ROLE OF MANGANESE IN THE FORMATION OF PROEUTECTOID FERRITE

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THE ROLE OF MANGANESE IN THE FORMATION

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PROEUTECTOID FERRITE

by

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SCOPE AND CONTENT:

The Fe-C-Mn phase diagram has been calculated from thermodynamic data. Experimentally determined tie-lines are in good agreement with the calculated diagram.

It has been shown that the assumption that the austenite-ferrite interface is in a local equilibrium condition during the late stages of the transformation in highly supersaturated alloys and at all times in alloys in an area of low supersaturation is justified. The approximate solution to the diffusion equations correctly predicts the experimentally determined manganese concentration profiles.

Hillert's concept of paraequilibrium has been examined and explicitly defined. The concentration given by a paraequilibrium calculation correctly predicts the experimentally observed growth rates of Kinsman and Aaronson (1967) for very highly supersaturated alloys.

A convolution technique for use in the interpretation of strongly localized concentration changes determined by electron beam microanalysis has been developed.

(ii)

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TABLE OF CONTENTS

1

INTRODUCTION

PART I	I	THE Fe-C-Mn PHASE DIAGRAM	3
	II	CALCULATION OF THE PHASE DIAGRAM	7
		 (a) Theory (b) Activity Coefficient Expressions (c) Activity Data (d) Free Energy of Transformation (e) Calculation 	7 8 10 11 14
	II	I EXPERIMENTAL DETERMINATION OF TIE-LINES	16
		 (a) Preparation of Materials (b) Analysis of Materials (c) Tie-Line Experiments 	17 17 18
	IV	RESULTS AND DISCUSSION	23
PART 2		INTRODUCTION	24
	۷	PROEUTECTOID FERRITE TRANSFORMATION	26
		 (a) Nucleation and Morphology (b) Effect of Alloying Elements (c) Theoretical Interpretations (d) Diffusion Data 	26 28 30 35
	VI	LOCAL EQUILIBRIUM MODEL .	37
		 (a) Diffusion Analysis (b) High Supersaturation: Carbon Impingement (c) Manganese Diffusion Control 	37 45 48
	VI	I PARAEQUILIBRIUM MODEL	52

	VIII EXPERIMENTAL PROCEDURES				56
	(a) Electron Probe Microanalysis Techniques				59
	IX EXPERIMENTAL RESULTS AND COMPARISON WITH THEORY				64
	(a) High Supersaturation, Long Times(b) Low Supersaturation				64 68
	X DISCUSSION				71
	XI CONCLUSIONS				77
REFERENCES		a N		•	79
	TABLES				83
FIGURES					88

LIST OF TABLES

- 1. Activity Data for the Fe-C-Mn System
- 2. Calculated Tie-Lines
- 3. Analysis of Melting Stock
- 4. Experimental Tie-Lines
- 5. Calculated Paraequilibrium Tie-Line
- 6. Data Required to Calculate Predicted Manganese Concentration Curves

LIST OF ILLUSTRATIONS"

- 1. Portion of the Fe-Fe₃C constitution diagram.
- 2. a) Fe-C-Mn isotherm after Purdy, Weichert and Kirkaldy (1964).
 - b) Fe-C-Mn isotherm after Wells (1948) and Aaronson et al (1966).
- 3. Activity coefficient of Fe-Mn alloys, after Roy and Hultgren (1967).
- 4. Standard free energy change for the ferrite to austenite transformation in iron.
- 5. Calculated standard free energy of transformation for hypothetical BCC graphite to FCC graphite.
- 6. Fe-Mn phase diagram.
- 7. Calculated standard free energy of transformation for hypothetical BCC Mn to FCC Mn.
- 8. Graphical solution of the tie-line equations.
- 9. Isotherm of the Fe-C-Mn system at 730°C.
- 10. Isotherm of the Fe-C-Mn system at 762°C.
- 11. Typical micrograph of the austenite-ferrite mixture in the equilibrium experiments.
- 12. Sample microprobe scan across an equilibrated Fe-C-Mn alloy.
 - All illustrations have been placed at the end of the thesis.

