solute concentration of the liquid at the interface lies somewhere on the metastable extension of the peritectic phase liquidus.

11. Steady state solidification of the peritectic phase takes
place if the primary phase does not nucleate at or near the peritectic phase/liquid interface.

Steady state solidification is defined as the production of a solid phase of solute concentration equal to that of the bulk liquid. The question of whether or not steady state solidification of the primary phase develops during solidification of these alloys has not been resolved in the literature. The model assumes that nucleation of the peritectic phase occurs sometime after steady state primary phase solidification is underway in order to provide a mathematical description of the solute profile ahead of the interface before transient peritectic phase solidification begins. It makes no statement about the undercooling required for nucleation of the peritectic phase.

Steady state freezing of the primary phase of a peritectic alloy, having a bulk composition lying within the limits of the peritectic isotherm, must occur from liquid having a solute concentration on a metastable extension of the primary phase liquidus, at a temperature below the peritectic temperature. In addition, solidification of the primary phase under steady state plane front conditions implies that the liquid ahead of the interface is superheated with respect to the primary phase liquidus temperature. However, since the metastable primary phase liquidus extension must lie below the peritectic phase liquidus, a region of liquid that is
undercooled, with respect to the peritectic phase liquidus, must exist for a short distance ahead of the primary solid/liquid interface as shown in Figure 8. Therefore, peritectic phase nucleation is not limited to the interface, but can occur in this undercooled liquid.

**Mathematical Description**

The purpose of the mathematical model is to predict whether or not the solute concentration in the liquid at the interface will lie on the metastable extension of the peritectic phase liquidus at some point during peritectic phase solidification. A mathematical description of the complete solute profile in the liquid versus time is not of concern to the topic under consideration. The phenomena of uni-directional transient solidification of the peritectic phase, 8, can be described as a moving boundary problem with unknown interface velocity-time laws and changing boundary conditions, i.e. interface concentrations and concentration gradient in the liquid. The solution to the one-dimensional solute balance equation, (18), at the solid/liquid interface will provide values of solute concentrations at the interface versus interface positions versus time for transient peritectic phase solidification.
\[ C_1^{\beta/1}(1-K^{\beta/1}) \nu_{\text{interface}} = D_1 \frac{dC_1}{dX} \bigg|_{x=x_{\text{interface}}} \]

The meaning of the symbols used in this equation are as follows:

- \( C_1 \) ... the solute concentration in the liquid
- \( C_1^{\beta/1} \) ... the solute concentration in the liquid at the \( \beta/\)liquid interface
- \( \nu_{\text{interface}} \) ... the interface velocity; referred to as \( \nu^i \) in subsequent equations.
- \( D_1 \) ... the diffusion coefficient of the solute in the liquid.
- \( dC_1/dX \) ... the concentration gradient of the solute in the liquid at the interface.
- \( x_{\text{interface}} \) ... the distance from the location at which the peritectic phase nucleated, along the length of the specimen; referred to as \( X^i \) in subsequent equations.

There are three unknowns in equation (18), the solute concentration and concentration gradient in the liquid at the interface and the interface velocity. The values for these variables as solidification progresses is a function of the rate of isotherm movement, since, the specimen is being moved through a furnace with a linear temperature gradient. An analytical solution to the solute balance equation is not easily obtained, however, discrete values of \( C_1 \), \( X^i \) and time,
can be obtained using an approximate description of equation (18). The manner by which a solution to an approximate description of equation (18) is obtained is described in Section 3.2.1.

3.2.1

The interface is assumed to move forward in steps of a fixed distance \( \Delta X' \); the new solute concentrations and concentration gradient at the interface for each step are then calculated. Figure 9 shows pictorially the re-distribution of solute when the interface takes the first and subsequent steps and the technique used to obtain an approximate solution for equation (18); frequent reference to this figure will prove helpful in following the method of solution of equation (18) described in subsequent sections. As stated earlier discrete values of solute concentration in the liquid at the interface, \( C_{l}^{i'/k}(X^i) \), versus interface position, \( X^i \), are the required model predictions. The approximate description of equation (18) is written as follows:

\[
(19a) \quad C^{g/1}_{l}(X^i) (1-k^{g/1}) \frac{\Delta X'}{\Delta t} = D_{l} \frac{\Delta C_{l}}{\Delta X''} |_{X=X'}
\]

\[
(19b) \quad \Delta C_{l} = C_{l}(X^i) - C_{l}(X^i+\Delta X'')
\]
Figure 9 A Schematic Showing how Solute Is Re-Distributed In The Manner Described By The Conceptual Model Outlined In Section 3.3.

The derivatives in equation (18), $v = \frac{dx}{dt}$ and $\frac{dc}{dx}$, have been replaced by the approximations, $\Delta x'/\Delta t$ and $\frac{\Delta c}{\Delta x''}$, respectively. The symbols (' and "') on $\Delta X$ in equation (19) are meant to indicate that these values are different from one another. The variable $\Delta X''$ is best understood by referral to Figure 9. Briefly the meaning of the symbols used in equation (19) and Figure 9 are as follows:

- $X'$ is the distance from the location at which the peritectic phase nucleated, along the length of the specimen.
- $\Delta X'$ is the distance the interface moves in each step; the value of $\Delta X'$ is constant throughout the calculations.
ΔX′_n is best understood by referral to Figure 9; n indicates the number of steps the interface has taken.

X_j=n^i is the distance from the location at which the peritectic phase nucleated, after (n) ΔX′ steps have been taken.

Δt is the time it takes for the interface to travel a distance ΔX′.

C_p^β/1(X^i) and C_t^1/β(X^i) are the peritectic and liquid phase solute concentrations at the solid/liquid interface.

C_t(X^i + ΔX″) is the solute concentration of the liquid at the position X^i + ΔX″, along the length of the specimen.

dC_t/dX |_{XXi} is the slope of the liquid solute profile at the interface.

C_t^α/1(X) is the steady state liquid solute profile from the previous primary phase solidification.

D_t is the diffusivity of the solute in the liquid.

In order to obtain values of C_t^1/β(X^i) and X^i from a solution to equation (19), this equation must be solved for values of three variables, ΔX′, ΔX″ and Δt. The concentrations in equation (19), C_t(X^i) and C_t(X^i+ΔX″), are a function of the variables ΔX′, ΔX″ and Δt. Specifying a step size ΔX′ reduces the number of unknowns in this equation to two, ΔX″ and Δt. Another constraint is required in order to obtain a unique solution of ΔX″ and Δt for a given ΔX″; this constraint is outlined in Section 3.2.2. An equality of areas approximation
described below is used to determine the values of the variables \( X^i, \Delta X^m, X^i+\Delta X^m, C_1^{1/β}(X^i) \) and \( C_1^{1/β}(X^i+\Delta X^m) \) as required by equation (19).

1. As the interface moves forward in small steps, \( \Delta X^i \), the solute concentrations at the interface are assumed to remain constant and equal to the value \( C(X^i) \) at the interface position \( X^i = \sum \Delta X_j, j=1,n. \) New solute concentrations at the interface are determined by the new interface temperature, at that position. The temperature at the new interface position is a function of the rate of isotherm movement which must be accounted for in this calculation; the first \( \Delta X^i \) step is assumed to take place isothermally.

2. For each step, the rejected solute per unit area, \( A_1 \), is assumed to fill an area in the solute layer, \( A_2 \), ahead of the interface as shown in Figure 9. A small step size (\( \Delta X^i \)) allows the use of simple geometric approximations. Equations (20), (21) and (22) are the mathematical expressions for the areas \( A_1 \) and \( A_2 \), written in a form for solution using a computer. Simultaneous solution of these expressions, \( A_1=A_2 \), provides values for \( \Delta X^m \), \( C_1^{1/β}(X^i) \) and \( C_1^{1/β}(X^i+\Delta X^m) \).

\[
(20) \quad A_1 = \left[ C_1^{5/β}(X_{j=n-1}^i) - k^{β/1} C_1^{5/1}(X_{j=n}^i) \right] \Delta X^i
\]

\[
\left[ \frac{C_1^{5/1}(X_{j=n-1}^i+\Delta X_{n-1}^m) - C_1^{5/1}(X_{j=n}^i)}{2\Delta X^m} \right] \Delta X^i \cdot \Delta X^m
\]
(21) \[ A_2 = A' + \left[ \frac{C_o D_1 (1-k^{s/l})}{2 k^{s/l} v_g} \right] \left[ \left( -\frac{v_g \Delta X_n''}{D_1} \right) - 2 \right] \exp \left( \frac{-v_g (X_{j,n} + \Delta X_n'')}{D_1} \right) \]

\[ \frac{\Delta X_n'' (C_1^{s/l} (X_{j,n}) - C_o)}{2} \]

(22) \[ A' = \left[ \frac{C_o D_1 (1-k^{s/l})}{2 k^{s/l} v_g} \right] \exp \left( \frac{-v_g (X_{j,n-1} + \Delta X_{n-1}'')}{D_1} \right) \]

\[ \frac{[C_1^{s/l} (X_{j,n-1} + \Delta X_{n-1}'') - C_1^{s/l} (X_{j,n-1})] \Delta X' (\Delta X_{n-1}'' - \Delta X')} {2 \Delta X_{n-1}''} \]

\[ \frac{[C_1^{s/l} (X_{j,n-1}) + C_1^{s/l} (X_{j,n-1} + \Delta X_{n-1}'')] (\Delta X_{n-1}'' - \Delta X')} {2} \]

New symbols introduced in these equations are as follows:

- \( C_o \) is the initial bulk alloy composition
- \( k^{s/l} \) is the partition coefficient for primary phase solidification
- \( v_g \) is the specimen travel velocity in the furnace. This velocity may not be equal to the interface velocity during the initial stages of transient peritectic phase solidification.
- as a reminder, \( X_{j,n} \) denotes the interface position after the
jth ΔX' step.

In order that unique values for ΔX'' and Δt for a specified ΔX' are obtained as a solution of both equations (20) and (21), another constraint condition is required. Section 3.2.2 outlines the constraint condition used to solve equations (20) and (21).

3. The value of Δt is used to calculate the solute concentration of the liquid at the interface, $C_i^{1/β}(X_i')$. One point on a plot of solute concentration of the liquid at the interface versus interface position has been obtained.

4. The values of $C_i^{1/β}(X_i')$ and ΔX' are substituted into equations (20) and (21) to obtain a value for ΔX''. An equation of the form $a + bΔX'' + cF(ΔX'')$ is solved for ΔX''.

5. The value of the solute concentration gradient at the interface is calculated given the previously calculated values for ΔX'' and $C_i^{1/β}(X_i')$ and the value of $C_i^{1/β}(X_i' + ΔX'')$, which is calculated from the expression describing the solute profile that existed ahead of the a/liquid interface.

6. The data required to calculate solute concentration in the liquid at the interface for the next ΔX' step is complete, ΔX'' and $C_i^{1/β}(X_i' + ΔX'')$.

3.2.2

An overall solute balance for solidification provides a relationship between ΔX' and Δt which could be used to
Figure 10 A Schematic Showing The Overall Solute Balance For Solidification Of The Primary Phase.

Figure 11 A Schematic Showing The Overall Solute Balance For Solidification Of A Peritectic Alloy After The Peritectic Phase Nucleates.
obtain a unique solution for $\Delta X''$ and $\Delta t$ for a specified value of $\Delta X'$; this relationship also defines the function $C_t(X_t)=F(X_t,t)$. Figures 10 and 11 illustrate the overall solute balances for steady state primary phase solidification, before the peritectic phase nucleates, and for peritectic phase solidification respectively. The total amount of solute (per unit area) re-distributed is assumed to remain constant and is equal to the amount of solute contained in the diffusion layer ahead of the steady state primary phase/liquid interface, which is represented by B1 on the diagram. The total amount of solute per unit area carried ahead of the $\alpha$/liquid interface is approximated by the expression:

$$B1 = \frac{D(C_1^{1/\alpha}(X_o) - C_o)}{2v_{\text{specimen}}}$$

$X_o$ is the position of the $\alpha$/liquid interface just before the peritectic phase is nucleated, along the length of the specimen.

The $\alpha$/liquid interface velocity is assumed equal to the specimen travel velocity in the furnace for steady state $\alpha$ phase solidification. The amount of solute per unit area in the diffusion layer ahead of the peritectic phase/liquid interface, B3 on Figure 11, is equal to the total, B1, minus what has been removed to form some peritectic solid, B2. If one assumes that the geometric approximation of the solute
profile ahead of the B/liquid interface is described by an exponential curve, then the amount of solute carried ahead of this interface can be approximated by the expression:

\[
B_3 = \frac{(C_i^{\beta/\beta}(X^i) - C_o) \Delta t}{2 \Delta X'}
\]

At any time \( t = \Sigma \Delta t \), equality of the global mass balances (23) and (24) yields the following equations which defines a relationship between \( \Delta X' \) and \( \Delta t \), for the \( j \)th step:

\[
[(\frac{D_1(C_i^{\beta/\beta}(X_o) - C_o)}{2 v_{specimen}})] - \Delta X'[((k^{\beta} + \Sigma_{j=1}^n C_j^{\beta/\beta}(X_j)) + (k^{\beta} C_j^{\beta/\beta}(X_{j+n}))) - nC_o - \nC_o]
\]

\[
= \frac{D_1 \Delta t_{j=n}(C_j^{\beta/\beta}(X_{j+n}) - C_o)}{2 \Delta X'}
\]

\[
C_j^{\beta/\beta}(X_{j+n}) = \frac{T_j + T_0}{m_j^{\beta/\beta}} + \left[ \frac{G_j}{m_j^{\beta/\beta}} (X_j^{i} - (v_s(t_{j-n-1} + \Delta t_n)) \right]
\]

\( X_j^i \) indicates interface position after the \( j \)th \( \Delta X \) step.

The liquidus temperature for the initial alloy composition and the melting point of the pure solvent with a peritectic phase crystal structure are denoted by the symbols \( T_i \) and \( T_0 \). The slope of the peritectic phase liquidus and the temperature gradient in the liquid are denoted by the symbols \( m_i^{\beta/\beta} \) and \( G_i \). Combining equations (25) and (26) yields a second order
equation in $\Delta t$ to be solved. This value of $\Delta t$ is used to calculate the liquid solute concentration at the interface $C_l^{1/\beta}(x_{jn})$.

The model predictions are presented in graphical form as a trace of the peritectic phase/liquid interface concentration versus interface position; zero is defined as the primary solid/peritectic phase interface position. A comparison of the curves of liquid solute concentration at the interface versus the interface position, for a moving and a stationary specimen, may show that an assumption of a stationary specimen during the peritectic phase solidification transient is a reasonable one. The temperature at any distance $X$ ahead of the $\alpha$/liquid interface is greater if the specimen is stationary than if it is moving by the value $vt$; $v$ is the specimen travel velocity in the furnace during the transient solidification of the peritectic phase. The peritectic and liquid concentrations, at any interface position $x_{jn}'$, would be the minimum possible value if the specimen was stationary during the period of transient peritectic phase solidification. Therefore, if calculations of a trace of $C_l^{1/\beta}(X_i)$ versus distance of interface position indicate that the interface conditions do not regain the stable $\alpha$ phase region on the binary phase diagram, then it is unlikely that this can occur under moving specimen conditions.
4.0 Modelling of the Diffusion Controlled Growth of the Peritectic Phase During Dendritic Solidification of Peritectic Alloys

This chapter contains a theoretical analysis of diffusion controlled peritectic phase growth which is proffered as part of the overall discussion in this work on peritectic alloy solidification in general. Details of the conceptual model of this phenomenon currently used were provided in Section 2.2; the model is pictorially represented in Figure 5. As stated in the summary of the literature review of diffusion controlled peritectic phase growth in Section 2.3, the present conceptual model describing this phenomenon does not provide a framework from which the following question could be considered: How does coupling amongst intrinsic factors such as solute constitutional and diffusional interaction and extrinsic factors such as cooling rate affect the solute composition of the peritectic phase and phase growth rate? A theoretical framework is presented in this chapter as a development of the present conceptual model which facilitates consideration of the question posed above. The ideas presented herein require that one put aside the traditional treatment of solute partitioning in multicomponent peritectic alloys, such as the
treatment of these alloys as pseudo-binaries and adopt a more holistic treatment. The subject of diffusion controlled peritectic phase growth for a binary system is treated in Section 4.1. A method of treating the non-isothermal aspect of the transformation and a mathematical description of the transformation are offered in the sub-section 4.1.1. A method of solving the problem for binary systems is outlined in sub-section 4.1.2. The transformation in a binary alloy is considered in this work in order to respond to some very basic questions: what factors control the transformation in a binary system, and do these same factors or different ones control the transformation in a ternary system? A development of the conceptual model of the peritectic transformation for ternary systems is elaborated in Section 4.3, which shows clearly what the important factors are with respect to solute partitioning during the peritectic transformation and how coupling amongst these factors expresses itself in terms of the magnitude of micro-segregation observed. Although the ternary mononvariant three phase reaction amongst the primary solid, secondary solid and liquid phases is not a ternary peritectic reaction, for the sake of clarity the secondary solid phase will be referred to as the "peritectic phase" when dealing with the ternary system.
4.1 Mathematical Modelling of Diffusion Controlled Peritectic Phase Growth during Binary Alloy Solidification

4.1.1 The Non-Isothermal Diffusion Controlled Peritectic Transformation

The phenomenon of non-isothermal diffusion controlled peritectic transformation is mathematically described by a moving boundary problem with unknown velocity-time laws and changing boundary conditions, such as solute concentrations at the interfaces. Kirkaldy and Brown's paper, "On diffusion behaviour in ternary multiphase systems" outlined clearly the mathematical complexities of solving this diffusion problem and the difficulty of envisioning multi-component system response, under non-isothermal conditions. Many analytical and numerical solutions describing isothermal diffusion controlled phase growth are available for binary systems in the literature, i.e. constant interface concentrations and diffusion coefficients. Modelling the non-isothermal transformation as a series of steps composed of an athermal growth portion and an isothermal diffusion controlled growth portion, makes the diffusion problem more tractable. The iron-

7. Note: Athermal solidification describes the solidification of an alloy under the conditions of complete mixing in the liquid and no solute diffusion in the solid. Values of interface concentration and phase fractions are obtained by integration of the Scheil-Chipman solute balance at the solid/liquid interface.
carbon and iron-carbon-manganese systems are used here to
develop and illustrate model predictions for binary and
ternary systems respectively. Athermal growth of the
peritectic phase is considered in this work, because in an
alloy system such as a steel the diffusivity of a solute in
delta-ferrite is usually several orders of magnitude greater
than the diffusivity of the same solute in austenite. This
allows one to assume complete mixing of the solute occurs in
the delta-ferrite phase as well as in the liquid phase.

The non-isothermal transformation is modelled in this
thesis using a stepwise approach:

1. Athermal growth of the peritectic phase occurs as the
temperature changes instantaneously from temperature $T_{i-1}$ to
$T_i$. The values of solute concentration at the interfaces and
interface position obtained are used as initial boundary
conditions for the isothermal diffusion portion of the
problem, at temperature $T_i$. [Note: The peritectic temperature
is represented by $T_i$ for the first athermal step].

2. The interfaces are allowed to move isothermally due to
solute diffusion through the peritectic phase, for a duration
At determined by the cooling rate.

3. The values of solute concentration and interface position
obtained at the end of the isothermal diffusion period are
used to calculate the values for these variables over the next
period of athermal growth, from $T_i$ to $T_{i+1}$. [Note: The final
interface position at $T_i$ is used to calculate the initial interface position at $T_{i+1}$.

The mathematical model calculates values for solute concentration at the interface and interface position versus temperature until either the delta-ferrite or liquid phase disappears. Athermal or "Scheil" growth is a useful reference point for the following reasons:

1. It takes solute constitutional interaction into account, as expressed by the phase diagram; although, it does not allow for consideration of ternary diffusional interaction, which is the influence of the presence of one solute on the diffusion of another.

2. A mathematical solution describing phase fractions and interface compositions is readily obtainable.

3. It can describe "non-equilibrium" solidification situations, i.e. diffusion controlled peritectic phase growth at temperatures other than the peritectic temperature. The equilibrium phase diagram cannot be used to determine primary, peritectic and liquid phase fractions since it predicts that either the primary or the liquid phase or both disappears at the peritectic temperature.

The purpose of this development of the present conceptual model is to facilitate an understanding of how coupling amongst intrinsic and extrinsic factors controlling the peritectic transformation govern the microsegregation of
solute during the transformation. Some examples of intrinsic factors are solute diffusivity, solute constitutional and diffusional interaction; extrinsic factors are those such as cooling rate. The purpose of the mathematical model presented herein is to provide predictions of solute concentration at the interfaces and interface position versus temperature which can be used to evaluate the ideas about solute partitioning suggested by the conceptual model development. [Note: All equations in this and other sections describe the transformation using the names and symbols associated with the primary and peritectic phases of an iron-carbon alloy, known as delta-ferrite ($\delta$) and austenite ($\gamma$) respectively]. The solute balances at the $\delta/\gamma$ and $\gamma$/liquid interfaces must be simultaneously solved to provide values of solute concentration at the interfaces and interface position versus temperature. The solute balances for each interface are given by equations (27) and (28) respectively:

$\delta/\gamma$ interface

$$
-C_i^\delta [\frac{1-k^{\delta/\gamma}}{k^{\delta/\gamma}}] v^{\delta/\gamma} = -x^{\delta/\gamma} \frac{\partial C_i^\delta}{\partial t} \bigg|_{x=x^{\gamma/\gamma}} + D_i^\gamma \frac{\partial C_i^\gamma}{\partial x} \bigg|_{x=x^{\gamma/\gamma}}
$$

$\gamma$/liquid interface

$$
C_i^\gamma (1-k^{\gamma/\gamma}) v^{\gamma/\gamma} = \left[\frac{L}{2} - x^{\gamma/\gamma}\right] \frac{\partial C_i^\gamma}{\partial t} \bigg|_{x=x^{\gamma/\gamma}} + D_i^\gamma \frac{\partial C_i^\gamma}{\partial x} \bigg|_{x=x^{\gamma/\gamma}}
$$
i = solute 1,2,...n. Briefly, the symbols used in these equations are as follows:

- $C_i^j$ is the solute concentration at either the $\delta/\gamma$ or $\gamma$/liquid interface; $j = \delta, \gamma, \text{liquid}$
- $k$ is the partition coefficient for the solute at the interface
- $v$ is the velocity of the interface
- $X$ is the interface position within the volume element; it has a value ranging from zero to one-half the interdendritic spacing ($L$)
- $D_i^\gamma$ is the diffusivity of solute $i$ in the austenite phase
- $dC_i/dX$ is the solute concentration gradient in the austenite phase at the interface$^8$

For all calculations the mole fraction of solute was used rather than weight percent, for solute concentration. The equations are coupled because interface movement is controlled by the diffusion of solute through the peritectic phase. Simultaneous solution of all the solute balances will give the interface position versus time relationship for each interface.