- 13. Typical calibration curve for the electron probe microanalyser.
- 14. Temperature composition regions in which the various morphologies form in iron-carbon alloys (from Aaronson, 1962).
- 15. Concentration profile in vicinity of advancing cementite interface (from Darken, 1961).
- 16. Schematic penetration curves in λ space for ferrite growth in Fe-C-Mn austenite.
- 17. Carbon concentration profile for the calculation of impingement line.
- 18. Time required for interface to reach 99% of X_{α}^{\dagger} .
- 19. Approximate concentration profiles for manganese diffusion control at long times in highly supersaturated alloys.
- 20. Schematic free energy surface for ferrite and austenite illustrating the paraequilibrium conditions.
- 21. Calculated paraequilibrium diagram for Fe-C-Mn alloys at 728°C.
- 22. Section of the paraequilibrium surface.
- 23. Electron probe microanalysis of a concentration step.
- 24. Micrograph typical of samples of alloy A transformed at 728°C.
- 25. Typical microprobe scan across a sample of alloy A transformed for 5.37X10⁶ sec at 728°C.
- 26. Microprobe analysis of alloy A transformed for 5.37 X 10⁶ sec at 728⁰C.
- 27. Microprobe analysis of alloy A transformed for 5.37 X 10⁶ sec at 728⁰C.

Microprobe analysis of alloy A transformed for 1.78 X 10⁶ sec at 728⁰C. 28. Microprobe analysis of alloy A transformed for 1.78 X 10⁶ sec at 728°C. 29. Microprobe analysis of alloy A transformed for 5.12 X 10^5 sec at 728°C. 30. Microprobe analysis of alloy A transformed for 5.12 X 10⁵ sec at 728°C. 31. Microprobe analysis of alloy A transformed for 1.6 \times 10⁵ sec at 728^oC. 32. The calculated relationship between C_{21} and ϕ for alloy A at 728°C. 33. 34. Typical micrograph of alloy B transformed for 8.6 X 10⁴ sec at 728°C. 35. Typical micrograph of alloy B transformed for 4.32 X 10⁵ sec at 728°C. 36. Typical micrograph of alloy B transformed for 3.15 X 10⁶ sec at 728⁰C. 37. Microprobe analysis of alloy B transformed for 4.32 X 10⁵ sec at 728°C. Microprobe analysis of alloy B transformed for 3 X 10⁶ sec at 728^oC. 38. Microprobe analysis of alloy B transformed for 8.59 X 10⁴ sec at 728°C. 39. Calculated parabolic rate constant for a 0.97 A% C, 1.53 A% Mn alloy. 40. 41. Comparison of Kinsman and Aaronson's experimental results with the various predicted parabolic growth rate curves. 42. Schematic representation of the local equilibrium-paraequilibrium areas at proeutectoid transformation in Fe-C-Mn alloys.

 Representation of the difference between the effect of manganese and nickel on the proeutectoid transformation assuming local equilibrium.

(ix)

INTRODUCTION

Nearly all of the common grades of steel (primarily alloys of iron and 0.02 - 1.5% carbon) are hot-worked in the austenite phase. The transformations which occur on cooling from austenite are therefore of great industrial importance. The effect of alloying elements (other than carbon) on these transformations is equally important.

When austenite is slow-cooled, the diffusion-controlled transformations are greatly influenced by alloying elements such as Mn, Mo, Cr, Si, or Ni. It is hoped that a theoretical understanding of the role of these elements will eventually lead to a replacement of empirical alloying and heat treating data with fundamental relationships.

The austenite to proeutectoid ferrite transformation is perhaps the simplest of the austenite decomposition reactions. However, even for this transformation in the Fe-C-Mn system, several models have been proposed to explain the retarding influence of Mn on the kinetics. The present investigation extends one of these models to the very late stages of the transformation in polycrystalline austenite. It demonstrates that at least for late times Kirkaldy's (1958) local equilibrium calculation is correct.

To be more specific one refers to a portion of the metastable Fe-Fe₃C phase diagram based on that of Hansen (1958) and modified to agree with the work of Smith and Darken (1959), (Figure 1). Iron on heating to 911° C undergoes an allotropic change from a body-centered cubic (BCC)

structure called ferrite or α -iron to a face-centered cubic (FCC) structure called austenite or γ -iron. This transformation is reversed at 1400^oC, a temperature much higher than considered in this study. Austenite will dissolve up to a maximum of about 8.7 atomic percent (A%) C (2 weight percent (wt.%)) at 1153^oC whereas ferrite has a maximum solubility of about only 0.1 A% C (0.02 wt.%). The interstitially dissolved carbon atoms occupy the octahedral sites in both phases (Petch, 1942, Zener, 1952). Cementite, or Fe₃C, a hard, brittle intermetallic compound, has a complex orthorhombic structure. Slow cooling of an austenitized eutectoid steel (about 0.8 wt.% C) below the eutectoid temperature produces a lamellar mixture of ferrite and cementite called pearlite. Quenching of austenite to room temperature produces a non-equilibrium body-centered tetragonal structure called martensite (α) having the same carbon content as the original austenite and formed by a shear process involving co-operative atom movements at the $\gamma - \alpha$ interface.

It is the purpose of the present study to investigate the effect of alloying elements on the kinetics of the diffusion-controlled austenite to proeutectoid ferrite transformation, especially in Fe-C-Mn alloys. This is a continuation of the work of Purdy (1962) and of Purdy, Weichert and Kirkaldy (1964).

Before a quantitative discussion of the austenite-proeutectoid ferrite transformation in these ternary alloys can be undertaken, it is necessary to establish with certainty the Fe-C-Mn phase diagram in the proeutectoid region. Accordingly, this thesis is divided into two parts, Part I dealing with the phase diagram and Part 2, with the transformation studies.

PART 1

I THE Fe-C-Mn PHASE DIAGRAM

A portion of the Fe-C phase diagram (Hansen, 1958, Smith and Darken, 1959) which forms one of the binary limits for the Fe-C-Mn ternary system is shown in Figure 1. This was briefly described in the preceding section.

The other limiting binary system, Fe-Mn, has been experimentally determined by Troiano and McGuire (1943). However, their experimental points for the $\alpha + \gamma / \gamma$ boundary at the higher temperatures (700[°] and 800[°]C) were unreliable and so they extrapolated this section of the boundary from the points at 600[°]C and below. They were able to experimentally determine the $\alpha + \gamma / \alpha$ boundary at 700 and 800[°]C as well as at the lower temperatures.

Recently Hillert, Wada and Wada (1967) experimentally determined a point on the $\alpha / \alpha + \gamma$ boundary at 820°C which is in good agreement with that of Troiano and McGuire. Hillert was unable to determine the corresponding point on the $\alpha + \gamma / \gamma$ boundary due to the steep manganese gradients in the austenite adjacent to the interface. However, calculations based on a regular solution model, and independent of the experimental result, indicate that the $\alpha + \gamma / \gamma$ boundary should be somewhat lower than that previously accepted. Hillert's calculated $\alpha / \alpha + \gamma$ boundary passing through his single experimental point lies very close to that of

Troiano and McGuire.

Ternary isotherms for this system have been published by Wells (1948) based on the earlier work of Walters and Wells (1936). These isotherms indicate that the $\alpha + \gamma / \gamma$ boundary is concave toward the Fe corner. When modified to agree with the newer binary data mentioned above, this curvature is even greater. However, the data on which the ternary surface was based is sketchy.

Purdy, Weichert and Kirkaldy (1964) attempted to determine experimentally the ternary surface by up-quenching martensitic alloys into the two-phase region. After holding at temperature to precipitate ferrite, the samples were quenched and examined metallographically to confirm precipitation on the austenite grain boundaries. The samples were then up-quenched to higher temperatures and held for times sufficient to redissolve all of the grain boundary ferrite (up to several hours.) The lowest temperature at which the ferrite completely dissolved was taken as a point on the $\alpha + \gamma / \gamma$ surface for the bulk composition of the sample. The limiting binaries used in their construction of the ternary isotherm were for Fe-C, the same as shown in Figure 1, and for Fe-Mn, the diagram of Troiano and McGuire.

Their results, shown in Figure 2a, indicated a phase boundary which is concave away from the Fe rich corner.

Unfortunately, in these experiments there is no certainty that the ferrite dissolving at the higher temperatures is in equilibrium with the austenite away from the interface. Indeed, the remainder of their paper is concerned with showing that ferrite formed on up-quenching in this manner does not lie on the equilibrium tie-line for the bulk com-

position and thus would not be in equilibrium with the austenite away from the interface. The times at dissolution temperatures were not sufficient to allow the equilibration of manganese throughout the sample and there would thus appear to be no basis for the assumption that the last bit of ferrite which dissolves at the higher temperatures is in equilibrium with austenite having a composition equal to the bulk composition of the sample.

Since the publication of these results, it was learned that the standardized thermocouple used in their experiments may have been incorrectly calibrated by the National Research Council (Purdy, 1970). This incorrect standardization could account for the recorded temperatures being as much as five degrees lower than the true temperatures. If this was so, this correction would result in a nearly linear $\alpha + \gamma / \gamma$ boundary.