---

8. Note: No effort was spared in order to be consistent in the use of symbols among equations (27), (28) and all other equations in this chapter. The meaning of any new symbols introduced in equations appearing in the rest of this chapter will be indicated below the equation in which they appear for the first time.
4.1.2 An Analytical Solution to the Diffusion Controlled Phase Growth Problem for a Binary Alloy

The solute concentrations at both the δ/γ and γ/liquid interfaces are uniquely determined for any given temperature, in a binary alloy. The factors that control the progress of the peritectic transformation in binary alloys are cooling rate, the magnitude of the temperature and possibly composition dependant solute diffusivity and whether or not the two phase region, δ/γ and γ/liquid, on the phase diagram opens or closes as the temperature decreases. This last factor determines whether or not the difference in solute concentration across an interface is increasing or decreasing: this is of some significance in determining how far an interface travels during the isothermal diffusion period, as determined by the solution of the solute mass balances. The model assumes that the peritectic phase appears at the binary peritectic temperature.

The time-dependant interface concentration changes in the solute balances (27,28) need not be considered during the isothermal period because the solute concentrations at the interfaces are fixed at any given temperature. Equations (27) and (28) reduce to equations (29) and (30):
\( \delta/\gamma \) interface

\[
C_\delta^\gamma \left[ \frac{1 - k^{\delta/\gamma}}{k^{\delta/\gamma}} \right] v^{\delta/\gamma} = D^- \frac{dC_\gamma^\delta}{dx}\bigg|_{x=x^{\delta/\gamma}}
\]

\( \gamma/\)liquid interface

\[
C_\gamma^\gamma \left( 1 - k^{\gamma/\gamma} \right) v^{\gamma/\gamma} = D^- \frac{dC_\gamma^\gamma}{dx}\bigg|_{x=x^{\gamma/\gamma}}
\]

\( D^- \gamma \) is temperature but not concentration dependant.

\[
-\left. \frac{dC_\gamma^\gamma}{dx} \right|_{x=x^{\gamma/\gamma}} = \left. \frac{dC_\gamma^\gamma}{dx} \right|_{x=x^{\gamma/\gamma}} = \frac{C_\gamma^{\gamma/\gamma} - C_\gamma^{\gamma/\gamma}}{W}
\]

\( W \) is the thickness of the peritectic phase

Equations (29) and (30) are re-arranged to obtain the interface velocity, \( v^{\delta/\gamma} = \frac{dx^{\delta/\gamma}}{dt} \) and \( v^{\gamma/\gamma} = \frac{dx^{\gamma/\gamma}}{dt} \), and are substituted into (31).

\[
\left. \frac{dx}{dt} \right|_{x=x^{\gamma/\gamma}} = \frac{dx^{\gamma/\gamma}}{dt} - \frac{dx^{\delta/\gamma}}{dt}
\]

\( dx^{\delta/\gamma}/dt \) is negative with respect to the direction of \( dx^{\gamma/\gamma}/dt \). Integration of equation (31) gives an equation which describes the variation of the peritectic phase thickness with time during the isothermal diffusion period.

For the first athermal step from the peritectic temperature to \( T_1 \), the liquid and \( \delta \)-ferrite phase fractions at
the peritectic temperature are calculated using the Lever Rule and the bulk alloy concentration $C_0$; the 'Scheil' interface positions at $T_i$ are calculated using the phase fractions and the width of the volume element which is one-half the primary dendrite spacing. Further athermal steps use the concentration tie-lines at $T_{i-1}$ and $T_i$ and the final interface position at $T_{i-1}$ to calculate the "Scheil" interface position at $T_i$. Equation (32) is the integrated version of equation (31) describing peritectic phase thickness, $w$, with time during the isothermal diffusion period.

\[ w = X^\gamma - X^\delta = \left[ 2At + (X_s^\gamma - X_s^\delta) \right]^{\frac{1}{2}} \]

$X_s$ is the interface position defined by "Scheil" solidification, at that temperature $T_i$.

$A$ is an integration constant which is defined as:

\[ A = D^\gamma \left[ \frac{1}{C^\gamma k^\gamma} + \frac{k^\delta}{C^\delta (1 - k^\delta)} \right] (C_i^\gamma - C_0^\gamma) \]

Equation (32) is used to determine the primary/peritectic and peritectic/liquid phase interface positions by substitution in either (29) or (30) and integration from $t=0$ to $t=At$. The transformation continues until either the $\delta$-ferrite or liquid phase disappears. The model prediction of phase fractions and concentrations during the peritectic transformation are
presented in Section 5.2.1 for an Fe-0.12 wt% C alloy.

4.2 Conceptual and Mathematical Modelling of Solute Partitioning During Diffusion Controlled Peritectic Phase Growth for a Ternary Alloy

In some useful multicomponent systems, i.e. Fe-C-X, solute diffusivities and the degree of chemical interaction can differ greatly between carbon and solute X, such that a limiting case analysis is useful in evaluating model assumptions about a system's behaviour. In the following subsections a development of the basic conceptual model is elaborated which makes clear the relative importance of these factors based upon a limiting case analysis. This analysis facilitates an understanding of how the coupling of factors such as the rates of solute diffusion, ternary solute constitutional and diffusional interaction and cooling rate influence the composition and growth of the peritectic phase; it also provides some ideas with respect to simplification of the calculations. The knowledge of how these coupled factors determine interface tie-lines and phase fractions allows one to better assess the assumptions of the conceptual model and provide more reasonable predictions for the same solute in several different base alloys. In a ternary system where there is a significant disparity between solute diffusivities, this
difference takes on a certain importance among the previously stated factors controlling the progress of the peritectic transformation. If one assumes that the interface tie-line for a ternary alloy at any temperature is given by the tie-line that passes through the initial alloy composition, then implicit in this assertion is the assumption that the diffusivities of the two solutes in all phases are equal and/or very large. If this assumption is not reasonable for the solutes in the alloy under consideration, then the interface tie-line must be obtained by solving the solute balances for the two solutes at each interface. Solute constitutional and diffusional interaction must also be taken into consideration because: 1. the former determines the tie-lines in the two-phase region on the ternary isotherm and 2. the choice of tie-line is influenced by the latter in a time-depndant way since diffusional interaction is a strong function of local concentrations, which increase in the interdendritic region as solidification progresses.

In the following two sub-sections, 4.2.1 and 4.2.2, two limiting cases to diffusion controlled growth of the peritectic phase are analyzed. In a ternary system, control of the growth of the peritectic phase by the diffusion of either solute through the peritectic phase represents a limiting case for diffusion controlled peritectic phase growth. To facilitate the limiting case analysis, assume that in the
ternary alloy under consideration there is a fast diffusing solute (1) and a slow diffusing solute (2) whose diffusivities differ by at least two orders of magnitude in the peritectic phase ie. C and X (substitutional) in Fe-C-X system. Section 4.2.1 contains an analysis of the situation in which the growth of the peritectic phase is controlled by the fast diffusing solute (1). Section 4.2.2 contains an analysis of the situation in which the growth of the peritectic phase is controlled by the slow diffusing solute (2). These two sections describe a development of the conceptual model, describing the phenomena of the peritectic transformation, proffered in this work.

4.2.1 Limiting Case 1...Peritectic Phase Growth Kinetics Controlled by the Fast Diffusing Solute During the Isothermal Diffusion Period

The conceptual model assumes that the peritectic phase is nucleated at the peritectic temperature within the small volume element shown in Figure 5. The delta-ferrite and liquid phase fractions at the peritectic temperature are determined by applying the Lever Rule to the δ/liquid tie-line of the three-phase tie-triangle, passing through the bulk alloy composition. Athermal solidification determines the initial phase fractions and solute concentrations at the interface at
a temperature \( T_i \), over the instantaneous temperature drop from
the temperature \( T_{i-1} \) to temperature \( T_i \). These values are
obtained by integration of the Scheil-Chipman mass balance
equations at each interface, from \( T_{i-1} \) to \( T_i \). The initial
solute 1 and 2 concentration profiles are as shown in Figure
12. Implicit in our use of athermal ("Scheil") growth to
define initial boundary conditions for the isothermal
diffusion problem is the assumption that the interfaces do not
move during the isothermal period. This constraint is a
consequence of the stepwise treatment of the non-isothermal
aspect of the problem. Two options that would allow the
interface to move during the isothermal diffusion period under
these initial conditions are either an instantaneous change
from the "Scheil" tie-line to one which allows the fluxes of
solute 1 and 2 through an interface to move it equal
distances or to allow partitioning of the slow diffusing
solute to be described by the Scheil-Chipman equation.

The first option implicitly assumes that the solute
concentrations at the interfaces remain constant throughout
the isothermal diffusion period. The second option allows the
interface to move without constraining the system in the
manner previously described. Solute 2 does not diffuse in the
austenite but partitions in a manner described by the Scheil
mass balance at the interface, in order to keep pace with the
fraction austenite versus time relationship described by the
Figure 12 A Schematic Showing The Scheil Concentration Profiles For The Two Solute In The Volume Element And Direction Of Tie-line Travel During The Isothermal Diffusion Period For Limiting Case 1.

fast diffusing solute's mass balance. As the transformation proceeds the volume fraction of the delta and liquid phases decrease. Scheil partitioning requires that the solute 2 concentration at the interface decrease and increase at the δ/γ and γ/liquid interfaces respectively. The interface tie-lines migrate in the direction of the arrows shown on the ternary isotherm in Figure 12. The concentration gradient of the fast diffuser in the austenite approaches zero during the isothermal period. Within the context of this limiting case, the system is self-moderating, in that interaction between the slow and fast diffusing solutes keeps the fast diffuser peritectic phase concentration gradient negligibly small.
throughout the peritectic transformation.

4.2.2 Limiting Case 2...Peritectic Phase Growth Kinetics

Controlled by the Slow Diffusing Solute During the

Isothermal Diffusion Period

In limiting case 2, there is no constraint on
diffusion of solute 2 in the austenite phase. Assume that the
same initial conditions, such as concentration at the
interfaces and interface positions for solutes 1 and 2 as used
in limiting case 1 apply to limiting case 2. As in case 1,
the solute fluxes through an interface must move it equal
distances. The mass balance equations for the interfaces
suggest that over some time period \(\Delta t\), the flux of solute 1
through the interface would be greater than that for solute 2.
As the \(\gamma/\text{liquid}\) interface moves forward, a portion of the
quantity of solute 1 swept by the interface would have to be
rejected into the liquid, in order for solute 1 to keep pace
with solute 2 as shown in Figure 13. As the solute 1 liquid
concentration increases, the \(\gamma/\text{liquid}\) tie-line on the ternary
isotherm changes in the direction of the arrows shown in
Figure 13. The concentrations of solute 1 and 2, at the
\(\gamma/\text{liquid}\) interface, increase and decrease respectively. The
interface concentrations at the \(\delta/\gamma\) boundary do not change
because the solute fluxes passing through the boundary move it
the same distance. As the transformation proceeds, the austenite concentration gradient of the slow diffusing solute decreases and that for the fast diffusing solute increases. At some point we must consider allowing the fast diffusing solute to take control of peritectic phase growth. The limiting case analysis is self-consistent in that consideration of either limiting case leads to the same conclusion...the system is self-moderating.

4.2.3 Mathematical Modelling of the Peritectic Transformation in Ternary Alloys

The limiting case analysis suggests that, in a system where solute diffusivities differ by several orders of magnitude, the calculations of phase composition and fraction for isothermal diffusion controlled growth of the peritectic phase, would be greatly simplified if:

1. That the interface mass balance equations for the fast diffuser are used to describe growth of the peritectic phase.
2. The slow diffusing solute is allowed to partition in a manner described by the Scheil mass balance equations.

The appropriate interface tie-line is determined simultaneously by the rate of diffusion of the slowest 8diffusing solute in solution, the cooling rate and the degree of constitutional chemical interaction among the various solutes, when ternary diffusional interaction is neglected.
The model predictions of the concentration versus time and velocity versus time relationship for the peritectic transformation are obtained by simultaneously solving the coupled mass balances for solute 1 (34 and 35) and the integrated Scheil equations for solute 2 (36 and 37), at the two interfaces.

Solute 1...1/γ interface

\[ C^1(1-\kappa t^{1/2}) t^{1/2} = \left( \frac{L}{2} - X_1^{1/2} \right) \frac{dC^1}{dt} \bigg|_{x=X_1^{1/2}} + D^1 \frac{dC^1}{dx} \bigg|_{x=X_1^{1/2}} \]

δ/γ interface
(35) \(-C^\delta \left[ \frac{1-k^{\delta/\gamma}}{k^{\delta/\gamma}} \right] \nu^{\delta/\gamma} = -X^{\delta/\gamma} \frac{dC^\delta}{dc} \bigg|_{x=x^{4/\gamma}} \gamma \frac{dC^\gamma}{dx} \bigg|_{x=x^{4/\gamma}}\)

Solute 2...1/\gamma interface

(36) \quad C^\delta = C^\delta_{\text{Scheil}} \left[ \frac{L - X^{\gamma/1}_{\text{Scheil}}}{L - X^{\gamma/1}} \right]^{1-k^{\delta/\gamma}}

\delta/\gamma interface

(37) \quad C^\delta = C^\delta_{\text{Scheil}} \left[ \frac{X^{\delta/\gamma}_{\text{Scheil}}}{X^{\delta/\gamma}} \right]^{\frac{(1-k^{\delta/\gamma})}{k^{\delta/\gamma}}}

The system of equations (34) to (37) are solved to determine the \(\delta/\gamma\) and \(\gamma/\text{liquid}\) interface positions, the interface concentration tie-lines and the concentration gradient across the \(\gamma\) phase. In this work, solution of the non-isothermal diffusion controlled growth problem was broken down into several sequential segments. The required calculations for each segment were done by computer programs written for that segment. The procedure followed to obtain a "final" concentration profile in the volume element at several temperatures, during the transformation, is described in the following sections entitled: calculation of the 'peritectic' corner of the ternary isotherm, the athermal step and the isothermal diffusion period.
Calculation of the 'Peritectic Corner of The Ternary Isotherm

The corner of the iron-carbon-manganese phase diagram, containing the monovariant three-phase equilibria amongst the delta-ferrite, austenite and liquid phases, was calculated for an alloy of composition of Fe-0.12wt%C-1.5wt%Mn. The carbon and manganese concentrations are representative of the Mn and C content of 'peritectic' steels usually produced in large tonnages for plate and tube applications. A series of ternary isotherms were calculated for chosen temperatures within the limits defined by the peritectic temperatures for the iron-carbon and iron-manganese systems, $T_p^{Fe-C} (1492K) < T < T_p^{Fe-Mn} (1472K)$. The procedure for constructing one of these isotherms for a particular temperature was divided into the four segments:

1. calculate the position of the $\delta$/liquid two-phase boundaries.
2. calculate the position of the $\gamma$/liquid two-phase boundaries.
3. find the point of intersection of the liquidus lines of the $\delta$/liquid and $\gamma$/liquid boundaries; this point locates two legs of the three-phase tie-triangle on the isotherm, ie. $\delta$/liquid and $\gamma$/liquid tie-lines.
4. calculate the position of the $\delta$/\gamma two-phase boundaries.

The general thermodynamic equations for calculation of
two-phase field tie-lines are:

\[
\Delta \mu_{\text{o.1/s}} = \ln K_{\text{o.1/s}} + \ln \Gamma_{\text{o.1/s}}
\]

\[
\Gamma = \frac{Y_1}{Y_2}, \quad Y = \text{activity coefficient}
\]

\[
\frac{\Delta \mu_1^{0.1/2} - \Delta \mu_2^{0.1/2}}{RT} = \ln \frac{K_1^{1/2}}{K_2^{1/2}} + \ln \frac{\Gamma_1^{1/2}}{\Gamma_2^{1/2}}
\]

\[
\frac{\Delta \mu_2^{0.1/2} - \Delta \mu_1^{0.1/2}}{RT} = \ln \frac{K_2^{1/2}}{K_1^{1/2}} + \ln \frac{\Gamma_2^{1/2}}{\Gamma_1^{1/2}}
\]

Note: in equations (38) to (43) \( Y \) represents the activity coefficient.

- \( \Delta \mu_i \) is the total change in the Gibbs Free Energy (chemical potential) of species \( i \), for the transformation; \( i = \text{solvent o, and solutes 1 and 2.} \)
- \( K_1 \) is the solute partition coefficient
- \( \Gamma_i \) is the ratio of the activity coefficient for species \( i \) in for the two phases indicated.

The two phase region's tie-lines are obtained from a solution of equations (29) to (31), when the temperature and one concentration term (expressed as mole fraction) are specified and the values of the ratios of the activity coefficients \( \Gamma_o \).
Γ₁, Γ₂ are known. The activity coefficients can be expressed using a low order Taylor expansion where the coefficients form a symmetric matrix.

If the solution is dilute, equations (38) to (40) reduce to:

\[ K₀ = \exp\left(\frac{-Δμ₀^o}{RT}\right) \]

\[ K₁ = \left(\frac{Y₁^{o,s}}{Y₁^{o,l}}\right) \exp\left(-\frac{Δμ₁^o}{RT}\right) \]

\[ K₂ = \left(\frac{Y₂^{o,s}}{Y₂^{o,l}}\right) \exp\left(-\frac{Δμ₂^o}{RT}\right) \]

The simplified equations for the calculation of two-phase field tie-lines and boundaries on ternary isotherms for dilute solutions, used in this work were published in a paper by Hone, Subramanian and Purdy. The information required for solution of the equations is obtainable from binary phase diagrams and known ternary solution parameters (Wagner interaction parameters), for the solutes in the phases concerned.

If one concentration is specified, i.e. \( X₁^s \), the values of the others \( X₁^l, X₂^l, X₂^s \) are determined by the following equations:
(41) \[ x_1^s = \frac{x_1^o}{k_1} \]

(42) \[ x_2^s = \left[ \frac{1 - k_2}{k_2 - k_o} \right] - \left[ \frac{k_1 - k_2}{k_2 - k_o} \right] x_1^l \]

(43) \[ x_2^s = k_2 x_2^l \]

The liquidus and solidus surfaces can be considered planar and the liquidus and solidus lines can be drawn by connecting the binary phase field endpoints. The binary values of the partition coefficients could be used in the equations above to yield tie-lines.

In the temperature range within which the monovariant three-phase reaction occurs, the portion of the ternary two-phase boundary, eg. \( \delta \)/liquid, connecting the stable phase field on a binary, Fe-Mn, to the three-phase region, \( \delta \)-\( \gamma \)-liquid, defines a thermodynamically stable phase field, on the ternary isotherm. The other part of this two phase region is an extrapolation of the stable field boundaries into other phase fields. The procedure for calculation of the two-phase boundaries is outlined using the \( \delta \)/liquid boundary as an example:

1. The binary manganese and carbon concentrations and the binary partition coefficients for the \( \delta \)/liquid boundary are
obtained from their respective phase diagrams.

2. The \( \delta / \) liquid phase field is stable on the Fe-Mn phase diagram; an extension of the \( \delta / \) liquid boundaries into the stable \( \gamma / \) liquid field is used to obtain carbon concentrations and partition coefficients. The binary iron partition coefficients obtained from each diagram were compared and found to differ in the third decimal place; one can be confident of these numbers to two decimal places. The ternary iron partition coefficient was allowed to vary with carbon content since the difference in the value of the third decimal place proved to be important in the calculation of the ternary tie-lines at the binary limits.

3. Equations (41) to (43) were simultaneously solved, using the binary solute and ternary solvent partition coefficients, as the carbon concentration in the \( \delta \) phase was varied from the maximum at the binary limit for the phase field to zero.

The Athermal Step

The interface tie-lines and interface positions calculated in this segment provide the initial boundary conditions for the isothermal diffusion period. The first athermal step is from the peritectic temperature to some temperature \( T_i \) since the model assumes that peritectic phase appears at the peritectic temperature. The \( \delta \)-ferrite and
liquid solute concentrations are given by the end points of the three phase tie-triangle; the phase fractions are calculated using the Lever Rule, on the ternary isotherm. For all further athermal steps from \( T_{i-1} \) to \( T_i \), the final interface positions and concentrations calculated for \( T_{i-1} \) are used.

The two Scheil solute balances at each interface must be simultaneously solved for values of solute concentration and \( \delta \) and liquid phase fractions at temperature \( T_i \). The integrated version of the Scheil solute balance at both interfaces is given by equations (44) and (45):

\[
(44) \quad C_j^\delta(T_i) = C_j^\delta(T_{i-1}) \left( \frac{X_i^\delta/T_i}{X_i^\delta/T_{i-1}} \right)^{1-k_i^\delta/\delta^j} X_i^\delta/T_i
\]

\[
(45) \quad C_j^\gamma(T_i) = C_j^\gamma(T_{i-1}) \left( \frac{L-\gamma/\gamma(T_{i-1})}{L-\gamma/\gamma(T_i)} \right)^{1-k_i^\gamma/\gamma^j}
\]

where \( C_j \) denotes the Scheil concentration of solute \( j = 1 \) or 2, at the specified temperatures, \( T_{i-1} \) and \( T_i \). 

\( X(T) \) is the interface position in the volume element at the specified temperature.

\( L/2 \) is one-half the primary dendrite spacing.
The Scheil mass balances are solved in four steps; this is illustrated below using the first athermal step from the alloy...
peritectic temperature to some temperature $T_i$. The solute balances for carbon were used to calculate the interface tie-line as follows:

1. the solute balances for manganese were re-arranged to provide a value for interface position, $X^{\delta/\gamma}$ and $X^{\gamma/\delta}$, at $T_i$ in terms of the manganese concentrations, $C_m^{\delta}$ and $C_m^{\gamma}$.

2. these were then substituted into the carbon balances to provide two equations with four unknowns, $C_c^{\delta}, C_c^{\gamma}, C_m^{\delta}, C_m^{\gamma}$.

3. these two equations were solved simultaneously for the solute composition of the interface subject to the constraints defined by equations (41) to (43), since the new solute composition of the interface must specify a tie-line in the two-phase field.

4. the tie-line at $T_i$ was used with the carbon mass balance to determine interface position at temperature $T$. We now have the initial boundary conditions for the isothermal diffusion period.

The Isothermal Diffusion Period

The model predictions final values of solute concentration at the interfaces and interface positions at the end of an isothermal diffusion period of duration $\Delta t$, for several $T_i$, provide an indication of the severity of microsegregation of solute during the peritectic
transformation. Values for solute compositions (tie-lines) at the interfaces versus interface position in the volume element were obtained as follows:

1. The $\gamma$/liquid interface was moved forward the pre-determined distance $\Delta X^{\gamma/\ell}$ shown on Figure 14. The movement of the $\delta/\gamma$ and $\gamma$/liquid interfaces during this period are coupled due to solute diffusion through the austenite phase.

2. The solute 2 liquid concentration $C_2^1$ was calculated using the integrated Scheil balance (36). Scheil partitioning of solute 2 is not time dependant during the isothermal diffusion period since the mass balance explicitly relates solute 2 concentrations at the interface to the fraction of delta-ferrite and liquid phases only.

3. The other three concentrations at the liquid interface, $C_1^1$, $C_1^\delta$, $C_2^\delta$, which define the tie-line were calculated using equations (41) to (43). The time dependance of the solute 1 concentration at the interface is eliminated since the two solutes concentrations are related through the ternary tie-line relationship.

4. Solute concentrations at the delta-ferrite interface and the delta-ferrite interface positions were calculated using an equality of areas approximation for partial integration of the mass balances; the solute flux through the $\gamma$/liquid interface represented by area $A_1$ on Figure 14 is equal to the solute flux through the $\gamma$/liquid interface represented by area $A_2$ on
Figure 14. These areas do not have the dimensions for a flux since Scheil partitioning of solute 2 eliminates the isothermal diffusion time dependance for the interface concentrations of both solutes, through the ternary tie-line relationship. The value of area $A_1$ on Figure 14 was calculated using the known values for interface position, $X_i = X_{i-1} + \Delta X^{\gamma/l}$, and the ends of the tie-line, $(C_1^1, C_2^1), (C_1^\gamma, C_2^\gamma)$.

5. The value of $A_2$ ($A_1 = A_2$), the integrated $\delta/\gamma$ Scheil mass balance for solute 2 (44) and equations (40) to (43) are used to calculate the new $\delta/\gamma$ interface position, $X_i = X_{i-1} - \Delta X^{\delta/l}$, and the tie-line.

6. An average value for the time, $\Delta t$, for either the $\gamma/l$ liquid or $\delta/\gamma$ interface to travel the distances $\Delta X^{\gamma/l}$ or $\Delta X^{\delta/l}$ respectively was retrieved using the interface solute balances for solute 1; it was obtained using the method described in the following paragraph, entitled: Procedure for Step 6.

7. Steps 1 to 6 are repeated for the duration of the isothermal diffusion period, defined by the cooling rate.

**Procedure For Step 6**

The equations (34) and (35) describing the relationship between the solute 1 $\delta$-ferrite and liquid concentrations, the austenite concentration gradient and interface position are not easily integrated. However, the variables $C_i(X), dC_i/dX, X_i^{\gamma/l}, dX_i^{\gamma/l}$ and $dt$ in equations (34)
and (35) can be separated and integrated using the equality of areas approximation because these variables are not time dependant, for the reason previously stated. The procedure by which this was done is illustrated with the austenite/liquid interface mass balance:

Solute $1...\gamma$/liquid interface

\[
C_1(1-k_1^{\gamma/2}) \frac{dx^{\gamma/2}}{dt} = (\frac{L}{2} - x^{\gamma/2}) \frac{dC_1}{dt} + D\gamma \frac{d\gamma}{dx} \Big|_{x=x^{\gamma/2}}
\]

\[
A_1 = \int [(1-k_1^{\gamma/2}) (C_1(x)) - (\frac{L}{2} - x) \frac{dC_1}{dx}] dx
\]

(i) The value for area $A_1$ shown in Figure 14 was calculated in
step 4.

(ii) A geometric approximation to the area, $A_3$, under the $(dC'/dX)|_{X=x_{1/2}}$ versus $X$ curve, over a distance $X$ was calculated using the values $x_{1/2}$, $\Delta x_{1/2}$ and the solute concentration at $X_i$ and $X_{i-1}$ calculated in step 5, as shown in Figure 15.

$$A_3 = \int \left[ \frac{dC'}{dX} \right]_{X=x_{1/2}}^X dX$$

$\frac{dC'}{dX}$ is a function of $X$

(iii) The average time for the liquid interface to move $X$ is given by: $\Delta t = A_1 / (D \times A_3)$. 
Figure 15 A Schematic Showing How The Area A3 Was Calculated In Order To Obtain An Approximate Solution To The Integral Of Equation (34).
5.0 Experimental Results and Model Predictions

Five sets of results are presented in this chapter: 1. A summary of observations made on the microstructure of plane front solidified Sn-1.21wt%Cd and Sn-2.58wt%Cd specimens. 2. Cooling curves and differential thermal curves used to determine the undercooling required for the nucleation of the primary and peritectic phases in tin-cadmium alloys containing, 1.06, 1.99, 3.13, 4.0wt%Cd (as weighed). Chemical analysis for each specimen after the cooling curves were obtained is given in each sub-section and observations on the microstructure of some of these specimens are also presented. 3. Calculations of values for thermodynamic factors which are important for nucleation of the peritectic phase on the primary phase/liquid interface. 4. Mathematical model predictions of the cadmium concentration in the liquid at the interface versus interface position, during the transient plane front solidification of the peritectic phase, β, in tin-cadmium alloys. 5. Mathematical model predictions of the delta-ferrite (δ)/austenite (γ) and austenite/liquid (l) interface tie-lines and fractions of delta-ferrite, austenite and liquid phase present during diffusion controlled growth of the peritectic phase (austenite) in an iron-carbon and an
iron-carbon-manganese alloy.

5.1 A Summary of the Solidification Conditions and Observations on the Microstructure of Plane Front Solidified Sn-1.21wt\%Cd and Sn-2.58wt\%Cd Specimens

Sn-1.21wt\%Cd

Five plane front solidified specimens of this alloy composition were produced; however, two were not usable for the purposes of this work due to problems with the specimen pushrod assembly during these two experiments. For the remaining three specimens, designated 12a, 12d and 12e, the solidification conditions and observations on the microstructure are summarized in Table I. The specimen travel velocity was 1.04x10^{-5} mm/s for all of these experiments; each experiment required approximately two and a half weeks for a specimen travel distance of 25 mm. The measured furnace temperature gradient at the center of the furnace was 2.5 K/mm, 2.2 K/mm and 1.9 K/mm for the three specimens 12a, 12d and 12e respectively.

Several microstructural features were observed to be common to all three specimens:
1. no evidence was found of an interface separating the solid phase grown during the experiment from the solid present at the beginning of solidification.
<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Composition (wt%Cd)</th>
<th>Furnace Temperature Gradient (K/mm)</th>
<th>Specimen Travel Velocity (mm/s)</th>
<th>Observations</th>
</tr>
</thead>
<tbody>
<tr>
<td>12a</td>
<td>1.207±0.010</td>
<td>2.5</td>
<td>1.74x10^-5</td>
<td>single phase α</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>no sign of initial s/l interface</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>quenched s/l interface is planar</td>
</tr>
<tr>
<td>12c</td>
<td></td>
<td>2.2</td>
<td></td>
<td>single phase α</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>no sign of initial s/l interface</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>quenched s/l interface is planar</td>
</tr>
<tr>
<td>12e</td>
<td></td>
<td>1.9</td>
<td></td>
<td>single phase α</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>no sign of initial s/l interface</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>quenched s/l interface is planar</td>
</tr>
</tbody>
</table>

2. The solid phase appeared to be single phase α in the optical micrographs; this is the 'high' temperature primary phase in the tin rich corner of the Sn-Cd phase diagram. The solid phase consisted of two or three 'columnar' grains as shown in Figure 16. Several small roughly elliptical discoloured patches were observed in the etched solid of

9. In this context, columnar grains are long, rectangular shaped grains with the longer boundary lying in a direction parallel to the solidification direction.
specimen 12e; these areas appeared to be randomly distributed in the solid phase. Scanning electron microscope examination of these areas showed a density of small holes which may be either etch pits in a more highly deformed region produced by metallographic polishing or a place where precipitates (possibly the Cd rich phase) might have been. 3. The solid/liquid interface was planar at the moment the specimen was quenched.

Sn-2.58wt%Cd

The results of these experiments are reported in two subsections. Group A specimens, numbered 25-1, 25-2, 25-4 and
25-7, were grown on a boron nitride surface. Group B specimens, numbered 25-5 and 25-6, were grown on a composite surface, composed of a rectangular piece of either pyrex or quartz, 9.5mm long, inset into the bed of the boron nitride crucible 22mm from the edge of the crucible, measured in the direction of solidification. Specimen 25-3 is included in this group although it was grown on a soda-lime microscope cover glass which replaced the normal bottom half of the boron nitride cell. The solidification conditions and observations of microstructure for these two groups are summarized in Tables II and III, respectively. The specimen travel velocity was 1.04x10^{-5} mm/s for six of the eight experiments; a velocity of 0.6x10^{-5} mm/s was used for specimen 25-4 and the average specimen travel velocity for specimen 25-5 was 1.67x10^{-5} mm/s. The measured temperature gradient at the center of the furnace was within the range of approximately 1.5 to 1.9K/mm for these experiments. The observations of the microstructure of the solidified specimens for Group A and Group B are described separately in the following two paragraphs.

**Group A.. Specimens Solidified on Boron Nitride Surface**

A combination of optical microscopy and wavelength dispersive x-ray spectrometry (WDS) revealed the following microstructures for specimens 25-1, 25-2 and 25-4.

No evidence was found in specimen 25-1 of an interface separating the solid produced during the experiment from the
solid present at the start of solidification. The solid phase grown in specimen 25-1 during the experiment was single phase α. Columnar grains were observed in this sample similar to those shown in Figure 16. The solid/liquid interface of specimen 25-1 at the moment the specimen was quenched was cellular. Optical microscopy indicated that the interface had degenerated from planar to cellular 2-3mm back from the quenched interface. Specimen 25-1 was cut into four 10mm long pieces and sent for chemical analysis. The results of that analysis from the four pieces are 1.667, 1.269, 1.473, 4.847wt%Cd, from initially solidified end to quenched liquid; the section of the specimen of average composition 4.847wt%Cd was comprised of quenched liquid and some α phase 2mm back from the quenched solid/liquid interface. The average cadmium content of the solid phase was 1.47wt%; this cadmium content is approximately 1.96 times the α phase peritectic cadmium content \(C_α = 0.75\text{wt}\%\text{Cd}\).

The portion of specimen 25-2 containing the initial solid/liquid interface was not prepared for metallographic examination. This specimen initially solidified as single phase α; β phase formed at a cellular α/liquid interface. Solidification of the β phase continued until the specimen was quenched. This specimen experienced two disturbances during solidification: 1. the pushrod velocity was increased from \(1.04\times10^{-5}\) mm/s to \(1.61\times10^{-5}\) mm/s for a period of time. Figure
17a is an optical micrograph which shows that 1.8 mm after the α/liquid interface degenerated to cellular, β phase covered the α/liquid interface. It had to be pushed past an obstruction in the furnace and it spent several days stationary in the furnace before it was quenched. There are two regions of large grained decomposed β phase separated by a fine grained region. This fine grained region, shown in Figure 17b, may be related to the period during which the specimen was pushed past an obstruction in the furnace; the final large grained region, near the quenched liquid interface, may have developed during the period where the specimen was stationary in the furnace before quenching. The solid/liquid interface was planar at the moment the specimen was quenched for specimens 25-2. Neither of the wavelength dispersive cadmium maps, Figures 17b and 17c, of the partially decomposed β region and the quenched solid/liquid interface region, respectively, provided any indication of the presence of decomposed β phase.

The initial solid formed in specimen 25-4 was α phase; after 2 mm of α phase solidification, some β phase formed at the center of the α/liquid interface. Solidification of both phases continued for approximately 0.3 mm at which point the α phase re-covered the entire solid/liquid interface; the α/liquid portion of interface was cellular during this transient. Degeneration of the α/liquid interface to cellular
<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Composition (wt%Cd)</th>
<th>Furnace Temperature (K)</th>
<th>Specimen Travel Gradient (K/mm)</th>
<th>Velocity (mm/s)</th>
<th>Observations</th>
</tr>
</thead>
<tbody>
<tr>
<td>25-1</td>
<td>2.581 ± 0.054</td>
<td>1.76</td>
<td></td>
<td>1.04 x 10^-5</td>
<td>Single phase α</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>quenched s/l interface is cellular, starting 2-3 mm back from the interface</td>
</tr>
<tr>
<td>25-2</td>
<td>=</td>
<td>1.83</td>
<td></td>
<td>1.04 x 10^-5</td>
<td>Single phase α; interface degenerated to cellular after an imposed specimen velocity disturbance.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>decomposed β phase</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>quenched s/l interface is planar</td>
</tr>
<tr>
<td>25-4</td>
<td>=</td>
<td>1.94</td>
<td></td>
<td>0.60 x 10^-5</td>
<td>Single phase α</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Initial α/l interface is visible</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Second s/l interface visible</td>
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<td>2 mm from the initial interface, the α/l interface degenerated to cellular and some β phase covered only the center portion of the α/l interface.</td>
</tr>
<tr>
<td></td>
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<td></td>
<td></td>
<td>The β phase disappeared (1.3 mm) and cellular solidification of α phase continued for 2.3 mm, until β phase covered the interface again.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>β phase solidification continued until the specimen was quenched.</td>
</tr>
<tr>
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<td></td>
<td></td>
<td></td>
<td>Quenched s/l interface is planar but ragged.</td>
</tr>
<tr>
<td>25-7</td>
<td>=</td>
<td>1.9</td>
<td></td>
<td>1.04 x 10^-5</td>
<td>Initially plane front α</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1 mm of partially decomposed β followed by 3-5 mm of recrystallized</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.5-0.8 mm of recrystallized columnar β grains followed by a transition region of partially decomposed and recrystallized β.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Planar quenched s/l interface.</td>
</tr>
</tbody>
</table>
Figure 17a An Optical Micrograph Of Specimen 25-2; α/liquid Interface Has Degenerated To Cellular. 25X

Figure 17b An Optical Micrograph Of The Fine Grained Decomposed β Phase Region Of Specimen 25-2. 10X
Figure 17c An Optical Micrograph Of The Region Near The Quenched Solid/Liquid Interface Of Specimen 25-2. 16X

Figure 17d A Wavelength Dispersive Cadmium Map Of The Re-solidified Region Near The Quenched Solid/Liquid Interface Of Specimen 25-2.
was most likely due to the fact that the specimen had stopped moving in the furnace for a period of time and had to be restarted. The presence of \(\beta\) phase in the cell boundaries removes the need for \(\beta\) phase nucleation at the interface; thereby increasing the probability of \(\beta\) phase growing on the \(\alpha/\text{liquid}\) interface. The \(\beta\) phase re-appeared at the \(\alpha/\text{liquid}\) interface after another 2.3 mm of cellular \(\alpha\) phase solidification. These three regions are visible in the macrograph shown in Figure 18a; the micrographs in Figures 18b, 18c and 18d provide a higher magnification view of these three regions. Solidification of the \(\beta\) phase continued until the specimen was quenched; Figures 18e and 18f are high magnification views of some areas in this region. The quenched solid/liquid interface was planar on a macro scale but ragged; Figure 18g is a high magnification view of the quenched \(\beta/\text{liquid}\) interface.

The solidification of specimen 25-7 was deliberately disrupted twice, for short periods of time. After 10mm of travel the specimen was quickly pushed 10mm into the cold end; after another 10mm of travel, the specimen travel velocity was increased to a value five times the initial velocity, for a duration of three hours. The speed was then decreased back to the initial velocity and the specimen solidified at this velocity for another five hours before it was quenched. Initially this specimen solidified as single phase \(\alpha\) with a
Figure 18a An Optical Micrograph of the Resolidified Region of Specimen 25-4. 3.32X

Figure 18b An Optical Micrograph of the Initial 2 mm of α Phase Solidification; β Phase Covers the Center Portion of the α/Liquid Interface. 25X
Figure 18c An Optical Micrograph Of The Final 2.3 mm Of α Phase Solidification: β Phase Covers The Entire α/liquid Interface. 25X

Figure 18d An Optical Micrograph Of The Cellular α/β Interface. 200X
Figure 18e An Optical Micrograph Of The Decomposed β Phase. 200X

Figure 18f An Optical Micrograph Of The Decomposed β Phase. 200X
planar interface; this phase is visible at the bottom of the macrograph of the sample shown in Figure 19a. For approximately 1mm beyond this, the solidified structure appears to be partially decomposed $\beta$ phase followed by 3 to 5mm of recrystallized $\beta$; it is possible that the partial decomposition $\beta$ phase observed in the region close to the interface was induced during metallographic preparation of the specimen. A 6 to 8mm long region of what appears to be recrystallized columnar $\beta$ grains follows next succeeded by a transitional region of partially decomposed and recrystallized $\beta$. Figures 19b, 19d and 19f are optical micrographs of the $\alpha/\beta$ interface, the transition zone 4-5 mm from the planar
quenched solid $\beta$/liquid interface and the solid $\beta$/liquid interface respectively. Figures 19c, 19e and 19g are WDS cadmium maps of these regions, respectively.
Figure 19b: An Optical Macrograph of the α/β Interface in Specimen 25-7. 50X

Figure 19c: A Wavelength Dispersive Cadmium Map of the Region 1 mm from the α/β Interface... Decomposed β Phase 25-7. 500X
Figure 19d: An Optical Macrograph Of The Decomposed β Phase Region 4-5 mm From The Quenched Solid/Liquid Interface In Specimen 25-7. 50X

Figure 19e: A Wavelength Dispersive Cadmium Map Of The Decomposed β Phase 4-5 mm From The Quenched Solid/Liquid Interface. 500X
Figure 19f An Optical Macrograph Of The Quenched Solid/Liquid Interface In Specimen 25-7. 50X

Figure 19g A Wavelength Dispersive Cadmium Map Of The Quenched Solid/Liquid Interface. 500X
Group B...Specimens solidified on a composite surface

Specimens 25-5 and 25-6 were grown on a boron nitride surface with a rectangular piece of pyrex and quartz, respectively, embedded in the bed of the crucible. Optical metallography of specimen 25-5 revealed that the specimen solidified in a dendritic mode during the entire specimen. The average travel velocity for this specimen was $1.67 \times 10^{-5}$mm/s; this velocity may have been fast enough to permit dendritic solidification of the specimen. This portion of specimen 25-5 containing the initial interface was not prepared for metallographic examination. Figure 20a and 20b are an optical micrograph and a WDS cadmium map of the region where the pyrex insert was located.

Optical metallography of specimen 25-6 revealed that the specimen solidified as a phase until it was quenched. Figure 21a is a micrograph of the quenched solid/liquid interface which shows the presence of two cell boundaries and a small region containing some peritectic and eutectic phase on the interface. Figure 21b is a 200X micrograph of the cell boundaries which shows more clearly the peritectic phase (darker) in the boundary; the two boundaries are less than 0.6mm long. The specimen was too thin for further polishing to remove the heavy deformation visible in Figure 21a.

Specimen 25-3 was solidified on a soda-lime microscope cover glass. The glass slide had to be cracked and pried off


<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Composition (wt%Cd)</th>
<th>Furnace Temperature (K)</th>
<th>Specimen Travel Gradient (K/mm)</th>
<th>Velocity (mm/s)</th>
<th>Observations</th>
</tr>
</thead>
<tbody>
<tr>
<td>25-5</td>
<td>2.581±0.054</td>
<td>1.48</td>
<td>1.67x10⁻⁵</td>
<td></td>
<td>.PYREX INSERT .dendritic α solidification</td>
</tr>
<tr>
<td>25-6</td>
<td>&quot;</td>
<td>1.62</td>
<td>1.04x10⁻⁵</td>
<td></td>
<td>.QUARTZ INSERT .WDS cadmium map shows the solid/liquid interface degenerated to cellular within 5 mm of the quenched solid/liquid interface. The WDS map provides no indication as to whether or not the solid was α or β phase.</td>
</tr>
<tr>
<td>25-3</td>
<td>&quot;</td>
<td>1.86</td>
<td>&quot;</td>
<td></td>
<td>.SCDA-LINE GLASS .4mm of uni-directional dendritically solidified α phase .4.5mm of non-directional, dendritically solidified α and β phase .uni-directional dendritically solidified α phase to the end of the sample</td>
</tr>
</tbody>
</table>

the specimen using the tip of a scalpel blade. Examination of this specimen in the optical microscope showed α phase dendrites had solidified uni-directionally for 4mm, from the beginning of solidification; Figure 22a is an optical micrograph of the initial solid/liquid interface. This was followed by 4.5mm of non-directional dendritic growth of both the α and β phase; this transition zone is shown the optical micrograph and WDS cadmium map of Figures 22b, 22c and 22d, respectively. Finally, unidirectional dendritic solidification of the α phase was re-established and continued to the end of the specimen; Figure 22e is an optical micrograph of this region.
Figure 20a: An optical micrograph of the dendritically solidified region of specimen 25-5 over the Pyrex insert. 25X

Figure 20b: A wavelength dispersive cadmium map of the dendritically solidified region of specimen 25-5 over the Pyrex insert.
Figure 21a An Optical Micrograph Of The
Quenched Solid/liquid Interface Of
Specimen 25-6. 12.5X

Figure 21b A Micrograph Of The Two Cell
Boundaries On The Quenched
Solid/liquid Interface Of Specimen
25-6. 200X
Figure 22a An Optical Micrograph Of The Initial Solid/Liquid Interface Of Specimen 25-3. 50X

Figure 22b An Optical Micrograph Of The Non-directionally Solidified α And β Phase Region Of Specimen 25-3. 50X
Figure 22c A Wavelength Dispersive Cadmium Map Of The Non-directionally Solidified α And β Phase Region Of Specimen 25-3.