Aaronson, Domian and Pound (1966) calculated tie-lines in the twophase region of the phase diagram based upon a prior experimental knowledge of the phase boundaries. In all their calculations, they have set the carbon content of the ferrite equal to zero. In a rigorous treatment this would imply that the partial molar free energy of carbon in ferrite is equal to minus infinity. They have also defined $\overline{G}_{S\alpha}^{\alpha\gamma}$ and $\overline{G}_{S\gamma}^{\gamma\alpha}$ as the partial molar free energies of substitutional atoms (both iron and manganese, irrespective of their identity) in ferrite and in austenite at the austenite-ferrite boundaries, respectively, and then set these equal. Since the condition for equilibrium which defines a tie-line is that the partial molar free energy of each component is uniform throughout the two-phase system, their premise would seem to leave their conclusions in doubt.

For the tie-line calculations, Aaronson et al have used the phase boundaries of Walters and Wells (1936). This diagram, with their calculated tie-lines, is shown in Figure 2b.

In view of the uncertainty in all of these diagrams, a re-calculation, including a number of tie-lines in the two-phase region, has been carried out following the method of Hone, Subramanian and Purdy (1969). As described in the next section, not all of the ternary data required for such a calculation are known, but in the case of terminal solid solutions such as these, the crucial data may be inferred from the limiting binary diagrams. In addition, confirmatory experiments using a new technique have been performed. A description of the theoretical calculation and the experiments follows.

II CALCULATION OF THE PHASE DIAGRAM

(a) Theory

The partial molar free energy of component i, \overline{G}_i , in any phase may be written

$$\overline{G}_i = G_i^0 + RT \ln a_i$$
 (1)

where G_i^0 is the free energy of the pure component i in its standard state and a_i is the activity of component i. In a ternary system there are three such equations for each phase.

At equilibrium the partial molar free energy of each component is uniform throught the two-phase systems, or

$$\overline{G}_{i}^{\alpha} = \overline{G}_{i}^{\gamma}$$
(2)

Therefore, the following three equations are valid in any twophase region of a ternary system.

$$\Delta G_i = RT \ln \frac{a_i}{a_i}$$
 $i = 0, 1, 2$ (3)

where $\Delta G_i = G_i^{0\alpha} - G_i^{0\gamma}$, the free energy change of the pure component i in transforming from the alpha to the gamma phase.

Equation 3 may be written

Primed quantities refer to the ferrite or alpha phase; unprimed, to the austenite or gamma phase. Subscripts 0, 1, 2 refer to the solvent iron (0) and the solutes carbon (1) and manganese (2).

$$\frac{\Delta G_i}{RT} = \ln \frac{X_i}{X_i} + \ln \frac{Y_i}{Y_i} \quad i = 0, 1, 2 \quad (4, 5, 6)$$

where X_i is the mole fraction and γ_i is the activity coefficient (equal to $\gamma_i = a_i/X_i$). It should also be noted that $X_0 = 1 - X_1 - X_2$, and $X_0 = 1 - X_1 - X_2$. Equations 4, 5 and 6 are the same as obtained by Hone (1969) by a more circuitous route.

If the activity coefficients and free energy of transformation of the pure components are known at a given temperature, one of the concentrations, X'_2 , may be specified, and equations 4, 5 and 6 solved for the three remaining concentrations. This yields one tie-line in the two-phase region. The procedure may be repeated at the same temperature for other values of X'_2 , completely determining the two-phase region of the isotherm. Other isotherms may be calculated in the same manner.

Although all of the required ternary thermodynamic data is not known for terminal solid solutions, the critical parameters can be inferred from the limiting binary phase diagrams (Hone, 1969).

(b) Activity Coefficient Expressions

Wagner (1952) has shown that the activity coefficients in multicomponent solutions may be expanded as a Taylor Series about the state of infinite dilution. Dropping the second and higher order derivatives the expression for solute 1 becomes

$$\ln \gamma_{1} = \ln \gamma_{1}^{0} + \frac{\partial \ln \gamma_{1}}{\partial X_{1}} X_{1} + \frac{\partial \ln \gamma_{1}}{\partial X_{2}} X_{2}$$
(7)

or

$$\ln \gamma_1 = \ln \gamma_1^0 + \varepsilon_{11} \chi_1 + \varepsilon_{12} \chi_2$$
(8)

Similarly for solute component 2,

$$\ln \gamma_2 = \ln \gamma_2^0 + \epsilon_{21} \chi_1 + \epsilon_{22} \chi_2$$
 (9)

It may also be shown as a Maxwell relation that $\varepsilon_{12} = \varepsilon_{21}$.

The expression for the solvent (component 0) may be obtained with the aid of the Gibbs-Duhem relation

$$\sum_{i=1}^{2} X_{i} d\ln \gamma_{i} = 0$$
(10)

Dropping the cubic terms, it may be shown that

$$\ln y_0 = - \frac{\varepsilon_{11} x_1^2}{2} - \varepsilon_{12} x_1 x_2 - \frac{\varepsilon_{22} x_2^2}{2}$$
(11)

In these expressions the γ_i^0 are the Henry's Law coefficients and the ϵ_{ij} are the Wagner interaction parameters.