Figure 22d A Wavelength Dispersive Cadmium Map Of The Non-directionally Solidified α And β Phase Region Of Specimen 25-3.
Figure 22c An Optical Micrograph Of The Second Region Of Uni-directionally Solidified $\alpha$ Phase Of Specimen 25-3. 50X
5.2 Results of Undercooling Experiments on Peritectic Tin-Cadmium Alloys

Cooling curves and differential thermal curves were obtained from these experiments for pure tin and four peritectic tin-cadmium alloys. The following data from the alloy specimen cooling curves is summarized in Table IV: the temperature at which solidification started, the temperature at which a recalcitrance maximum was observed, the temperature at which the peritectic transformation started and the eutectic temperature. A cooling curve for pure tin is presented in Figure 23; the melting temperature obtained from such cooling curves was 505.4±2.2K, in reasonable agreement with the known melting point of 505.97K (231.97°C).

Sn-4wt%Cd

Several cooling curves and differential thermal curves were obtained for a Sn-4wt%Cd specimen (composition as weighed). The final alloy concentration as determined by chemical analysis after the cooling curves were obtained was 2.003±0.009wt%Cd. Figures 24 and 25 show three cooling curves and differential thermal curves obtained for this alloy specimen. The data from these curves is summarized in Table IV. The start of solidification was indicated by the first deviation of the differential curve from a straight line. The
TABLE IV
A Summary Of The Phase Transformation Temperatures Versus Alloy Composition From the Bulk UnderCooling Experiments

<table>
<thead>
<tr>
<th>Composition (wt% Cd)</th>
<th>$T_{\text{start solid}}$</th>
<th>$T_{\text{max recal}}$</th>
<th>$T_{\text{start transf}}$</th>
<th>$T_{\text{start eutect}}$</th>
<th>$T_{\text{end eutect}}$</th>
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</thead>
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<tr>
<td></td>
<td>$\pm 2.2K$</td>
<td>$\pm 2.2K$</td>
<td>$\pm 2.2K$</td>
<td>$\pm 2.2K$</td>
<td>$\pm 2.2K$</td>
</tr>
<tr>
<td>Sn-4wt% Cd</td>
<td>495.80</td>
<td>494.22$^1$</td>
<td>460.38</td>
<td>452.77</td>
<td></td>
</tr>
<tr>
<td></td>
<td>491.41</td>
<td>496.22</td>
<td>447.53</td>
<td>443.08</td>
<td></td>
</tr>
<tr>
<td></td>
<td>491.66</td>
<td>499.42</td>
<td>496.17</td>
<td>461.00</td>
<td>454.98</td>
</tr>
<tr>
<td>Sn-3wt% Cd</td>
<td>491.87</td>
<td>493.37</td>
<td></td>
<td>(2)</td>
<td>(2)</td>
</tr>
<tr>
<td></td>
<td>491.80</td>
<td>498.15</td>
<td>495.19</td>
<td>447.53</td>
<td>440.53</td>
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<td>492.05</td>
<td>498.28</td>
<td>495.55</td>
<td>447.53</td>
<td>441.78</td>
</tr>
<tr>
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<td>499.02</td>
<td>494.55</td>
<td>460.38</td>
<td>452.77</td>
</tr>
<tr>
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<td>498.14</td>
<td>500.00</td>
<td>494.80</td>
<td>(3)</td>
<td>(3)</td>
</tr>
<tr>
<td></td>
<td>495.30</td>
<td>498.03</td>
<td>494.80</td>
<td>446.28</td>
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<tr>
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<td>489.58$^6$</td>
<td>504.90$^6$</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Sn-1.914wt% Cd$^5$</td>
<td>498.28</td>
<td>500.00</td>
<td>496.05</td>
<td>459.05</td>
<td>452.77</td>
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<td>Sn-1wt% Cd</td>
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</tr>
<tr>
<td></td>
<td>491.58</td>
<td>501.75</td>
<td>493.51</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pure Sn</td>
<td>494.80</td>
<td>505.73</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>495.08</td>
<td>506.08</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

1. Small arrest not associated with a second peak on the differential thermal curve
2. No differential thermal curve recorded
3. No discernible peak on the differential thermal curve
4. Curves obtained from a specimen that was not melted under flux
5. Nucleation of the solid phase initiated by insertion and removal of a piece of metal wire
6. A slight change in slope observed on the cooling and differential thermal curve
Figure 23 A Cooling Curve For Pure Tin Obtained From The Bulk Undercooling Experiments.

Figure 24 Cooling Curves For Sn-4wt%Cd Specimen Obtained From Bulk Undercooling Experiments.
observed solidification start temperature in three successive runs (curves a, b and c in Figure 24) was $495.8 \pm 2.2\, K$, $491.4 \pm 2.2\, K$ and $491.7 \pm 2.2\, K$. These temperatures are $2.2\, K$, $4.6\, K$ and $4.3\, K$ below the peritectic temperature ($496\, K$), respectively. The temperature at which a maximum in recalescence was observed is $496.2 \pm 2.2\, K$ and $499.4 \pm 2.2\, K$ for curves (b) and (c) respectively; the $\alpha$ liquidus temperature for a Sn-$4.0\, wt\%$ Cd alloy is $495.1\, K$ and it is calculated using the data published by Hanson and Pell-Walpole. The start of a second peak on the differential thermal curve, for the second experiment with this alloy, signalled the start of the peritectic transformation at $496.2 \pm 2.2\, K$. A slight change in
the slope of the cooling curve was observed at this temperature. No second peak was observed on the differential thermal curve for the first and second experiments. A third small peak was observed on the three differential thermal curves over the temperature range 461K to 443K: the eutectic temperature is 449K for this alloy system. Optical metallography of an area near the thermocouple showed the microstructure of this specimen to be α dendrites, with interdendritic β phase and eutectic as shown in Figure 26.

Sn 2–3wt% Cd

The appropriate amounts of tin and cadmium were mixed to provide alloys containing 2 and 3wt% Cd. The cadmium concentration for the Sn-2wt% Cd alloy, determined by chemical analysis after the cooling curves were obtained is 0.039±0.004; it is not representative of the alloy composition for the first three experiments. No flux was used the fourth time a cooling curve was obtained for this specimen; the temperature at which maximum recrystallization occurred was essentially the melting temperature of pure tin. This fact taken in conjunction with the finding that no indication of a peritectic transformation nor a eutectic reaction was observed on the differential thermal curve indicated that a substantial amount of cadmium was lost had occurred during the fourth experiment. The cadmium
concentration for the Sn-3wt% Cd alloy was 1.777±0.006, after
the cooling curves were obtained. Figures 27, 28 and 29, 30
show the cooling curves and differential thermal curves for
the 2 and 3wt% Cd alloys respectively. The data from these
curves is summarized in Table IV. The start of solidification
was indicated by the first deviation of the differential curve
from a straight line. The average value of the observed
solidification start temperatures is 497.0±2.2K and 491.9±2.2K
for the 2wt% Cd and 3wt% Cd alloys respectively; the peritectic
temperature is 496K. The average value of the observed
temperature at which a maximum in recalescence occurred was
499.0±2.2K and 496.9±2.2K; the α phase liquidus temperature
for these two alloy compositions are 499.6K and 495.9K,
respectively. The start of a second peak on the differential
thermal curve signalled the start of the peritectic
transformation at 494.7±2.2K and 495.4±2.2K, for the two
alloys respectively. A slight change in slope of the cooling
curves was observed. A third small peak was observed on the
differential thermal curve over the temperature range 460K to
440K. Optical metallography of an area near the thermocouple
showed the microstructure of the Sn-3wt% Cd specimen to be α
dendrites with interdendritic β phase and eutectic as shown in
Figure 31.

Figure 32 shows the cooling curve and differential
thermal curve for a Sn-1.914wt% Cd alloy, for which nucleation
Figure 26  An Optical Micrograph of the Sn-4wt%Cd Specimen Taken After All the Cooling Curves Were Obtained. (Final Alloy Composition: Sn-2.003 \pm 0.009wt%Cd). 50X

Figure 27  Cooling Curves For The Sn-2wt%Cd Specimen Obtained From The Bulk Undercooling Experiments.
Figure 28 Differential Thermal Curves For The Sn-2wt\%Cd Specimen Obtained From The Bulk Undercooling Experiments.

Figure 29 Cooling Curves For The Sn-3wt\%Cd Specimen Obtained From The Bulk Undercooling Experiments.
Figure 30 Differential Thermal Curves For The Sn-3wt%Cd Specimen Obtained From The Bulk Undercooling Experiments.

Figure 31 An Optical Micrograph Of The Sn-3wt%Cd Specimen Taken After All The Cooling Curves Were Obtained. (Final Alloy Composition: Sn-1.777 ± 0.006wt%Cd). 50X
of the solid phase was initiated by quickly inserting in and removing from the melt a piece of metal wire, at a temperature just below the liquidus temperature for this alloy. The solidification start temperature was 498.3±2.2K. The temperature at which maximum recalcitrance was observed is 500.0±2.2K. The start of the second peak on the differential curve was observed at 496.0±2.2K. A third small peak was observed on the differential thermal curve, over the temperature range 459.1±2.2K to 452.8±2.2K.

Sn-1wt%Cd

The cadmium concentration determined by chemical analysis after the cooling curves were obtained is 0.072. Figures 33 and 34 show representative cooling curves and differential thermal curves for this alloy. The values of the temperature at which solidification started are 498.5±2.2K and 491.6±2.2K, for the two successive experiments. The temperature at which a maximum in recalcitrance occurred was 500.8±2.2K and 501.8±2.2K for the two experiments; the α phase liquidus temperature is 501.9K. A slight change in the slope of the cooling and differential thermal curve suggested the possibility of a peritectic transformation occurring in these specimens. The temperature at which the peritectic transformation was observed to start are 494.2±2.2K and
493.2±2.2K. No third peak was observed on the differential thermal curve near the eutectic temperature.
Figure 33 Cooling Curves For The Sn-1wt%Cd Specimen Obtained From The Bulk Undercooling Experiments.

Figure 34 Differential Thermal Curves For The Sn-1wt%Cd Specimen Obtained From The Bulk Undercooling Experiments
5.3 Calculation of Thermodynamic Variables for the Nucleation of the Peritectic Phase at a Planar Primary Phase/Liquid Interface

The Thomson and Spaepen\textsuperscript{26} calculations were carried out for a Sn-2.5wt\%Cd alloy, solidifying with a cadmium concentration in the $\alpha$ and liquid phases at the interface of 1.5wt\% Cd and 7.6 (7.5988) wt\%Cd respectively; the value 1.5wt\%Cd is the average value of cadmium concentrations in the $\alpha$ phase obtained in specimen 8c, 1.269 to 1.667wt\%Cd. The $\alpha$ liquidus temperature for a cadmium concentration in the liquid of 7.60wt\% is 486.23K; the $\beta$ liquidus temperature is 487.58K. The $\alpha$/liquid interface temperature is 1.35K below the $\beta$ liquidus temperature and it is 9.77K below the peritectic temperature. For the purpose of these calculations, the value of the temperature at the $\alpha$/liquid interface was varied over a temperature range up to 175K below the $\beta$ liquidus temperature and values for the following thermodynamic factors were calculated at each temperature:

- the composition of the $\beta$HCP nucleus,
- the molar volume and entropy of fusion of the $\beta$HCP phase,
- the interfacial free energy for the $\beta$HCP/liquid interface,
- the Gibbs volume free energy for solidification of the $\beta$HCP phase,
- the critical nucleus' diameter,
the Gibbs free energy for homogeneous and heterogeneous nucleation of the BHCP phase,
the steady state homogeneous and heterogeneous nucleation rate,
The free energy for heterogeneous nucleation and the steady state nucleation rate of the BHCP phase was calculated for several different values of the surface free energy for the \( \alpha/\text{BHCP} \) interface, i.e. 100, 75, 59, 40, 30, 20, 10, 5 \text{nmJ/m}^2. Calculations of free energy for heterogeneous nucleation and the steady state nucleation rate were repeated for a \( \beta \text{SHP} \) phase, using the following values for the \( \beta \text{SHP/liquid surface free energy: 55, 50, 40, 30, 20, 10, 5nmJ/m}^2, \) and the values given above for the \( \alpha/\beta \) interfacial free energy. The data from these calculations dealing with the subject of homogeneous and heterogeneous nucleation of the BHCP phase at the \( \alpha/\text{liquid} \) interface are presented separately in the sub-sections below.

**Homogeneous Nucleation of the BHCP Phase at a Planar \( \alpha/\text{Liquid} \) Interface**

Figure 35 is a plot of the calculated cadmium concentration of a critical size BHCP nucleus versus the \( \alpha/\text{liquid} \) interface temperature. The same data are superimposed upon a plot of the equilibrium \( \beta \) solidus in Figure 36. The \( \beta \) solidus composition at the \( \beta \) liquidus temperature for the
liquid at the α/liquid interface is Sn-4.1994wt%Cd. At all values of undercooling, 1.35K to 175K, the cadmium concentration of the nucleus which varies from, 4.18 to 1.85wt%Cd with decreasing undercooling, lies well within the β phase field of the tin-cadmium phase diagram. Graphs of the calculated values of the molar volume and entropy of fusion for the βHCP phase as a function of interface temperature are presented in Figures 37 and 38. The values of the molar volume range from 16.14×10⁻³ to 16.22×10⁻³ mm³/mol for interface temperatures within the range 486.23K to 313K. For the purposes of comparison, the molar volume of pure Sn and pure Cd are 16.28×10⁻³ mm³/mol and 12.99×10⁻³ mm³/mol, respectively. Values of the entropy of fusion, for solidification of an βHCP phase from liquid of cadmium composition 7.60wt%Cd, ranged from 17.29 to 17.47 J/molK for interface temperatures within the range 486.23K to 313K. The entropy of fusion ΔS, of pure Sn and pure Cd are 13.21 J/molK and 10.29 J/molK; pure tin at these temperatures has a body centered tetragonal crystal structure (B.C.T), while pure cadmium is hexagonal close packed (H.C.P). For these calculations the entropy of fusion of pure tin solidifying to a hexagonal close packed (ΔGI) was required. The calculated entropy of fusion for the solidification of pure tin to the hexagonal closed packed structure was obtained from calculations of lattice stability.
Figure 35 A Plot Of The Calculated Cadmium Concentration Of A Critical Size $\beta$HCP Nucleus As A Function Of Temperature. (The dependant variable is plotted on the abscissa for comparison with Figure 36).

Figure 36 A Plot Of A Portion Of The Sn-Cd Phase Diagram ... $\beta$ Phase Solidus With Data Of Figure 35 Superimposed Upon This Plot.
Figure 37 A Plot Of The Calculated Value Of The Molar Volume Of The $\beta$HCP Phase As A Function Of Temperature.

Figure 38 A Plot Of The Calculated Value Of The Entropy Of Fusion For The $\beta$HCP Phase As A Function Of Temperature.
(\Delta G^0) using tin-cadmium phase diagram data, giving the value 17.61J/molK.

Figures 39, 40 and 41 are graphs showing the interfacial free energy of the BHCP/liquid interface, the diameter of the critical size BHCP nucleus and the Gibbs volume free energy for solidification of the BHCP phase as a function of interface temperature. The calculated values for the interfacial free energy of the BHCP/Liquid interface lie within the range 13.06 to 86.91mJ/m² for interface temperatures of 486.23K to 313K; for the purposes of comparison, the \(\alpha\)/liquid interface energy of pure tin is 59mJ/m². A diameter of 0.369x10⁻³mm was obtained for a critical size BHCP nucleus at a planar \(\alpha\)/liquid interface with an interface temperature of 486.23K. Figures 42 and 43 show the Gibbs free energy for the nucleation of critical size BHCP nuclei and the steady state nucleation rate for homogeneous nucleation of this phase, both as a function of temperature. The Gibbs free energy for homogeneous nucleation of critical size BHCP nuclei is 19.14x10⁻¹⁵J at a temperature of 486.23K; this value decreases to 30.83x10⁻²⁰J at an interface temperature of 313K. The steady state nucleation rate plotted in Figure 43 is 3.18x10⁻²mm⁻³s⁻¹ at an undercooling of -170K, below the BH liquidus temperature.
Heterogeneous Nucleation of the βHCP Phase at a Planar α/liquid Interface

Figure 44 and 45 are graphs showing the free energy for heterogeneous nucleation and the steady state heterogeneous nucleation rate of critical size βHCP nuclei as a function of interface temperature, respectively, for several values of $\gamma^a/\betaHCP$, ie. (100, 59, 20 and 1mJ/mm$^2$). The nucleation rate is greater than $10^{-4}$mm$^{-3}$s$^{-1}$ at approximately 165, 135, 100 and 80K undercooling, respectively, for the values of $\gamma^a/\betaHCP$ given above. These values are at least an order of magnitude greater than the values obtained in the undercooling experiments, ~1-2K. Some values of the steady state nucleation rate as a function of interface temperature and α/βHCP interfacial free energy are tabulated in Table V. The free energy for nucleation and steady state nucleation rate of a βSHP phase was calculated as a function of temperature, βSHP/liquid interfacial energy (55, 50, 40, 30, 20, 10, 5mJ/m$^2$) and α/βSHP interfacial energy (55, 50, 40, 30, 20, 10, 5mJ/m$^2$); the value of the βSHP/liquid interfacial energy is unknown at present. Some calculated values of the nucleation rate at undercoolings of 2.6K, 4.6K and 9.6K versus $\gamma^{\betaSHP/l}$, $\gamma^{a/\betaSHP}$ are given in Table VI.
Figure 39 A Plot Of The Calculated Value Of The Interfacial Free Energy Of The βHCP/Liquid Interface as A Function Of Temperature.

Figure 40 A Plot Of The Calculated Value Of The Diameter Of A Critical Size βHCP Nucleus As A Function Of Temperature.
Figure 41 A Plot Of The Calculated Values Of The Gibbs Volume Free Energy For Solidification Of the βHCP Phase As A Function Of Temperature.

Figure 42 A Plot Of The Gibbs Free Energy For Homogeneous Nucleation Of A Critical Size βHCP Nucleus As A Function Of Temperature.
Figure 43 A Plot Of The Steady State Homogeneous Nucleation Rate As A Function Of Temperature.

Figure 44 A Plot Of The Free Energy For Heterogeneous Nucleation Of A Critical Size $\beta$HCP Nucleus As A Function Of Temperature, For $\gamma_{\beta \beta} = 100, 59, 20, 1\text{mJ/m}^2$. 
Figure 45 A Plot Of The Heterogeneous Nucleation Rate Of A Critical Size βHCP Nucleus As A Function Of Temperature, For $\gamma^{a/b} = 100, 59, 20, \text{lmJ/m}^2$. 
<table>
<thead>
<tr>
<th>T (K)</th>
<th>α/βHCP Interfacial Free Energy (mJ/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>100.0</td>
</tr>
<tr>
<td>423</td>
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<td>313</td>
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### TABLE VI

Selected Values Of The βSHP Phase Steady State Heterogeneous Nucleation Rate (mm$^3$s$^{-1}$) As A Function Of Undercooling, βSHP/liquid And α/βSHP Interfacial Energy

<table>
<thead>
<tr>
<th>$\gamma_{\beta S H P/\beta}$ (mJ/m$^2$)</th>
<th>$\gamma_{\alpha/\beta S H P}$ (mJ/m$^2$)</th>
<th>Undercooling</th>
<th>2.6K</th>
<th>4.6K</th>
<th>9.6K</th>
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<td>55</td>
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<td>0.0</td>
<td>7.6x10$^{-56}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>1.7x10$^{-52}$</td>
<td>1.5x10$^5$</td>
<td>6.0x10$^{23}$</td>
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<tr>
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<td>10</td>
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<td>5.0x10$^{-1}$</td>
<td>1.8x10$^{28}$</td>
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<tr>
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<td>20</td>
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<td>10.0x10$^{-10}$</td>
<td>3.8x10$^{26}$</td>
<td></td>
</tr>
<tr>
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<td>30</td>
<td>2.9x10$^{-247}$</td>
<td>7.8x10$^{-57}$</td>
<td>9.4x10$^{22}$</td>
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</tr>
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<td>0.0</td>
<td>1.2x10$^{-250}$</td>
<td></td>
</tr>
</tbody>
</table>
5.4 Mathematical Model Predictions for the Transient Plane Front Solidification of the Peritectic Phase in Tin -Cadmium Alloys

The mathematical model described in Section 3.3 was developed to predict whether or not cadmium concentrations and interface temperatures could be obtained in the liquid at the peritectic phase/liquid interface, which would be conducive to nucleation of a new band of primary phase, after some period of peritectic phase (β) solidification. Steady state solidification of the α phase is assumed to be established on extensions of the α liquidus and solidus lines. Figure 46 shows the calculated steady state cadmium profile in the liquid ahead of the α/liquid interface for four values of velocity, 8.5x10⁻³ mm/s, 4.25x10⁻³ mm/s, 1.7x10⁻³ mm/s and 1.7x10⁻⁵ mm/s. The β phase is nucleated and instantly covers the planar α/liquid interface. Transient growth of the β phase occurs during which the solute that had accumulated in the solute diffusion layer ahead of the α/liquid interface is used up, since the β phase solidifies at higher cadmium concentrations than the α phase; this is described by the phrase 'α solute layer depletion'¹⁰ in this section. The

¹⁰. The phrase, 'α solute layer depletion' describes the situation where the initial stages of β solidification uses up the solute that had accumulated in the diffusion layer ahead of the α/liquid interface, prior to the appearance of
model assumes that the steady state velocity of the \( \alpha \)/liquid interface, prior to the appearance of the peritectic phase, and the temperature gradient in the liquid are equal to the value of the specimen travel velocity and the furnace temperature gradient, respectively. Calculations of solute concentration and interface position stop when '\( \alpha \) solute layer depletion' ends.

Mathematical model predictions of cadmium concentration in the liquid at the \( \beta \)/liquid interface as a function of interface position are presented as graphs in this section for: two alloy compositions, Sn-1.3wt\%Cd and Sn-2.5wt\%Cd, at two values of furnace temperature gradients, 31.7 and 1.8K/mm, and two values of specimen travel velocities, \( 8.5 \times 10^{-3} \) and \( 1.74 \times 10^{-5} \) mm/s. These values define the limits of the solidification conditions under which Sn-Cd alloys have been solidified in work presented in the literature\(^1\) and this experimental work. Observations for peritectic tin-cadmium alloys solidified under these conditions as to whether or not banding occurred are available for comparison with that predicted by the model. Model predictions are presented separately for the following solidification conditions: (a) the \( \beta \) phase. It is considered over if either the solute is used up or the solute gradient in the liquid ahead of the interface can no longer sustain interface motion. This idea is elaborated further in the section containing the discussion of these results.
different steady state α/liquid interface velocities at a constant value for the temperature gradient in the liquid and a constant value for the steady state velocity for different values of the temperature gradient in the liquid. (b) moving isotherms (i.e., moving furnace) versus stationary isotherms. and (c) a comparison of the solidification path for intermediate values of steady state α/liquid interface velocity i.e. $4 \times 10^{-3}$ mm/s and $1.7 \times 10^{-3}$ mm/s with that for the velocities used for the first three conditions. Observations of the microstructure of peritectic tin-cadmium alloys solidified at these velocities is also available in the literature.

**Variations of the Steady State α/Liquid Interface Velocity and Temperature Gradient in the Liquid**

**Different Velocities at a Constant Temperature Gradient**

Figures 47 and 48 show plots of cadmium concentration in the liquid at the interface as a function of interface position, along the length of the specimen, for an alloy of composition Sn-1.3 wt% Cd. The value of the distance moved by the interface on these plots is measured from the point at which the B phase nucleated. The temperature gradients
Figure 46 A Plot Of The Cadmium Profile In The Diffusion Layer Ahead Of The Steady State α/liquid Interface. C₀=1.3 wt% Cd

Figure 47 A Plot Of Cadmium Concentration In The Liquid At The β/liquid Interface Versus Interface Position With Respect To The Previous α/liquid Interface. C₀=1.3 wt% Cd... G=31.7 K/mm
Figure 48 A Plot Of Cadmium Concentration In The Liquid At The β/liquid Interface Versus Interface Position With Respect To The Previous α/liquid Interface. 
C₀ = 1.3wt%Cd....G = 1.8K/mm

are 31.7K/mm and 1.8K/mm for these figures, respectively; the steady state α/liquid interface velocities are 8.5x10⁻³mm/s and 1.7x10⁻⁵mm/s in each figure. Figure 49 is a plot of these same variables for a bulk alloy composition of 2.5wt%Cd and temperature gradient of 31.7K/mm.

The values for the total distance the interface moves assumes that the 'α solute layer depletion' portion of β phase solidification has ended. Given a temperature gradient of 31.7K/mm in the liquid and an alloy composition of Sn-1.3wt%Cd, the predicted value of the total distance that the β/liquid interface would move is 133x10⁻³mm and 12.9x10⁻³mm, for steady state α/liquid interface velocities of 8.5x10⁻³mm/s
and $1.7 \times 10^{-5} \text{mm/s}$, respectively, before 'α solute layer depletion' would end. The β/liquid interface of a Sn-2.5wt% Cd specimen would move a total distance of $110 \times 10^{-3} \text{mm}$ for a steady state α/liquid interface velocity of $8.5 \times 10^{-3} \text{mm/s}$. Given a temperature gradient of $1.8 \text{K/mm}$ and an alloy composition of Sn-1.3wt% Cd, the predicted total distance that the β/liquid interface would move is $123 \times 10^{-3} \text{mm}$ and $25.3 \times 10^{-3} \text{mm}$, for steady state α/liquid interface velocities of $8.5 \times 10^{-3} \text{mm/s}$ and $1.7 \times 10^{-5} \text{mm/s}$ respectively.

The final cadmium concentration in the liquid at the interface is the liquid concentration at the end of the 'α
solute layer depletion' portion of β phase solidification. Given a temperature gradient of 31.7K/mm, an alloy containing 1.3wt% Cd is predicted to have a final cadmium concentration in the liquid at the interface of 5.8828wt% Cd and 6.9571wt% Cd for steady state α/liquid interface velocities of 8.5x10^{-3}mm/s and 1.7x10^{-5}mm/s respectively. An alloy containing 2.5wt% Cd is predicted to have a final cadmium concentration in the liquid at the interface of 13.7243wt% Cd for a steady state α/liquid interface velocity of 8.5x10^{-3}mm/s. Given a temperature gradient of 1.8K/mm, an alloy containing 1.3wt% Cd is predicted to have a final cadmium concentration in the liquid at the interface of 6.9129wt% Cd and 6.9649wt% Cd for steady state α/liquid interface velocities of 8.5x10^{-3}mm/s and 1.7x10^{-5}mm/s respectively.

Constant Velocity and Different Temperature Gradients

Figures 50 and 51 are essentially a re-arrangement of the data presented in Figures 47 and 48. Given the steady state α/liquid interface velocity of 8.5x10^{-3}mm/s and an alloy composition of Sn-1.3wt% Cd, the model predicts that the β/liquid interface would have moved approximately the same distance, 133x10^{-3}mm and 123x10^{-3}mm, for temperature gradients of 31.7K/mm and 1.8K/mm respectively. Given a steady state α/liquid interface velocity of 1.7x10^{-3}mm/s the β/liquid interface for this alloy would have moved further for the low
Figure 50 A Plot Of Cadmium Concentration In The Liquid At The β/liquid Interface Versus Interface Position With Respect To The Previous α/liquid Interface. C₀=1.3wt%Cd. V=8.5x10⁻⁷mm/s

Figure 51 A Plot Of Cadmium Concentration In The Liquid At The β/liquid Interface Versus Interface Position With Respect To The Previous α/liquid Interface. C₀=1.3wt%Cd. V=1.7x10⁻⁷mm/s
value of temperature gradient 1.8K/mm, than for a gradient of 31.7K/mm, ie. 25.2x10^{-3}mm versus 12.9x10^{-3}mm. The higher the temperature gradient in the liquid, at a given value of steady state α/liquid interface velocity, the lower is the final value of the cadmium concentration in the liquid at the interface predicted to be, ie. 5.8828wt%Cd versus 6.9129wt%Cd, when the 'α solute layer depletion' portion of β phase solidification ends.

Predictions for a Moving Isotherm Versus a Stationary Isotherm

In section 3.2.2 it was suggested that for a stationary isotherm condition, ie. specimen stationary in the furnace, during the 'α solute layer depletion' part of peritectic phase solidification, the final value of the cadmium concentration in the liquid at the interface would be the lowest possible for the system, compared to that for moving isotherms. Figures 52 and 53 show plots of the cadmium concentration in the liquid at the interface as a function of the interface position for stationary and moving isotherms, at two steady state α/liquid interface velocities, 8.5x10^{-3}mm/s and 1.7x10^{-5}mm/s respectively, for an alloy composition of 1.3wt%Cd and a liquid temperature gradient of 31.7K/mm. The velocity of the moving isotherm (specimen travel velocity) is equal to the steady state α/liquid interface velocity.

The predicted value of the total distance that the
Figure 52 A plot of cadmium concentration in the liquid at the β/liquid interface versus interface position for a stationary and a moving specimen $C_0=1.3$ wt% Cd, $G=31.7$ K/mm, $V=8.5 \times 10^{-3}$ mm/s.

Figure 53 A plot of cadmium concentration in the liquid at the β/liquid interface versus interface position for a stationary and a moving specimen $C_0=1.3$ wt% Cd, $G=31.7$ K/mm, $V=1.7 \times 10^{-3}$ mm/s.
The predicted value of the final cadmium concentration in the liquid at the interface is 4.828 wt% Cd and 5.8828 wt% Cd for stationary and moving isotherms, respectively, given an α/liquid steady state velocity of 8.5x10^{-3} mm/s. The predicted cadmium concentration in the liquid at the interface is 6.9464 wt% Cd and 6.9571 wt% Cd for stationary and moving isotherms, respectively, given a steady state α/liquid interface velocity of 1.7x10^{-5} mm/s.

Predictions for Intermediate Values of a Steady State α/Liquid Interface Velocity

Figure 54 shows a plot of the cadmium concentration in the liquid at the interface as a function of interface position for steady state α/liquid interface velocities of 8.5x10^{-3} mm/s and 4.25x10^{-3} mm/s and a temperature gradient of 31.7K/mm in the liquid. The predicted value of the total distance the B/liquid interface would move is 233x10^{-3} mm and 260x10^{-3} mm versus 133x10^{-3} mm for a steady state α/liquid
interface velocity of $4.25 \times 10^{-3} \text{mm/s}$, $1.7 \times 10^{-3} \text{mm/s}$ and $8.5 \times 10^{-3} \text{mm/s}$ respectively. The model predicted that the final cadmium concentration in the liquid at the interface is 5.4 wt% Cd and 6.130 wt% Cd versus 5.8827 wt% Cd for these velocities, respectively. Figure 55 shows a comparison of the plots of the solute concentration in the liquid at the interface as a function of interface position for stationary and moving isotherms, given a steady state $\alpha$/liquid interface velocity of $4.25 \times 10^{-3} \text{mm/s}$. The predictions of the final solute concentration in the liquid at the interface are 6.5968 wt% Cd and 5.4 wt% Cd for a stationary isotherm and one moving at
Figure 55 Cadmium Concentration In The Liquid At The 
β/liquid Interface Versus Interface Position 
For A Stationary And A Moving Specimen. 
\( V=4.25 \times 10^{-3} \text{mm/s} \), \( C_0=1.3 \text{wt}\% \text{Cd} \), \( G=31.7K/\text{mm} \)

the specimen travel velocity of \( 4.25 \times 10^{-3} \text{mm/s} \), respectively. Similar predictions of final cadmium concentration are obtained for a steady state \( \alpha/\text{liquid} \) interface velocity (equal to the specimen travel velocity) of \( 1.7 \times 10^{-3} \text{mm/s} \): 6.9211wt\% Cd and 6.130wt\% Cd for a stationary and a moving isotherm respectively. The values predicted for distance moved by the interface and final cadmium concentration in the liquid at the interface as a function of velocity and temperature gradient are contrary to those obtained for the limiting conditions. The linear geometric approximations used in the model to solve the transient solidification problem are no longer appropriate
at a certain stage in the calculations for these velocities; this will be elaborated upon in the discussion of these results.

5.5 Model Predictions for Diffusion Controlled Peritectic Phase Growth for Iron-Carbon Based Alloys

In Chapter 4 a theoretical framework was presented which facilitates an understanding of how coupling amongst those factors controlling the peritectic transformation govern microsegregation of solute during the transformation. The material presented in the following two sub-sections on binary and ternary iron-carbon alloys is used in the discussion presented in Section 6.2, to frame a response to three basic questions with respect to solute segregation and the diffusion controlled peritectic transformation:

1. what factors control the transformation in a binary alloy?
2. do the same factors or different ones control the transformation in the ternary system?
3. if different factors control the transformation in a ternary system then what are the reasons for this?

Predictions of δ-ferrite (δ)/austenite (γ) and austenite/liquid (l) phase fractions and carbon concentration at the interfaces as a function of various combinations of cooling rate and carbon diffusivity in austenite, based on the
conceptual model presented in Section 4.1, for a binary iron-carbon alloy (Fe-0.12wt%C) are presented in the subsection entitled 'Peritectic Iron-Carbon Alloy'. The cooling rates used in these calculations were 2.5K/s, 2.5x10⁻¹K/s, 2.5x10⁻²K/s and 2.5x10⁻⁴K/s; these cooling rates are order of magnitude variations of the cooling rate used by Chuang and Schwerdtfeger¹⁹ in their work on binary iron-carbon alloys. The carbon diffusivity was varied over four orders of magnitude, by multiplying the value of the temperature dependant diffusivity of carbon in austenite (0.761*exp(-16109/T+273)) by 10⁻² and 10⁻⁴. Predictions of initial and final ternary interface tie-lines for the isothermal diffusion period at two temperatures, 1759K and 1752K, are required in order to illustrate the concepts elaborated in Section 4.2. These predictions for a ternary alloy (Fe-0.12wt%C-1.5wt%Mn) are presented in the subsection titled 'Peritectic Iron-Carbon-Manganese Alloy'. The carbon and manganese concentrations of these alloys are representative of the Mn and C content of a plain carbon peritectic steel for plate and tubular applications.

Peritectic Iron-Carbon Alloy

The model assumes that the austenite phase appears at the binary peritectic temperature of 1766K. The transformation finish temperature and temperature range for several
diffusivity and cooling rate combinations are presented in Table VII. The dividing line drawn through Table VII separates diffusivity and cooling rate combinations for which the liquid phase is predicted to disappear from those for which the δ-ferrite phase is predicted to disappear, at the end of the transformation. Figures 56 and 57, 58 and 59, 60 and 61, show plots of the carbon concentration in the δ-ferrite and liquid phases at their respective interfaces as a function of interface position, in a volume element of width $180 \times 10^{-3}$mm, for a given value of carbon diffusivity and varying cooling rate. All concentrations are expressed as mole fraction in the calculations instead of weight percent carbon, in order to facilitate a comparison with the ternary alloy predictions, 0.12wt% C is equal to a mole fraction of 0.006 in the alloy.

The calculations predict that for a diffusivity equal to the measured value of carbon diffusivity in austenite, the predicted transformation finish temperature decreases from 1764.8K to 1751K as the cooling rate increases from $2.5 \times 10^{-2}$K/s to 2.5K/s. Although the mathematical model used to solve this diffusion problem was not a sophisticated one, the model predictions agreed reasonably well with Chuang's\textsuperscript{19} experimental observation that the transformation is over within a 2 to 10K temperature range, for a value of carbon diffusivity equal to that measured for carbon in austenite, $D=10^{-4}$ mm$^2$/s. At all three cooling rates, the model predicts that the liquid phase
### TABLE VII

Transformation Finish Temperature (K) (And Transformation Temperature Range (K)) Versus Cooling Rate (K/s) and Solute Diffusivity (mm²/s) in Austenite

<table>
<thead>
<tr>
<th>Diffusivity (mm²/s)</th>
<th>Cooling Rate (K/s)</th>
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</thead>
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<tr>
<td>2.5x10⁻⁴</td>
<td>2.5x10⁻² 2.5x10⁻¹ 2.5</td>
</tr>
<tr>
<td>10⁻⁴</td>
<td>1764.8K 1761.8K 1751K*</td>
</tr>
<tr>
<td>10⁻⁶</td>
<td>1751.5K* 1707.8K 1679K</td>
</tr>
<tr>
<td></td>
<td>(14.5K) (4.2K) (15K)</td>
</tr>
<tr>
<td>10⁻⁸</td>
<td>1679K</td>
</tr>
<tr>
<td></td>
<td>(82K)</td>
</tr>
</tbody>
</table>

\( f_1 \rightarrow 0 \quad \text{and} \quad f_g \rightarrow 0 \)

---

**Figure 56** A Plot Of Carbon Concentration In The \( \delta \) Phase At The \( \delta/\gamma \) Interface Versus Interface Position In The Volume Element (D...10⁻⁴ mm²/s).
Figure 57 A Plot Of Carbon Concentration In The Liquid Phase At The $\gamma$/liquid Interface Versus Interface Position In The Volume Element (D...$10^{-6}$mm$^2$/s).

Figure 58 A Plot Of Carbon Concentration In The $\delta$ Phase At The $\delta$/\gamma Interface Versus Interface Position In The Volume Element. (D...$10^{-6}$mm$^2$/s).
Figure 59 A Plot Of Carbon Concentration In The Liquid At The $\gamma$/liquid Interface Versus Interface Position In The Volume Element. ($D ... 10^{-8} \text{mm}^2/\text{s}$).

Figure 60 A Plot Of Carbon Concentration In The $\delta$ Phase At The $\delta/\gamma$ Interface Versus Interface Position In The Volume Element. ($D ... 10^{-8} \text{mm}^2/\text{s}$).
would disappear at the end of the peritectic transformation. The austenite phase fraction at the end of the peritectic transformation is 0.4954, 0.5231 and 0.6362 for cooling rates of 2.5x10^-2K/s, 2.5x10^-1K/s and 2.5K/s respectively. An austenite phase fraction determined using the Lever Rule at the predicted transformation finish temperatures for these cooling rates are 0.5124, 0.5775 and 0.849 respectively; this phase fraction can be calculated only in those instances where the transformation finish temperature is greater than the austenite solidus temperature for a given alloy composition.

Calculations using these same cooling rates and
smaller values of diffusivity for carbon in austenite show that: 1. As the cooling rate increases, the transformation finish temperature decreases (transformation temperature range increases), for a constant value of the solute diffusivity; a transition point is reached eventually where the phase predicted to disappear at the end of the transformation is no longer the liquid phase but the δ-ferrite phase. 2. As the values of the diffusivity decrease at a constant value of the cooling rate, the phase predicted to disappear at the end of the transformation is no longer the liquid phase but the δ-ferrite phase.

Given a diffusivity for carbon of the order \( D = 10^{-6} \text{mm}^2/\text{s} \), the transformation finish temperature decreases from 1751.5K to 1679K as the cooling rate increases from 2.5x10^{-2}K/s to 2.5K/s. The calculations predict that the austenite phase fraction at the end of the transformation is 0.632, 0.998 and 0.991 for the cooling rates, 2.5x10^{-2}K/s, 2.5x10^{-1}K/s and 2.5K/s respectively. At a cooling rate of 2.5x10^{-2}K/s, the liquid phase disappears at the end of the transformation, leaving δ-ferrite and austenite; the austenite phase fraction calculated using the Lever Rule is 0.835. At cooling rates of 2.5x10^{-1}K/s and 2.5K/s, the model predicted that the δ-ferrite phase disappeared at the end of the transformation, leaving liquid and austenite. The equilibrium phase diagram indicates that the fraction of austenite should
be one, at the transformation finish temperature for these two cooling rates. Given a diffusivity for carbon of the order $D = 10^{-5} \text{mm}^2/\text{s}$, the predicted austenite phase fractions are 0.9918, 0.9912 and 0.9912 for the cooling rates $2.5 \times 10^{-2} \text{K/s}$, $2.5 \times 10^{-1} \text{K/s}$ and $2.5 \text{K/s}$, respectively. The $\delta$-ferrite phase is predicted to disappear at the end of the transformation for all three cooling rates. The graphs for $2.5 \times 10^{-1} \text{K/s}$ and $2.5 \text{K/s}$ lie almost one atop the other for most of the transformation.

Figure 62 show plots of the carbon concentration at the $\delta$-ferrite interface as a function of interface position for the following diffusivity and cooling rate combinations:
(a) \( D = 10^{-8} \text{mm}^2/\text{s} \) and \( T = 2.5 \times 10^{-2} \text{K/s} \), (b) \( D = 10^{-8} \text{mm}^2/\text{s} \) and \( T = 2.5 \times 10^{-2} \text{K/s} \) and (c) \( D = 10^{-8} \text{mm}^2/\text{s} \) and \( T = 2.5 \text{K/s} \); these combinations are indicated with an asterisk on Table V. The graphs for combinations (a) and (b) coincide and that for combination (c) lies fairly close to the others; the transformation finish temperature for all three is 1753K. At the end of the transformation, the \( \delta \)-ferrite concentration for combination (a) and (b) is 1.004 times greater than that for combination (c).

**Peritectic Iron-Carbon-Manganese Alloy**

The monovariant three phase reaction, \( \delta + \alpha \rightarrow \gamma \), exists in the iron rich corner of the ternary isotherm; the bulk alloy composition is indicated by a cross on the three isotherms presented in Figures 63, 64 and 67, for the temperatures 1759.4K, 1759K and 1752K respectively; the compositions are given in mole fractions on these isotherms. It is assumed that for the alloy, of composition Fe-0.12wt%C-1.5wt%Mn, the austenite phase appears at this temperature and the phase compositions are given by the ends of the ternary tie-triangle in Figure 63. The calculated temperature at which the monovariant three-phase reaction occurs is 1759.4K for an alloy of composition Fe-0.12wt%C-1.5wt%Mn (in mole fractions, Fe-0.006C-0.0152Mn). The width of the volume
element used in these calculations is $180 \times 10^{-3}\text{mm}$, equal to one-half the primary dendrite spacing. At 1759.4K, the calculated value for the position of the $\delta$/liquid interface in the volume element is $162.83\times10^{-3}\text{mm}$.

At 1759K (Figure 64), the calculated values for the
Figure 64 "Peritectic" Portion Of The Fe-Mn-C Ternary Isotherm At 1759K.

initial position of the $\delta/\gamma$ and $\gamma$/liquid interfaces are $158.39 \times 10^{-3}$mm and $163.204 \times 10^{-3}$mm, respectively. [Note: Initial interface tie-lines, for the isothermal diffusion period at temperatures 1759K and 1752K are indicated by the dashed lines labelled initial tie-lines on their respective isotherms]. At the start of the isothermal diffusion period, the mole
fraction of carbon and of manganese in the liquid is 0.02409 and 0.02011 respectively; the initial mole fraction of carbon and of manganese in the \( \delta \)-ferrite is 0.00426 and 0.01478 respectively. The final tie-lines shown in Figure 64 are determined based on the assumption that the carbon concentration gradient in the austenite is zero at the end of the isothermal diffusion period, at 1759K. The calculated value of the mole fraction of carbon and of manganese in the liquid is 0.02282 and 0.02408 respectively at the end of the isothermal diffusion period; the calculated value of the mole fraction of carbon and of manganese concentrations in \( \delta \)-ferrite is 0.00419 and 0.00578 respectively. At the end of the isothermal diffusion period, the calculated value of the position of the \( \delta/\gamma \) and \( \gamma/\)liquid interfaces is 100.4x10^{-3}mm and 169.32x10^{-3}mm respectively. Figure 65 shows plots of the carbon and manganese concentrations in the liquid at the \( \gamma/\)liquid interface as a function of the interface position in the volume element, for the isothermal diffusion period. Figure 66 plots these same variables for the delta-ferrite phase at the \( \delta/\gamma \) interface.

At 1752K, the calculated values of the \( \delta/\gamma \) and \( \gamma/\)liquid interfaces are 88.484x10^{-3}mm and 171.19x10^{-3}mm. The mole fraction of carbon and of manganese in the liquid is 0.028864 and 0.024176 at the start of the isothermal diffusion period; the initial mole fraction of carbon and of manganese
in $\delta$-ferrite is 0.00386 and 0.00702 respectively. At 1752K the peritectic transformation is over $(f_\delta \to 0)$ before the austenite carbon concentration gradient becomes zero, during this isothermal period; the final tie-lines shown on Figure 67.
are those for the interfaces just before the transformation is completed ($f_x = 0.0055$). The predicted value of the mole fraction of carbon and of manganese in the liquid is 0.0245 and 0.03724 respectively; the predicted $\delta$-ferrite carbon and manganese concentration is 0.003861 and 0.00063
respectively at a fraction $\delta$-ferrite of 0.0055. The calculated values of the mole fraction of manganese in the $\delta$-ferrite is three times smaller than that given by the tie-line passing through the bulk alloy composition, at this temperature. The $\gamma$/liquid interface position at the end of the peritectic transformation is $178.512 \times 10^{-3}$ mm. Figure 68 shows graphs
of the carbon and manganese concentrations in the liquid at the \( \gamma/\text{liquid} \) interface as a function of the interface position in the volume element, for the isothermal diffusion period. Figure 69 shows plots for these same variables for the
Figure 69 A Plot Of Carbon And Manganese Concentration In The $\delta$ Phase At The $\delta/\gamma$ Interface Versus Interface Position In The Volume Element. (concentration expressed as mole fraction).

delta-ferrite phase and the $\delta/\gamma$ interface.
6.0 Discussion

The material to be presented in this section includes a discussion of the formation of banded structures during plane front solidification of alloys in peritectic systems as well as a discussion of diffusion-controlled growth of the peritectic phase in iron-carbon alloys. The nucleation of the peritectic phase and the growth of banded structures in plane front solidified peritectic alloys are addressed in Section 6.1; this discussion is based upon the results of the plane front solidification experiments and the undercooling experiments for tin-cadmium alloys, the Thomson-Spaepen analysis of crystal nucleation in a binary melt and modelling of the peritectic phase solidification transient for tin-cadmium alloys. The results of the mathematical modelling of the diffusion controlled growth of the peritectic phase, during dendritic solidification of iron-carbon binary and ternary alloys, is discussed in Section 6.2.
6.1 Nucleation of the Peritectic Phase and Growth of Banded Structures in Plane Front Solidified Tin-Cadmium Peritectic Alloys

6.1.1 Plane Front Solidification: Discussion of Experimental Results for Tin-Cadmium Peritectic Alloys

As reported earlier, no evidence of the peritectic phase \( \beta \) was found in any of the three Sn-1.207wt% Cd specimens solidified uni-directionally during this study; although banding has been previously reported\(^1\) in Sn-Cd alloys of similar composition. The specimens were placed in the furnace temperature gradient so that approximately 25-30mm of the 42mm long solid specimen was expected to melt at the start of the experiment. The absence of signs of this initial interface suggested that the entire solid specimen may have melted. The distance that must be solidified in order that the cadmium concentration in the liquid, at the advancing solid-liquid interface of the solidifying melt, would reach the liquidus concentration at the peritectic temperature was calculated using an approximate solution, developed by Smith, Tiller and Rutter,\(^2\) describing the solute concentration profile for the initial and final transients of a plane front solidified specimen of finite length. This calculation showed that for the Sn-1.207wt% Cd specimens, 37.7mm of the specimen would have had to solidify as an initial transient before the peritectic
isotherm liquidus concentration would be reached in the liquid at the interface. The specimen length was 42mm; therefore, the peritectic cadmium concentration would be reached within 5mm of the end of the specimen. However, the diffusion length at these specimen travel velocities is 100mm. The concentration of the liquid ahead of the interface should have been increasing faster than that calculated for a specimen whose length is several times greater than the diffusion length. The solid and liquid concentrations at the interface could have attained their respective peritectic compositions before the specimens were quenched; the quenched solid/liquid interface was 10-12mm from the end of the crucible. Sn-2.581wt%Cd specimens were used for all further experiments, because, for this Cd concentration, the transient distance required to reach the liquidus concentration at the peritectic temperature, 6.3mm, is much shorter than the specimen length.

The α phase was observed to be the initially solidified phase in these specimens; initial α phase solidification was reported for alloys of similar composition in previous work. It is possible that due to the slow specimen travel velocities, there is sufficient time for growth of α phase from the initial solid. According to the phase diagram, the initial solid is comprised of α phase and a cadmium rich phase in the proportions given by the Lever Rule. Specimen 25-1 and 25-6 were both grown under stable
conditions on boron nitride and quartz/boron nitride composite surfaces, respectively. Specimen 25-1 solidified as primary phase, \( \alpha \), until it was quenched. The chemical analysis carried out on 1cm long sections of specimen 25-1 showed that the \( \alpha \) phase solidified with an average cadmium concentration in these sections ranging from 1.269wt%Cd to 1.667wt%Cd; these cadmium concentrations are substantially higher than the \( \alpha \) phase composition, 0.75wt%Cd, at the peritectic temperature, indicating metastable solidification of the \( \alpha \) phase at a temperature below the peritectic isotherm. This point will be discussed further in connection with the results of the undercooling experiments. Specimen 25-5 solidified as \( \alpha \) phase until it was quenched. The solid/liquid interface degenerated to a cellular shape within 0.6mm of the quenched solid-liquid interface position. The peritectic phase \( \beta \) was observed in Sn-2.581wt%Cd specimens, which were subjected to some disturbance during solidification, ie. sudden increase in specimen travel velocity or change in local temperature. Banding was observed in specimen 25-4 during a period of solidification where \( \alpha \) phase never completely disappeared from the solid/liquid interface. Nucleation of the \( \beta \) phase at the \( \alpha \)/liquid interface was not necessary since \( \beta \) phase was present in the \( \alpha \) cell boundaries; \( \beta \) phase covered less than one-half of the solid/liquid interface. The \( \alpha \) phase re-covered the entire solid/liquid interface and continued solidifying with a
cellular interface until finally β phase covered the entire interface. This period of solidification appeared to be characterized by competition between α and β phases at the interface. However, once β phase covered the interface, α phase never reappeared at the β/liquid interface during a period of stable solidification conditions, even in specimen 25-4 which showed some evidence of banding in the initial stages of solidification. The results of this work with Sn-1.207wt%Cd and Sn-2.581wt%Cd alloys indicate that peritectic Sn-Cd alloys solidified horizontally would solidify as α (primary) phase under stable plane front conditions, obtained with low furnace temperature gradients and specimen travel velocities.

Specimen 25-3 solidified in the form of dendrites on a soda-lime microscope cover glass, under solidification conditions which produced plane front solidification in the other specimens. It should be noted that the alloy wetted the glass and the glass had to be broken and pried off the specimen. It is probable that some leaching of the glass occurred, thereby introducing other elements into the specimen in sufficient quantity to promote dendritic solidification. A region containing a mixture of α and cadmium rich (β phase?) dendrites was observed in this specimen; it is not known whether or not the wetting of the glass or the introduction of other solute elements from the glass promoted
conditions conducive to the nucleation of the phase, in this instance.

6.1.2 How much Undercooling is Required to Nucleate the Peritectic Phase in the Presence of the Pre-Peritectic Phase?...A Discussion of the Results of the Undercooling Experiments and the Thomson-Spaepen Analysis.

An extrapolation of the α solidus and liquidus lines, based on the original data of Hanson and Pell-Walpole\textsuperscript{27} for the Cd-Sn system, showed that the metastable α liquidus temperatures for the range of cadmium concentrations found in specimen 25-1 (Sn-2.581wt% Cd), must have ranged from 490K to 485K. These temperatures are 6 to 10K below the peritectic temperature of 496K. From the experimental observations made in this study on plane front solidified Sn-Cd specimens, it became clear that nucleation of the β phase is an extremely important factor in determining the microstructure produced in a peritectic alloy during freezing and it was this result that led to the carrying out of the undercooling experiments reported above. It is important, therefore, to consider the factors that may influence the nucleation behaviour of alloy systems of the peritectic type, if a clear understanding of the microstructures produced is to be achieved. In this regard, the undercooling experiments and the Thomson and
Spaepen analysis of heterogeneous nucleation in a binary melt were two approaches taken to answer the question posed in the title of this section. It was felt that an attempt to apply the Thomson-Spaepen analysis to the present system would emphasize the important factors in the nucleation process, since it is the most recent theoretical work concerned with nucleation in alloy melts rather than only single component systems. It must be noted, however, that the data necessary for any accurate calculations based on this theory are not available for the phases involved in the present study. On the other hand, Sundquist and Mondolfo's experimental study of nucleation in binary alloy systems provide some experimental observations of nucleation phenomena in similar binary alloy systems, including some of the peritectic type, and may, therefore, give an indication of what could be expected in the present case.

Undercooling Experiments

The solidification sequence suggested by the phase diagram for alloys having compositions within the range of the peritectic isotherm is as follows: initially, nucleation and dendritic solidification of the \( \alpha \) phase occurs. Dendritic solidification occurs because the solid is growing into an undercooled melt. During this solidification process,
segregation occurs so that the composition of the remaining liquid moves to the liquidus composition at the peritectic temperature. Nucleation of the $\beta$ phase is then expected, followed by the peritectic reaction at the peritectic temperature. Further solidification of the $\beta$ phase will occur until the composition of the remaining liquid reaches that of the Sn-Cd eutectic point. Nucleation of the cadmium rich phase should then occur and the solidification sequence will be completed by eutectic freezing, at the eutectic temperature. Thus, on a differential thermal analysis curve for these alloys, one would expect to see three peaks, each representing a stage in the solidification sequence for the alloy. This is precisely what was observed on the differential thermal curves: the first peak was attributed to the solidification of the $\alpha$ phase while the second, which occurred as a small peak on the side of the first, was attributed to the formation of the $\beta$ phase by the peritectic transformation.

The undercooling experiments were done in order to provide some indication of the effectiveness of the $\alpha$ phase as a nucleation catalyst for the $\beta$ phase. Figure 70 is a convenient reference diagram which summarizes the experimental temperature data presented in Section 5.2, (i.e. the temperature at which solidification started, the maximum recalescence temperature and the temperature at which the peritectic transformation began), on a plot of the tin-cadmium
phase diagram. Since no solid formed in the melt, for all but the ~2wt% Cd specimen, until the melt temperature dropped 2K to 5K below the peritectic temperature, it is conceivable that there was no significant substrate for $\alpha$ phase nucleation and that $\alpha$ phase was the most significant substrate available for
nucleation of the \( \beta \) phase, in these experiments. If the \( \alpha \) phase is an effective catalyst for the nucleation of the \( \beta \) phase, then in the presence of \( \alpha \) phase, one would expect to observe evidence of the start of the peritectic transformation in the specimen, at some temperature no more than a few degrees below the peritectic temperature; the differential thermal curves showed that the second peak occurred, at a temperature 1-2K below the peritectic temperatures, after the first phase had formed. This result was confirmed by one experiment in which a cold piece of bare thermocouple wire was inserted into the melt to initiate \( \alpha \) phase solidification at a temperature well above the peritectic temperature; this curve also exhibited a second peak 1-2K below the peritectic temperature, showing that \( \beta \) is nucleated by \( \alpha \) at an undercooling of 1-2K. The final small peak occurred at or near the known eutectic temperature, clearly identifying that thermal indicator.

Although an undercooling of 1-2K was sufficient to nucleate \( \beta \) phase in the bulk undercooling experiments, an undercooling of \(-1.4K\) was not sufficient to produce \( \beta \) phase at the metastable \( \alpha \)/liquid interface in the plane front solidified specimen 25-1.[Note: The value of 1.4K was determined by extrapolating the \( \alpha \) liquidus data of Hanson and Pell-Walpole,\(^{27}\) into the metastable range to the Cd concentration reached in specimen 25-1, as shown in Figure 70.]
It appears that nucleation of $\beta$ by $\alpha$ would be marginally possible under these conditions, especially in view of the limited accuracy of the data available. Therefore, provided that solidification conditions are sufficiently stable to prevent introduction of additional (local) undercooling (thermal or constitutional) single phase $\alpha$ solidification is to be expected, as observed]. The apparently conflicting information provided by the plane front solidification and undercooling experiments has a relatively simple explanation. The undercooling experiments show the effectiveness of $\alpha$ as a nucleation catalyst for $\beta$ from liquid having a composition within the peritectic isotherm composition range. Convection during solidification of a bulk alloy sample, in the undercooling experiments, mixes the liquid such that the overall liquid composition would lie within the peritectic isotherm range. As the undercooling experiment sample continues to cool, the solid is more likely to be brought into contact with liquid with which it is not in equilibrium; the driving force for nucleation of the peritectic phase is probably considerable as the temperature of the liquid falls below the peritectic temperature. The plane front solidification experiments show the effectiveness of $\alpha$ as a nucleation catalyst for $\beta$ from liquid, at the metastable $\alpha$/liquid interface, with a Cd concentration greater than that for the liquid on the peritectic isotherm. The question still
remains as to what undercooling is necessary, in metastable solidification of \( \alpha \) under plane front solidification conditions, to nucleate the \( \beta \) phase?

The Thomson-Spaepen Analysis

As outlined in an earlier section of this thesis, the Thomson-Spaepen analysis of crystal nucleation in binary metallic melts was used to determine order of magnitude values for the interface undercooling required to homogeneously, and heterogeneously nucleate the peritectic phase. A value of Cd concentration of 1.5wt\% was chosen for this calculation because it represents a value in the middle of the \( \alpha \) phase concentration range for specimen 25-1. (The corresponding Cd concentration for the liquid phase is 7.6wt\%). The results of the calculations shown earlier gave values of critical nucleus size of \( 0.369 \times 10^{-3}\text{mm} \) to \( 1.8 \times 10^{-6}\text{mm} \), for the range of undercooling from 1.35K to 175K, comparable to typical values found in the literature. It is of interest to note that the predicted value of Cd content for the critical nucleus lies wholly within the \( \beta \) single phase region over this entire range of undercooling, although the Cd content of the critical nucleus was calculated to decrease by about 55\% with increasing undercooling over that range. Predicted values of the interfacial free energy between the \( \beta \) phase, which was
taken to be hexagonal close packed (HCP) in structure to make calculations tractable, and the liquid were comparable to typical values of solid-liquid interfacial free energy found in the literature, 25 to 200mJ/m².\textsuperscript{28}

The undercooling required for nucleation of the $\beta$ phase was taken to be that at which the calculated nucleation rate differed significantly from zero. This gave, for homogenous nucleation of $\beta$, a value of about 175 to 180K for the required undercooling. This may be compared with the well known value generally accepted for homogeneous nucleation, i.e. 0.2 times the liquidus temperature of the material. This gives an undercooling value of about 100K. In view of the approximations involved, this agreement is considered satisfactory.

It is more likely, however, that the $\beta$ phase will be nucleated heterogeneously by the $\alpha$ phase, with which the liquid is in contact (or possibly by some foreign catalyst particles in the melt). In this case, the value of the Gibbs free energy for heterogeneous nucleation of the $\beta$ phase, and hence the nucleation rate, are essentially functions of the surface energies of three interfaces, i.e. $\alpha$/liquid, $\beta$/liquid and $\alpha/\beta$ (as well as a function of undercooling). Thus, a solid catalyst will nucleate a phase from the melt at small undercooling if there is enough energy available from replacing catalyst-liquid interface by catalyst-solid plus
solid-liquid interfaces to substantially reduce the free energy barrier to nucleation. For present purposes, the $\beta$HCP/liquid interfacial free energy was calculated using equation (12), yielding a value of 134 to 8.7mJ/m$^2$ and the $\alpha$/liquid interfacial free energy taken as 59mJ/m$^2$. The $\alpha/\beta$ interfacial free energy was not calculable and, therefore, this quantity was allowed to vary over a range of values and the critical free energy for heterogeneous nucleation calculated for each chosen value.

For values of $\alpha/\beta$HCP interface energy within the range 100mJ/m$^2$ to 1mJ/m$^2$, the undercooling required for heterogeneous nucleation was within the range 165K to 80K. These values are at least an order of magnitude greater than some typical values of undercooling for solidification of a phase on a reasonably good catalyst, found in Sundquist and Mondolfo's$^{30}$ study on nucleation in binary metallic melts. The values of solid-solid interphase energy required, according to the Thomson-Spaepen analysis are smaller than the low end of the range of experimentally determined values disclosed in the literature and values predicted using physical models of phase nucleation, 100mJ/m$^2$ to 300mJ/m$^2$,$^{31}$ shaped by current thought as to the magnitude of the total phase interface energy due to the individual contributions of the components of the interface energy, i.e. structural and chemical. In order to obtain an undercooling of the order of magnitude predicted by
classical nucleation theory, not only should the solid-liquid interfacial energy of the nucleating phase be smaller than that of the catalyst, but also, the magnitude of the solid-solid interfacial energy should be a minimum. Therefore, the calculations were repeated for a \( \beta \text{SHP} \) phase using values for the solid-liquid interfacial energy that were less than the \( \alpha \)/liquid interfacial energy. The nucleation rates were substantially larger at an undercooling of 9.6K than at either 2.6K or 4.6K for most of the chosen values for \( \gamma^{\text{SHP}/\alpha} \): 55, 50, 40, 30, 20mJ/m\(^2\). A reasonable nucleation rate was possible at 4.6K if \( \gamma^{\text{SHP}/\alpha} \) equals 55mJ/m\(^2\) and \( \gamma^{\alpha/\beta \text{SHP}} \) equals 5mJ/m\(^2\). The results of the Thomson-Spaepen analysis suggested that an undercooling of 5-10K may be reasonable for nucleation of the \( \beta \text{SHP} \) phase at a planar \( \alpha \)/liquid interface.

The situation existing in the present work is similar to that studied by Sundquist and Mondolfo.\(^{30}\) in their experiments on nucleation in binary alloys. These authors were concerned with the heterogeneous nucleation of one phase of a binary alloy system by another of the same system, such as the nucleation of Pb by Sn and of Sn by Pb in the Pb-Sn system. Moreover, the systems that they studied were mainly composed of low melting point metals, similar to (but not including) the present system, and some were of the peritectic type. Therefore, it seems reasonable to expect similar behaviour in the present case. They found values of undercooling for
heterogeneous nucleation as low as 0.25K (for Pb by Sn, Zn by Bi and Tl by Sn). The results of the Thomson-Spaepen analysis for this system appear to support the heterogeneous nucleation theory requirement that the value of the solid-solid interphase energy (structural and chemical components) must be very small, in order to obtain these small undercoolings. The structural component of the solid-solid interphase energy would be minimized if the nucleus βSHP was fully coherent with the substrate; a fully coherent interface is considered herein to be one with a minimum of mismatch between the two different crystal structures, over a few atom layers. Although the volume elastic strain energy would be substantial for a fully coherent nucleus, this energy term is not considered part of the interphase energy term in the calculation of the Gibbs volume free energy for the liquid-solid phase transformation; it is usually described by a separate work energy term. There is no information available on the possibilities for the following crystal structure combinations: body centered tetragonal (α) and simple hexagonal packing (βSHP), and body centered tetragonal (α) and hexagonal close packed (βHCP). In some of the alloys systems studied by Sundquist and Mondolfo, the crystal structures of the nucleating phase and the primary phase substrate are so different as to suggest that coherent interfaces would be unreasonable. The phase diagram does not predict the existence of an intermediate phase in many of
these systems; therefore, one could be certain that there was no other phase present separating the nucleating phase and the primary phase substrate. These results appear to belie the necessity for the structural component of interfacial energy to be of the order of that for a fully coherent nucleus.

The chemical component of the solid-solid interphase energy is comprised of that due to a difference in chemical composition across the boundary (bonding energy considerations) and the extent to which the interphase energy is reduced per unit area of boundary, by the presence of solute. The difference in cadmium concentration across the α/βHCP interface was approximately 3wt%, as calculated using the Thomson-Spaepen analysis; therefore, it is likely that the magnitude of the chemical component of this portion of the "chemical" interphase energy is not as significant as the structural component. The contribution to interphase energy due to solute segregation to the interphase boundary in the Sn-Cd system is not calculable; it is a function of what impurities are present in the melt among other things.

The Thomson-Spaepen analysis was an invaluable aid to interpreting the apparently conflicting information provided by the plane front solidification and bulk undercooling experiments. It put into perspective what the important factors are, that determine whether or not the peritectic
phase would appear during plane front solidification: the supersaturation in existence at the $\alpha$/liquid interface and interphase boundary energies. It cannot provide an order of magnitude value for the undercooling required to nucleate the $\beta$ phase at the plane front, metastable $\alpha$/liquid interface, without some input on the values of the $\alpha/\beta$ interphase energies.

An undercooling of 1-2K at the metastable $\alpha$/liquid interface was not sufficient for nucleation of the $\beta$ phase, during horizontal solidification of thin specimens under the stable thermal conditions and low solidification velocities used in this work. Larger values of undercooling could be produced more readily in the Bridgeman type solidification furnaces used in previous plane front solidification studies of peritectic alloys. It is more difficult to maintain stable conditions at the solidification front, in view of the high specimen travel velocities and high temperature gradients in the liquid used in previous solidification studies. Fluctuations in heater temperature would move the solid/liquid interface small distances. In this regard, it should be noted that a 1mm change in the solid/liquid interface isotherm would correspond to a local temperature change of 10 to 40K, given the large values of temperature required for plane front solidification at the higher growth rates used. In addition, convection of hotter liquid close to and away from the
interface can create a situation where part of the solid is re-melted. Since the re-melted \( \alpha \) solid contains less solute than the liquid from which it was freezing, the re-melting will temporarily decrease the solute content in the liquid at the interface, thereby creating increased local undercooling with respect to the \( \beta \) liquidus and enhancing the probability of \( \beta \) phase nucleation, (e.g., in the Cd-Sn system, freezing with metastable \( \alpha \) phase forming at a temperature below the peritectic isotherm, remelt will move the local composition toward the Sn side of the phase diagram, putting that composition farther below the \( \beta \) liquidus line).

6.1.3 Solidification Microstructures of Tin-Cadmium Peritectic Alloys... Plane Front and Cellular Solidification

Nucleation of the peritectic phase has been the focus of this discussion till now. The plane front solidification experimental results showed that once the difficulty of nucleating the peritectic phase was overcome and \( \beta \) phase solidification was established, the \( \alpha \) phase did not re-appear, at the \( \beta \)/liquid interface. The discussion presented below in Section 6.1.3.1 expands on the question of whether or not banding could occur during plane front solidification of the peritectic phase under very stable conditions, using the predictions of the conceptual/mathematical model presented in
Section 3.3. Much of the discussion in the literature concerning planar solidification of peritectic alloys focused on the possibilities for co-operative lamellar growth of the primary and peritectic phases, in a manner similar to that observed in eutectic alloy solidification. Some comments on this topic as well as on cellular solidification of peritectic alloys are presented in Section 6.1.3.2. These ideas evolved out of the work done in developing the conceptual model.

6.1.3.1 Banding in Plane Front Solidified Peritectic Alloys

A discussion of the model predictions for two Sn-Cd peritectic alloys, Sn-1.3wt%Cd and Sn-2.5wt%Cd) is presented in the section entitled 'Prospects for Obtaining Conditions at the β/liquid Interface Conducive to α Phase Nucleation in a Sn-1.3wt%Cd and a Sn-2.5wt%Cd Alloy During α Solute Layer Depletion'. Second, in the section entitled 'The Evolution of a Solidification Microstructure for Plane Front Solidified Peritectic alloys', a description is presented of the evolution of a plane front solidification microstructure for a bulk alloy composition less than the equilibrium composition of the peritectic phase on the peritectic isotherm. A similar description is presented for a bulk alloy composition greater than the equilibrium composition of the peritectic phase on the peritectic isotherm. Third, a few comments on the
possibility of co-operative lamellar solidification occurring in two phase peritectic alloys is presented in a similarly titled section.

Prospects for Obtaining Conditions at the $\beta$/liquid Interface Conducive to $\alpha$ Phase Nucleation in a Sn-1.3wt%Cd and a Sn-2.5wt%Cd Alloy During The $\alpha$ Solute Layer Depletion Transient

The results of the mathematical modelling of plane front solidification of peritectic Sn-Cd alloys show that it is not likely that conditions conducive to nucleation of stable $\alpha$ phase would be obtained at the $\beta$/liquid interface, after some period of peritectic phase $\beta$ solidification. An adjustment of the amount of solute carried in the solute layer, ahead of the interface, during the initial transient in $\beta$ phase solidification ($\alpha$ solute layer depletion transient) results in decreasing values of the solute concentrations at the interface with a corresponding increase in the value of the interface temperature. [Note: the phrase 'a solute layer depletion' was previously defined in Section 5.4]. However, whether or not conditions conducive to stable $\alpha$ phase nucleation occurs is strongly dependent upon the value of two factors which control the amount of excess solute to be removed from the $\beta$/liquid interface: how close the bulk alloy
cadmium concentration \( C_0 \) is to the equilibrium \( \alpha \) phase cadmium concentration \( pC_0 \), at the peritectic temperature and the value of the specimen travel velocity.

The specimen travel velocity and bulk alloy composition govern the values of three significant variables in the calculations for a solution of the mathematical transient problem, namely:

1. the excess solute to be removed from the solute layer ahead of the \( \beta \)/liquid interface. Excess solute is herein defined as the difference between the amount of solute that would be carried ahead of a steady state \( \alpha \)/liquid interface (\( C_\alpha = C_0 \)) and that carried ahead of a steady state \( \beta \)/liquid interface (\( C_\beta = C_0 \)).

2. the magnitude of the solute concentration gradient which exists in the liquid at the \( \beta \)/liquid interface, at the start of peritectic phase solidification. The initial magnitude of the concentration gradient for the purposes of these calculations depends upon the value of the solute concentration on the \( \beta \) liquidus at the steady state \( \alpha \) phase solidification interface temperature \( T_0 \) and the value of the gradient in the liquid which existed prior to peritectic phase nucleation.

3. the rate of decrease of the value of the concentration gradient at the interface as peritectic phase solidification continues. The magnitude of the temperature gradient in the
liquid and the specimen travel velocity, determine the equilibrium cadmium concentration in the liquid at the interface and therefore the rate of decrease of the magnitude of the concentration gradient, during peritectic phase solidification.

The closer the value of $C_0$ is to $P_{C_\alpha}$, the greater the probability of obtaining conditions at the interface characterized by a point on the metastable extension of the $\beta$ liquidus, into the stable $\alpha$ phase region on the phase diagram, after some period of transient peritectic phase, $\beta$, solidification. The specimen travel velocity appeared to be more important than the temperature gradient in the liquid in determining how far up on the $\beta$ liquidus the solute concentration at the interface would be at the end of the transient. Table VIII provides a useful summary of: the ratio of the cadmium concentration in the liquid at the interface, at the end of the $\alpha$ solute layer depletion transient versus equilibrium cadmium concentration of the liquid on the peritectic isotherm, $C_i/P_{C_\alpha}$, and the distance moved by the $\beta$/liquid interface versus temperature gradient in the liquid and specimen travel velocity, for the Sn-1.3wt%Cd alloy. The results for the Sn-2.5wt%Cd alloy were similar. The predicted ratio $C_i/P_{C_\alpha}$ at the end of the transient was smaller at the greater specimen travel velocity for both values of the temperature gradient; the difference between the values of
TABLE VIII

A Summary Of The Model Predictions For Peritectic Phase Solidification For A Sn-1.3wt%Cd Alloy

<table>
<thead>
<tr>
<th>Temperature Gradient (K/mm)</th>
<th>Specimen Travel Velocity (mm/s)</th>
<th>Ratio Of $C_l$/$P_c$</th>
<th>Distance Moved By The $\beta$/liquid Interface (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>31.7</td>
<td>8.5x10^{-3}</td>
<td>1.548</td>
<td>133.0x10^{-3}</td>
</tr>
<tr>
<td>1.8</td>
<td>8.5x10^{-3}</td>
<td>1.819</td>
<td>123.0x10^{-3}</td>
</tr>
<tr>
<td>1.8</td>
<td>1.7x10^{-3}</td>
<td>1.831</td>
<td>25.3x10^{-3}</td>
</tr>
<tr>
<td>31.7</td>
<td>1.7x10^{-3}</td>
<td>1.833</td>
<td>12.9x10^{-3}</td>
</tr>
</tbody>
</table>

This ratio for the two values of specimen travel velocity was significant for the steeper temperature gradient. The relatively steep concentration gradient which would exist in the liquid at the interface, at the higher specimen travel velocity aids the rapid removal of solute and promotes high initial velocities for the $\beta$/liquid interface, during the early stages of peritectic phase solidification. The excess solute in the solute layer is depleted before the magnitude of the solute gradient decreases to the point at which it can no longer remove solute from the layer. Figure 71 shows a schematic of the evolution of $\beta$ phase solidification which illustrates this point.

The shallow concentration gradient that exists in the liquid at the $\alpha$/liquid interface, at the lower specimen travel
velocity, does not promote rapid removal of excess solute and high $\beta$/liquid interface velocities, initially during the transient. In this instance, the $\alpha$ solute layer depletion transient essentially ended when the magnitude of the solute gradient, in the liquid at the interface, was such that no
further solute could be removed from the diffusion layer before the amount of excess solute carried in the solute layer was depleted. A schematic of the evolution of $\beta$ phase solidification which illustrates this point is shown in Figure 72.

The distance travelled by the $\beta$/liquid interface during the transient was predicted to be a stronger function of the specimen travel velocity than of the temperature gradient in the liquid; it was also more susceptible than the ratio $C_{\text{f}}/\beta C_{\text{i}}$ to variation in values of specimen travel velocity and temperature gradient respectively. This was probably due to the fact that different variables were controlling the progress of the transient at each velocity.

In Section 3.2.2 it was suggested that the stationary isotherm approximation, i.e. specimen stationary in the furnace during the $\alpha$ solute layer depletion transient, would provide values of the solute concentrations in the liquid at the interface which would be a lower limit to the values of the solute concentration in the liquid at the interface, in comparison to those for a moving isotherm condition, when the transient ends. Since the mathematical solution for the stationary isotherm problem is simple to obtain, it would be easier to determine whether or not, for a given alloy composition, the $\beta$ phase solidification transient would lead to interface conditions conducive to nucleation of the $\alpha$ phase
at the β/liquid interface. This idea was substantiated by the model predictions presented in Section 5.4. However, the lower interface temperatures and corresponding higher solute concentrations at the interface, for a moving furnace promotes steeper concentration gradients and correspondingly faster
interface velocities, thereby allowing the β/liquid interface to travel farther than under a stationary furnace approximation.

The model predictions obtained for intermediate values of velocity are unrealistic because the geometric approximations made in the calculations with respect to the variables A2 and dC/dX are inappropriate for the exponential solute concentration profile in the liquid at these velocities. These variables were defined in Section 3.3; Figure 9 shows clearly how they enter into the calculations. Perhaps the assumption that the point \( (X_{in} + \Delta X'', C_i(X_{in} + \Delta X'') \) lies on the α/liquid concentration profile no longer holds and would be indicated by a prediction of a negative value of \( \Delta X'' \) at some \( i^{th} \) interface step. Figure 46 shows that the liquid concentration profiles are reasonably linear for the limiting velocities used in these calculations, although they are described by an exponential function; the linear geometric approximations made in order to calculate the values of the variables A1 and A2, for these two velocities are reasonable over the distances travelled by the β/liquid interface during the transient.
The Evolution of a Solidification Microstructure for Plane Front Solidified Peritectic Alloys

The solidification microstructures obtained during uni-directional solidification of peritectic alloys, at a planar isothermal interface where local equilibrium applies, are strongly influenced by factors other than the familiar G/V-interface morphology relationship. The analysis of plane front solidification of these alloys in this work and the experimental results of Boettinger's\textsuperscript{1} work suggest that nucleation considerations for the $\alpha$ and $\beta$ phases and the bulk alloy composition are significant determinants of microstructure and solute concentration profile along the length of a solidified specimen. This is best illustrated by the description of the solidification of these alloys provided in the following two sections.

The generally accepted physical model of the evolution of banding in Sn-Cd peritectic alloys, and other alloy systems with a similar phase diagram, requires that after a period of primary $\alpha$ phase growth, assuming that each band is a complete, single phase layer: (i) the peritectic phase nucleate in undercooled liquid (with respect to the $\beta$ liquidus) at or near the $\alpha$/liquid interface, (ii) after some period of peritectic phase growth, the conditions in the liquid adjacent to the interface promote the nucleation of primary phase and (iii)

the primary phase nucleates and grows with a planar interface. The process would then repeat to form additional bands as freezing proceeds. During plane front solidification of a peritectic alloy, \( (C_a < C_o < C_f) \), it is to be expected that the \( \alpha \) phase would form first; as freezing proceeds, a solute (Cd) rich layer would be established in the liquid adjacent to the growing \( \alpha \) solid. Solidification of the \( \alpha \) phase would continue, reaching the metastable extensions of the \( \alpha \) solidus and liquidus lines, so that the liquid becomes undercooled with respect to formation of \( \beta \). At this point there are two possibilities: either there is no catalyst present for \( \beta \) phase nucleation or the \( \alpha \) phase (or some foreign particles) act as a catalyst for \( \beta \) nucleation. If there is no effective nucleation catalyst for \( \beta \) present, highly non-equilibrium solidification of \( \alpha \) must occur, at a temperature well below the peritectic temperature. The composition of the metastable \( \alpha \) formed and the amount of undercooling present with respect to nucleation of \( \beta \) will depend on the relative positions on the phase diagram of the metastable extensions of the \( \alpha \) solidus and liquidus lines and the stable \( \beta \) liquidus. It is not possible to state how long metastable \( \alpha \) phase solidification would continue under these circumstances.

Assuming that \( \beta \) phase nucleation takes place in the liquid adjacent to the advancing \( \alpha \) interface: this liquid will be undercooled with respect to \( \beta \) phase nucleation since the \( \alpha \)
phase growth is metastable. If the $\alpha$/liquid interface is completely covered by the $\beta$ phase during this transient solidification, the microstructure obtained upon further solidification will depend upon whether or not the Cd content in the initial melt is less than or greater than that for the peritectic point ($C_p$) on the peritectic isotherm. A discussion of possible solidification microstructures which could evolve in these two instances is presented in the following two sections.

In the first case, ie. that in which the initial melt composition is less than that of the peritectic point, ($C_o < C_p$), transient growth of the $\beta$ phase will occur as discussed earlier: The solute concentration in the liquid at the interface decreases and interface temperature increases, as prescribed by the $\beta$ liquidus. Banding and $\beta$ phase solidification are the possible outcomes:

1. Nucleation and growth of the $\alpha$ phase could occur, leading to development of a banded microstructure. Solidification conditions described by points lying on the metastable extension of the $\beta$ liquidus would be favourable for growth of the $\alpha$ phase, provided a catalyst is available for nucleation of the $\alpha$ phase.

2. Steady state solidification of the $\beta$ phase ($\beta/C_p = C_o$ at steady state) could be established, until the final transient is reached near the end of the sample, since, ultimately the
α solute layer depletion transient would end once steady state solidification of the β phase is possible. However, in this instance, the steady state solidification of β cannot occur at a temperature below the peritectic temperature. Thus, conditions conducive to steady state solidification of the metastable β phase could be obtained only if after a time, during the α solute layer depletion transient, the solute concentration in the liquid at the interface and interface temperatures were described by points lying on the metastable extension of the β liquidus.

3. "Normal" solidification of the β phase could occur, if the solute concentration in the liquid at the interface does not fall below that for the liquid on the peritectic isotherm, during the α solute layer depletion transient. Normal solidification describes a situation where, after the α solute layer depletion transient ends, continued solidification of the β phase occurs due to isotherm movement, since the specimen is moving through a fixed temperature gradient. The temperature at the interface decreases and the solute concentration at the solid/liquid interface increases as prescribed by the β solidus and liquidus.

In the second case, \( C_0 > P_{C_3} \), since the melt composition is richer in Cd than the peritectic point \( C_0^β \), β phase solidification is the only possible outcome:

1. If steady state solidification of the α phase occurred
before the $\beta$ phase nucleated, then the solidification conditions at the $\beta$/liquid interface would be evolving upwards on the $\beta$ liquidus towards the condition for steady state solidification of $\beta$ phase ($C_\beta = C_\alpha$ at steady state). Thus steady state solidification of the $\beta$ phase could be established during the $\alpha$ solute layer depletion transient. If this does not occur, then "normal" solidification of the $\beta$ phase would follow after the $\alpha$ solute layer depletion transient ends.

2. If steady state solidification of the $\alpha$ phase did not occur before the $\beta$ phase nucleated, and the solidification conditions at the $\beta$/liquid interface did not reach the metastable extensions of the $\beta$ liquidus, during the $\alpha$ solute layer depletion transient, then "normal" solidification of the $\beta$ phase would occur until the conditions for steady state $\beta$ phase solidification ($C_\beta = C_\alpha$) are reached. Steady state $\beta$ phase solidification would then continue until the final transient is reached near the end of the sample.

Banding phenomena cannot occur unless the $\alpha$ phase is nucleated by some heterogeneous nucleation catalyst, either the $\beta$ phase or an impurity or the crucible surface. Since, in the bulk Sn-Cd alloy undercooling experiments of this work, a large undercooling was obtained before nucleation of the $\alpha$ phase occurred, it is clear that the present alloys did not contain any effective heterogeneous nucleating catalyst for the $\alpha$ phase. Thus, if $\beta$ phase nucleation and growth had
occurred in the plane front solidification experiments of this work, re-establishment of the α phase after formation of a β band would be a very difficult process in this alloy system. It seems likely that, in cases in which banding is observed in peritectic Sn–Cd alloys, the α phase is never completely eliminated from the interface, so that re-nucleation of the α phase is never required.

6.1.3.2 Cooperative Lamellar Solidification and Cellular Solidification in Two Phase Peritectic Alloys

Lamellar solidification of binary eutectic and peritectic alloys, where $C_a < C_o < C_p \ldots C_o$ lies within the two phase $\alpha + \beta$ region on the phase diagram, appear to be very similar cases of two phase growth, and were treated as such in Boettinger's\(^1\) theoretical treatment describing steady state lamellar solidification of binary peritectic alloys, outlined in Section 2.2. The assumption of growth at a planar isothermal interface where local equilibrium applies is germane to Boettinger's\(^1\) discussion of this topic. However, there are two ideas, implicit in the development of the theory of co-operative lamellar solidification of binary eutectic alloys, which are not relevant to a discussion of lamellar two phase solidification of peritectic alloys. In this section, some thoughts on the possibility of co-operative lamellar two
phase solidification are presented which evolved out of the work done in developing a conceptual model of uni-directional plane front solidification of peritectic alloys.

Boettinger's\textsuperscript{1} theoretical treatment of lamellar two phase solidification of peritectic alloys was based on the theory developed for co-operative lamellar solidification of eutectic alloys. This treatment provided a relationship among the variables: interface velocity, interface undercooling and lamellar spacing, analogous to that for eutectic systems which suggested that lamellar solidification may be possible in some peritectic systems and suggested criteria for which lamellar growth of the two phases at a plane front would be possible in peritectic systems. This treatment of lamellar solidification of peritectic alloys did not explicitly state that lamellar two phase solidification of peritectic alloys, at a planar interface, cannot be considered co-operative, given the generally accepted definition of the word for binary eutectic systems. The phrase 'co-operative lamellar solidification of binary eutectics' incorporates two ideas: 1. each phase rejects the element required for the growth of the other phase and 2. ahead of either solid phase, the solute rejected into the liquid is removed from the interface by lateral diffusion of solute to the other phase and is subsequently incorporated in that phase, rather than by long range diffusion of solute into the liquid. During lamellar solidification of a two phase
peritectic alloy, the same element is rejected at the primary and peritectic solid-liquid interface and long range diffusion in the liquid is required for the continued growth of both phases. A consequence of the need for long range diffusion to remove solute from the interface is that prolonged lamellar two phase solidification, at any temperature, would eventually lead to the removal of one phase from the interface. This idea is communicated to better effect in the description of lamellar two phase growth provided in the following paragraphs, at the peritectic temperature and at a temperature below or above the peritectic temperature.

Consider then the uni-directional, lamellar solidification of a binary peritectic alloy, with a planar interface, at an interface temperature equal to the peritectic temperature. Initially, if the interface is stationary and the effect of curvature of the interface is neglected, then the equilibrium concentration of the solute in the liquid at the interface is the same ahead of each phase, \( C_l = C_i \). Assume also that the magnitude of the solute concentration gradient is the same in the liquid ahead of each phase. Once the interface starts moving, solute rejected into the liquid ahead of the primary (\( \alpha \)) and peritectic (\( \beta \)) phase lamellae would have to be removed from the interface by long range diffusion. However, since the solute concentration of the two solid phases is not equal, the amount of solute rejected into the liquid ahead of
each phase is also not equal; a greater amount of solute would be rejected ahead of the α phase lamellae. Some of the solute rejected into the liquid ahead of the α phase would accumulate ahead of the β phase due to lateral diffusion of solute. The β phase can continue solidifying at higher solute concentrations only if the β/liquid interface temperature falls. As a result the β phase should fall back from the interface, and the α phase would take on a morphology prescribed by the solute environment that it is in, e.g. cellular or dendritic. Lamellar solidification of the primary and peritectic phases cannot continue at a moving interface.

If the interface temperature is at some temperature lower than the peritectic temperature, then the phase diagram prescribes that the equilibrium concentration of the solute in the liquid, at the solid/liquid interface, at the center of an α lamellae be less than that in the liquid at the center of a β lamellae. The value of the concentration gradient in the liquid ahead of the α lamellae should theoretically be less than that ahead of the β lamellae. Solute diffusing laterally into the liquid ahead of the α lamellae, from the liquid ahead of the β lamellae would accumulate ahead of the α phase, due to the inability of the concentration gradient in the liquid ahead of the α phase lamellae to remove the excess solute. The equilibrium interface temperature for the liquid ahead of the primary phase would decrease as more solute accumulated in
this area. As solidification progressed, the $\alpha$ phase would eventually drop back from the solidification front, and the $\beta$ phase would take on a morphology prescribed by the solute environment it is in, e.g. cellular or dendritic.

The situation is similar for the case where the solid-liquid interface temperature is greater than the peritectic temperature. In this instance the concentration of the solute in the liquid, at the solid/liquid interface, at the center of a $\beta$ phase lamellae, would be less than that ahead of the center of an $\alpha$ phase lamellae. Solute would accumulate ahead of this portion of the solid-liquid interface with a corresponding decrease in the liquidus temperature for that portion of the interface. As solidification progressed, the $\beta$ phase would eventually drop back from the solid-liquid interface, and the $\alpha$ phase would take on a morphology prescribed by the solute environment it is in, e.g. cellular or dendritic.

Hillert\textsuperscript{7} envisaged a peritectic system where the conditions at a lamellar $\alpha$ and $\beta$ solid-liquid interface would be similar to that for eutectic solidification. Consider the uni-directional, plane front solidification of a peritectic alloy, where not only is the peritectic phase composition stoichiometric, but also the solute solubility in the $\alpha$ phase is negligible; a phase diagram for this alloy is provided in Figure 73a. Assume that at the initial solid-liquid interface
Figure 73a A Schematic Of A Peritectic Phase Diagram, Where The Peritectic Phase Has A Stoichiometric Composition.

Figure 73b A Schematic Of A Eutectic Phase Diagram.

The composition of the liquid is $C_o$, and both $\alpha$ and $\beta$ phase nucleate at some temperature lower than the peritectic temperature; the interfacial energy balance at the solid-liquid interface allows the two phases to grow side by side. The solid-liquid interface is assumed to be isothermal and
local equilibrium applies. At any temperature lower than the melting temperature of $\beta$ phase, the $\beta$ phase can exist in stable equilibrium with liquid of composition greater than $C_o$ and in metastable equilibrium with liquid of composition less than $C_o$. If the stable $\beta$/liquid equilibrium is established, the same considerations discussed previously apply. If the metastable $\beta$/liquid equilibrium is established, short range diffusion of solute can take place and both phases continue to grow; Hillert suggests that this situation is similar to that for the eutectic solidification situation shown in Figure 73b. It is not possible to say 'a priori' whether or not prolonged lamellar growth would be possible. A stability analysis of this situations is required which takes into account two opposing forces that influence interface temperature and velocity:

1. The mass balance at the metastable $\beta$/liquid interface requires that the solute concentration of the liquid at the interface decrease as $\beta$ phase solidification progresses, in the absence of an influx of solute from somewhere else. The interface temperature would not remain constant (isothermal) because the phase diagram predicts that the interface temperature would decrease as the liquid concentration decreases. This situation is conducive to nucleation of the $\alpha$ phase ahead of the metastable $\beta$/liquid interface since the local undercooling for nucleation of $\alpha$ phase increases as both
the $\beta$/liquid interface temperature and the solute concentration in the liquid at the interface falls. Plane front solidification conditions provide an extra degree of freedom whereby the liquid composition and temperature at the solid/liquid interface can vary with interface movement.

2. Solute diffusion from the $\alpha$/liquid interface to the metastable $\beta$/liquid interface would counteract the trend of decreasing solute concentration in the liquid at the moving $\beta$/liquid interface. The interface temperature would not remain constant (isothermal) because the phase diagram predicts that the temperature would rise as the solute concentration at the $\beta$/liquid interface rises.

An oscillating interface temperature, about the stability regimes of both phases, could allow one or the other of the phases to cover the entire interface. If one or the other phase covers the entire interface, at some point during solidification, then the solidification path would follow that described in Section 6.1.3.1 for these alloys. Interface velocity changes during lamellar two phase solidification could provoke a change in the interface morphology; this hinges on whether or not the value of the G/V ratio used is sufficient to maintain plane front solidification conditions. The mathematical description of the initial period of $\beta$ phase solidification must be solved to determine whether or not rapid growth of the either phase would occur.
One final comment with regard to cellular solidification of two phase peritectic alloys:

Prolonged cellular solidification of either phase is possible if the temperature at the cell tip was within the appropriate range for the stable phase field of that phase. However, assuming that the influence of curvature on interface stability can be neglected, sustained cellular growth of the metastable α phase, at a temperature lower than the peritectic temperature is not likely, since the liquid at the interface would be supercooled with respect to the stable peritectic (β) phase, under uni-directional solidification conditions. The presence of some peritectic phase in the intercellular region would preclude the necessity for its homogeneous nucleation in the supercooled liquid either at or ahead of the interface. The stable peritectic phase could grow out to cover the interface. This would provide a solidification microstructure similar to that observed by Titchener and Spittle⁶ in Ag-Zn peritectic alloys: a banded structure consisting of alternating layer of cellular primary phase in a peritectic phase matrix and peritectic phase. If metastable cellular solidification of the peritectic phase took place at some temperature above the peritectic temperature, whether or not prolonged cellular solidification of this phase would take place under these conditions depends upon the efficacy of the peritectic phase as a nucleation catalyst for the primary
phase. If the primary phase is a good catalyst for the peritectic phase, it is unlikely that the peritectic phase is a good catalyst for the primary phase or vice versa.\textsuperscript{31}

6.2 Microsegregation of Solute and the Diffusion Controlled Peritectic Transformation in Binary and Ternary Alloy Systems

The conceptual model currently used to describe solute segregation during the diffusion controlled peritectic transformation does not make clear:

1. what factors control solute segregation and the rate of the transformation in binary and ternary (multicomponent) alloys nor

2. how these factors work in unison to determine the degree of microsegregation obtained during the transformation.

The approach used to solve the mathematical problem of non-isothermal diffusion controlled phase growth in this work, outlined in Section 4.1, revealed some important differences between binary and ternary systems with respect to those factors that influence solute segregation during the transformation and what phases remain at the end of the transformation. Prior reflection on the transformation in a binary system is a useful starting point in developing an understanding of how the extra degree of freedom of the
ternary system, due to the presence of a second solute, influences the degree of solute segregation obtained during the transformation. An analysis of the significance of the model predictions for the binary alloy, Fe-0.12wt%C, with respect to the transformation is presented in Section 6.2.1. Solute segregation in a ternary alloy and possible consequences for ternary systems which are obscured by current conceptual/mathematical treatments of the topic are presented in Section 6.2.2, based on the model predictions for the iron-carbon-manganese alloy, Fe-0.12wt%C-1.5wt%Mn. Section 6.2.3 constitutes an attempt to summarize the ideas presented in Sections 4.0, 6.2.1 and 6.2.2, in order to bring into sharper focus the important differences between binary and ternary systems with respect to solute segregation.

6.2.1 Binary Alloy...Iron-Carbon

For the Fe-0.12wt%C alloy, equilibrium solidification predicts that δ-ferrite (δ) and austenite (γ) would be the phases remaining at the end of the isothermal peritectic reaction. Upon further cooling, γ phase only would exist at temperatures lower than 1737K. However, the diffusion controlled peritectic transformation is not an isothermal process and it is those factors that control the transformation temperature range which determine the transformation rate and the phase fractions of the phases
existing at the end of the transformation. The solute distribution amongst the phases during the transformation could be considered pre-determined, because, the solute concentration of two phases at an interface is fixed at any temperature for binary systems. Therefore, the solute concentrations in the δ and liquid phases are known at any time during the transformation; the solute concentration gradient in the austenite phase is determined by the rate of the transformation (thickness of the austenite phase), since the solute concentration in the austenite at the δ/γ and liquid/γ interfaces is fixed for a given temperature. In the case of binary systems, the cooling rate and the magnitude of the temperature and/or composition dependant solute diffusivity in austenite appear to be the only factors that determine the transformation temperature range, and the rate of progress of the transformation. In addition, these two factors in unison seem to determine the transformation temperature range, in a manner that is unclear. However, it seems that whether or not the two phase fields, primary and peritectic and peritectic and liquid, open or close with decreasing temperature is the more influential factor in determining the transformation rate during the later stages of solidification, and ultimately, which phases remain at the end of the transformation.

The model was not as helpful as one would have hoped
in sorting out whether or not cooling rate was more important than solute diffusivity or vice versa, in determining the temperature range over which the non-isothermal transformation would take place. The transformation temperature range was predicted to increase one order of magnitude for a two order of magnitude change in either cooling rate at a constant value for the carbon diffusivity or diffusivity at a constant value for the cooling rate. The plots of solute concentration at an interface versus interface position in the volume element shown in Figure 62 (Section 5.5) illustrate this point. The transformation finish temperature, γ phase fraction and phases remaining at the end of the transformation are essentially the same for the case where the three combinations of solute diffusivity in austenite and cooling rate used have the same value of the ratio of solute diffusivity to cooling rate. The values of the transformation finish temperature for these combinations have an asterisk beside them on Table VII.

The model also predicted that at small values for the transformation temperature range, 1-15K, the δ and γ phases remain at the end of the transformation. However, as the transformation range is extended to lower temperatures, the phase that disappears at the end of the transformation would no longer be the liquid phase but the δ-ferrite phase. In the case of the alloy composition considered, it is possible to have liquid existing at lower temperatures and at higher
solute concentrations than expected. Although the cooling rate and solute diffusivity in the austenite phase have a role to play in determining the transformation temperature range, it is the closure of the $\delta/\gamma$ two phase field, in the iron-carbon system, which ultimately determines at what temperature the transformation ends and what phases exist at that point. The boundaries of the $\delta/\gamma$ and $\gamma$/liquid two phase fields on the phase diagram define: the solute concentrations in the three phases at the $\delta/\gamma$ and $\gamma$/liquid interfaces and the magnitude of the difference in the solute concentrations across each interface. As the transformation is forced to lower and lower temperatures, due to a combination of high cooling rates and/or low solute diffusivity in the $\gamma$ phase, the narrowing gap (decreasing to zero) between the solute concentration in the $\delta$ and $\gamma$ phases at the $\delta/\gamma$ interface and the widening gap between the solute concentration in the liquid and $\gamma$ phases at the liquid/$\gamma$ interface, forces relatively larger displacements of the $\delta/\gamma$ interface near the end of the transformation, as compared to that at the beginning of the transformation for a similar value of solute flux. The degree to which this factor, closure of one or both of the two phase fields, takes precedence over cooling rate and solute diffusivity in limiting the transformation temperature range and determining what phases exist at the end of the transformation is alloy system specific. It may remain relatively unimportant in
systems where the two phase regions do not close but extend and expand to low temperatures, i.e. Sn-Cd.

6.2.2 Ternary Alloy...Iron-Carbon-Manganese

Equilibrium solidification, (complete diffusion of solute in all three phases), of the Fe-0.12wt%C-1.5wt%Mn alloy predicts a path similar to that for the Fe-0.12wt%C alloy:

1. At the ternary peritectic temperature for this alloy, 1759.4K the austenite (γ) phase would appear. [Note: although in the ternary system the reaction δ + liquid \(\rightarrow\) γ is a monovariant three phase equilibrium, it is referred to in this work as the peritectic reaction/transition for the sake of simplicity, with respect to comparisons made with the binary peritectic reaction.] The ternary peritectic temperature for this alloy is approximately 7K less than that for the binary alloy. In the three dimensional space of the ternary phase diagram, the three phase δ-γ-liquid region exists for less than a degree for this alloy.

2. At the end of the transformation, only δ and γ phases exists with solute concentrations in each phase defined by the ends of a tie-line through the alloy composition, on the ternary phase diagram. The temperature at which the bulk alloy composition lies wholly within the γ phase region was not calculated for this alloy.

As for the binary system, the progress of the non
Isothermal peritectic transformation appears to be controlled by the cooling rate and diffusivity of the two solutes in the austenite phase. However, the extra degree of freedom in a ternary system allows the solute concentrations at the interfaces, δ/γ and liquid/γ, to take a range of equilibrium values at any given temperature; these values are defined by the tie-lines of the two phase regions. It is a combination of cooling rate, solute diffusivity, constitutional solute interaction and diffusional solute interaction which determines the progress of the transformation and the degree of solute segregation in the three phases. Constitutional solute interaction defines the phases, phase boundaries and tie-lines in a multi-component system. Diffusional solute interaction describes the influence of the presence of one solute on the diffusion of other solutes in solution; the strength of this interaction is formally expressed by the sign and magnitude of the off-diagonal diffusivities in a matrix of diffusion coefficients for the system. The approach used to solve the mathematical problem describing diffusion controlled austenite phase growth in the iron-carbon-solute(x) system revealed much with respect to how the factors listed above work in unison to control the re-distribution of solute, during the transformation. The assumptions made in order to simplify the problem are outlined in Section 4.2 and therefore, are not repeated in this discussion.
Three significant concepts are suggested by the model predictions of interface tie-lines, for the peritectic transformation in an Fe-0.12wt%C-1.5wt%Mn alloy, with respect to solute segregation in the ternary system. These three ideas are discussed in the following paragraphs; briefly they are:

1. The tendency to minimize the concentration gradient of the fast diffusing solute in the $\gamma$ phase and constitutional solute interaction induce a greater degree of segregation of the slow diffusing solute in all phases, in comparison with solute segregation in the "Scheil" case and an "equilibrium solidification" case.

2. Diffusional solute interaction may amplify or diminish the influence of constitutional solute interaction on microsegregation of solute in the ternary system.

3. At the liquid/$\gamma$ interface, the possibility of metastable $\gamma$ solidification or nucleation of the $\delta$ phase exists throughout the transformation. Metastable solidification of the $\gamma$ phase is the case where the solute concentrations at the liquid/$\gamma$ interface are given by a tie-line on the metastable extension of the boundaries of the ternary $\gamma +$liquid two phase region.

Constitutional solute interaction defines a range of possible equilibrium tie-lines for the $\delta/\gamma$ and liquid/$\gamma$ interfaces, for the transformation at any temperature. The "no diffusion in the austenite...Scheil" condition provides tie-lines which define an upper and lower limit to this range for
the \( \delta/\gamma \) and liquid/\( \gamma \) interfaces respectively. An equilibrium solidification path gives a tie-line for the \( \delta/\gamma \) interface only, (that tie-line upon which the bulk alloy composition lies), at temperatures below the lower three phase equilibrium temperature for this alloy. The model predictions of initial and final tie-lines shown in Figures 64 and 67 are respectively, the Scheil reference tie-line and that for which the carbon concentration gradient in the \( \gamma \) phase is virtually zero at the end of the isothermal diffusion period. The combination of tie-lines chosen for the two interfaces at any temperature, minimizes the concentration gradient of the fast diffusing solute in the \( \gamma \); therefore, the tie-lines must lie "above" and "below" the Scheil tie-lines for the \( \delta/\gamma \) and liquid/\( \gamma \) interfaces, respectively. A comparison of the Scheil, equilibrium and final tie-lines in these figures shows how much greater the segregation of the slow diffusing solute would be due to constitutional solute interaction. Constitutional solute interaction determines the "slope" of the two-phase field boundaries. At the \( \delta/\gamma \) and liquid/\( \gamma \) interfaces the manganese concentration is much lower and higher, respectively, than for either the no diffusion in the \( \gamma \) phase or the complete diffusion in all phases case. In this system, the carbon concentration in the \( \delta \) phase remains relatively unchanged throughout the entire transformation due to the influence of constitutional solute interaction; this
was not the case in the binary system.

In both Figures 64 and 67, the final tie-line for the liquid/\gamma interface lies very close to the three phase region of the ternary isotherm; how close depends upon the "slopes" of the boundaries for the two, two-phase fields and cooling rate. However, the influence of diffusional solute interaction has not been taken into account in the calculations of these final tie-lines. In some systems, diffusional solute interaction may play an important role in determining the choice of interface tie-lines and cannot be discounted as negligible in mathematical modelling of solute re-distribution during the transformation. Solute diffusional interaction, as expressed by the value and sign of the off-diagonal diffusivities, may amplify or diminish the influence of constitutional solute interaction on microsegregation tendencies of the system. Using the Fe-0.12wt%C-1.5wt%Mn alloy as an example, the concentration gradient of the manganese (slow diffusing solute), in the \gamma phase, imposes a gradient in the activity of the carbon (fast diffusing solute). In response to this activity gradient, diffusion of the carbon would take place in order to minimize the activity gradient. The predicted manganese concentration gradient in the \gamma phase results in a variation in the carbon activity coefficient across the \gamma phase ranging from 0.049 at the \delta/\gamma interface to 0.052 at the liquid/\gamma interface, which is not enough to
significantly alter the predicted carbon distribution in the γ phase. A schematic showing the direction in which the carbon concentration profile would be adjusted, on the ternary isotherm, is provided in Figure 74. The final tie-line at the liquid/γ interface would lie closer to the three phase region than for that obtained for the case of negligible diffusional solute interaction. If the solute diffusional interaction for X-C in an Fe-C-X system was similar to but stronger than that for Mn-C, then the possibility of metastable γ solidification or the appearance of δ phase at the liquid/γ interface would be more likely in the Fe-C-X system, especially during the early stages of the transformation. It would be less likely if the sign of the X-C off-diagonal diffusivities in the Fe-X-C system is opposite to that for Mn-C, since the final tie-line would lie closer to the Scheil tie-line, on the ternary isotherm. The re-appearance of the δ phase would depend upon factors other than the existence of liquid of a composition with which the stable δ phase could co-exist, as discussed in Section 6.1. Solute diffusional interaction would take on greater importance as the transformation progressed because the influence of the presence of one solute on the diffusion of the other is a function of composition. As the transformation progresses, it is to be expected that an increasing concentration of X in the liquid would exert a stronger influence on the diffusion of carbon in the γ phase.
6.2.3 Binary to Ternary...An Extra Degree of Freedom

The treatment of the diffusion controlled peritectic transformation used in this work, modelling the non-isothermal transformation as a series of isothermal steps, exposed several aspects of the problem in binary and ternary systems, which are obscured by some of the more sophisticated mathematical methods of solving this problem. Superficially,
it appears that solute diffusivity in the peritectic phase and cooling rate are the only two factors that need be considered in any discussion of the peritectic transformation, since growth of the peritectic phase occurs due to diffusion of solute through the phase. However, this is not the entire story for either binary or ternary alloys.

In the binary case, closure of one of the two-phase fields dramatically affects the transformation rate during the later stage of the transformation, if the transformation is forced to completion at temperatures approaching the temperature for the solid/solid transformation in the pure solvent. The extra degree of freedom of a ternary system, allows for a range of equilibrium tie-lines for an interface; the system has some means of accommodating the restrictions placed on the transformation rate in the binary system, due to a fixed solute concentration-temperature relationship. In the ternary case, solute constitutional and diffusional interaction play an important role in determining the progress of the transformation in the early and later stages of the transformation, respectively. It is likely that a situation may not be reached where closure of one of the two-phase fields becomes important. In both the binary and ternary situation, it is possible under certain conditions to be left with liquid at the end of the transformation, when an equilibrium solidification path predicts that it would not
exist at the end of the transformation. In the binary system, the solute content of the liquid would be less than that predicted by the Scheil case, (no diffusion in the γ phase), since "Scheil solidification" would result in the disappearance of the δ phase at even lower temperatures than the diffusion controlled peritectic transformation, although not lower than the temperature for the solid-solid phase transformation in the pure solvent, eg. the δ → γ transformation in pure iron. In the ternary system, the solute content of the slow diffusing solute would be much greater than that predicted by the Scheil case, due to a combination of the tendency to minimize the concentration gradient of the fast diffusing solute in the γ phase and constitutional and diffusional solute interaction. There is also the added twist of the possibility of re-appearance of the δ phase at the liquid/γ interface which is the starting point for deliberations strikingly reminiscent of that concerning the nucleation of the primary phase at the peritectic phase/liquid interface with respect to the evolution of banded microstructures, although it is admittedly not the same problem at all.
7.6 Summary

Plane Front Solidification of Sn-Cd Peritectic Alloys

Sn-1.2wt% Cd alloys did not solidify with a banded structure; the solid phase formed was the primary phase. Sn-2.58wt% Cd alloys solidified as primary phase under stable growth conditions. The peritectic phase was observed in only those specimens which were purposely disturbed during solidification. A banded structure was observed in one Sn-2.58wt% Cd specimen where the primary phase/liquid interface had degenerated from planar to cellular. The peritectic phase grew in the cell boundaries and partially covered the solid/liquid interface during this period of solidification; the primary phase never completely disappeared from the solid/liquid interface. When peritectic phase solidification was firmly established the primary phase did not re-nucleate at the solid/liquid interface. In one other Sn-2.58wt% Cd specimen which experienced a sudden temperature drop across the length of the specimen, the solid formed was the peritectic phase.

The bulk undercooling experiments on Sn-Cd peritectic
alloys showed that in the presence of primary phase, an undercooling of 1-2K below the peritectic temperature was sufficient to nucleate the peritectic phase. The undercooling required to heterogeneously nucleate the primary phase was greater, 5-10K below the liquidus temperature, than that for nucleation of the peritectic phase.

The calculated undercooling (Thomson-Spaepen analysis) required for heterogeneous nucleation of a peritectic HCP phase ranged from 80 to 165K, as the primary/peritectic interphase energy was varied from 1 to 100mJ/m². The undercooling required for heterogeneous nucleation of a peritectic SHP phase ranged from 3 to 10K as the peritectic SHP phase/liquid and primary/peritectic interphase energy was varied between 5 to 55mJ/m².

Mathematical modelling of the initial stages of plane front solidification of the peritectic phase predicted it would not be possible to obtain conditions at the peritectic phase/liquid interface conducive to nucleation of the primary phase at either low temperature gradient and specimen travel velocity conditions or high temperature gradient and specimen travel velocity conditions. However, the closer the value of the bulk alloy composition is to the primary phase composition on the peritectic isotherm, the greater the probability of
obtaining these conditions. How far up on the peritetic phase liquidus the solute concentration at the interface would be at the end of the transient was more strongly influenced by the specimen travel velocity than the temperature gradient in the liquid.

Microsegregation of Solute and the Diffusion Controlled Peritectic Transformation in Fe-C and Fe-C-X Peritectic Alloys

Fe-C Alloy

The non-isothermal peritectic transformation temperature range was predicted to increase one order of magnitude for a two order of magnitude change in either cooling rate at a constant value for the carbon diffusivity or diffusivity at a constant value for the cooling rate. At small values of the transformation temperature range, 1-15K, the δ-ferrite and austenite phases remain at the end of the transformation. As the transformation range is extended to lower temperatures, the model predicted that the phase which would disappear at the end of the transformation would no longer be the liquid but the δ-ferrite phase. The calculated value of the transformation finish temperature, austenite phase fraction and phases remaining at the end of the transformation are essentially the same for the case where the
three combinations of solute diffusivity in austenite and cooling rate used have the same value of the ratio of solute diffusivity to cooling rate.

Fe–C–X Alloy

The model predictions of initial and final tie-lines show that the carbon concentration gradient in the austenite phase is virtually zero at the end of each isothermal diffusion period; the non-isothermal transformation was modelled by a series of isothermal steps. At the δ-ferrite/austenite (γ) and liquid/γ interfaces, the calculated value of the manganese concentration is much lower and higher, respectively than for either the no diffusion in the γ phase case or the complete diffusion in all phases case. The predicted carbon concentration in the δ-ferrite phase remains relatively unchanged throughout the entire transformation; this was not the case in the binary system.
8.0 Conclusions

Plane Front Solidification of Sn-Cd Peritectic Alloys

It appears that a Sn-Cd peritectic alloy would solidify as primary phase during horizontal, plane front solidification at the low specimen travel velocities and furnace temperature gradients used in this work, if it is not subjected to any disturbances. Banding in Sn-Cd peritectic alloys may be a response to erratic changes in local solidification conditions, eg. a situation where both phases are growing at the interface and nucleation is not an issue or fluctuations in local interface temperature or solute concentrations at the interface.

The undercooling experiments showed that the primary phase is an effective nucleation catalyst for the peritectic phase, an undercooling of 1–2K below the peritectic temperature, in liquid having a composition within the peritectic isotherm composition. However, it appears that an undercooling of the order of 1.4K was not sufficient to produce the peritectic phase at the metastable primary phase/liquid interface in the plane front solidified
Sn-2.58wt%Cd specimens. The results of the Thomson-Spaepen analysis suggested that an undercooling of 5-10K may be reasonable for nucleation of the SHP peritectic phase at a planar metastable primary phase/liquid interface, solute composition of the liquid is greater than the solute composition of the liquid on the peritectic isotherm.

Microsegregation of Solute and the Diffusion Controlled Peritectic Transformation in Binary and Ternary Peritectic Alloys

The treatment of the diffusion controlled peritectic transformation used in this work, modelling the non-isothermal transformation as a series of isothermal steps, exposed several aspects of the problem in binary and ternary systems, which are obscured by some of the more sophisticated mathematical methods of solving this problem.

Binary Peritectic Alloy

The model was not as helpful as one would have hoped in sorting out whether or not cooling rate was more important than solute diffusivity or vice versa, in determining the temperature range over which the non-isothermal transformation would take place. However, although the cooling rate and
solute diffusivity in the austenite phase have a role to play in determining the transformation temperature range, it is the closure of the δ-ferrite/austenite phase field, in the iron-carbon system, which ultimately determines at what temperature the transformation ends and what phases exist at that point. The degree to which this factor takes precedence over cooling rate and solute diffusivity in limiting the transformation temperature range and determining what phases exist at the end of the transformation is alloy system specific.

Ternary Peritectic Alloy

The extra degree of freedom of a ternary system, allows for a range of equilibrium tie-lines for an interface; the system has some means of accommodating the restrictions placed on the transformation rate in the binary system, due to a fixed solute concentration-temperature relationship. Three significant concepts suggested by the model predictions of solute segregation in the ternary system are:
1. The tendency to minimize the concentration gradient of the fast diffusing solute in the austenite phase and constitutional solute interaction induce a greater degree of segregation of the slow diffusing solute in all phases, in comparison with solute segregation in the no diffusion in the austenite case and the complete diffusion in all phases case.
2. Diffusional solute interaction may amplify or diminish the influence of constitutional solute interaction on micro-segregation of solute in the ternary system.

3. At the liquid/austenite interface, the possibility of metastable austenite solidification or nucleation of the δ-ferrite phase exists throughout the transformation.
LIST OF REFERENCES


31. J.W. Rutter.....Private Communication