In any two-phase region of a ternary system there are six expressions in all, one for each component in each phase.

Although these expressions are strictly applicable for infinitely dilute solutions, they have been shown experimentally to apply in Fe-C-Mn austenite up to quite high concentrations (Brown and Kirkaldy, 1964).

(c) Activity Data

The activity of carbon in Fe-C alloys (austenite and ferrite) and in Fe-C-Mn alloys (austenite only) has been determined by Smith (1946, 1948). The Henry's Law coefficients (graphite standard state) and the interaction parameters determined from these data (Brown and Kirkaldy, 1964) are given in Table 1. Although Smith has compiled these data only for the temperature range of 800 to 1200° C they have been used in these calculations by extrapolation down to 700° C. The experimental points for the ferrite phase (Smith, 1946) are too scattered to allow extraction of a meaningful parameter ε_{11}° . However, since this interaction parameter is multiplied in equation 3 by the very low concentration of carbon in ferrite, any error introduced by setting $\varepsilon_{11}^{\circ} = 0$ is negligible.

Since no direct information is available on the cross interaction in ferrite and since theoretically there is no reason to believe that this parameter should differ substantially between equilibrated phases, ε_{12} has been set equal to that in austenite.

Roy and Hultgren (1965) have measured the activity of manganese in Fe-Mn austenite at 1450° K (manganese standard state). Their results, shown in Figure 3, give a self interaction parameter, ϵ_{22} , of -0.65. Using a 1/T dependence for extrapolation (Kirkaldy, 1962) a value of -1 at 730°C is estimated. As no data is available on the ferrite phase, the self interaction parameter, ϵ_{22} , has been set equal to zero. Since there is no reason to believe that ϵ_{22} should be large and since it is multiplied by X_2 , a relatively small value, any error introduced by this approximation will be negligible. All of the thermodynamic data used are summarized in Table 1.

(d) Free Energy of Transformation

The free energy of transformation of iron from ferrite to austenite, ΔG_0 , has been calculated by Johansson (1937), Zener (1946), Fisher (1949), Darken and Smith (1951) and most recently by Kaufman, Clougherty and Weiss (1963). These values are shown in Figure 4.

The free energy of transformation of a hypothetical FCC graphite to BCC graphite, ΔG_1 , has been calculated using the following equation, the binary (0 - 1) analogue of equation 5 and the appropriate activity expressions.

$$\frac{\Delta G_{1}}{RT} = \ln \frac{X_{1}}{X_{1}} + \ln \frac{Y_{1}^{0}}{Y_{1}^{0}} - \varepsilon_{11}X_{1}$$
(12)

The values of X_1 and X_1 were taken from the Fe-C phase diagram of Hansen (1958), and extrapolated to lower temperatures (Figure 1). Equation 12 was solved for ΔG_1 at ten-degree intervals from 700°C to 850°C. The calculated values, shown in Figure 5, are somewhat scattered due to the error in choosing the concentrations from the phase diagram. A linear least square fit of these points gives

$$\Delta G_1 = 11.539T^0 K - 15,347$$
(13)

Over a larger temperature range, ΔG_1 may not be a linear function of tempera-

ture (Hillert, 1967). However, as may be seen from Figure 5, any error introduced by using a linear relation over the limited temperature range involved here is small.

Equation 13 was used to calculate the value of ΔG_1 at the temperatures of interest.

To check for internal consistency of the data, equation 12, and the binary (0 - 1) form of equation 4

$$\frac{\Delta G_0}{RT} = \ln \frac{1 - X_1}{1 - X_1} + \frac{\varepsilon_{11} X_1^2}{2}$$
(14)

were simultaneously solved at ten-degree intervals to re-calculate the binary phase diagram (ΔG_1 values from equation 13). Good agreement with Hansen's diagram could be obtained only if the values of ΔG_0 were altered slightly from those given by Kaufman, Clougherty and Weiss(1963). These adjusted values are also shown in Figure 4 and were used in all following calculations. As may be seen from this figure, the values used fall within the scatter of the data from the various investigators.

As discussed in the previous section concerning the limiting binary phase diagrams, Troiano and McGuire (1943) experimentally determined the ferrite-austenite region of the iron-manganese phase diagram and Hillert (1967) has claimed that their austenite boundary is in error at high temperatures. Hillert presented a calculated diagram which is in good agreement with the experimental ferrite boundary but which indicates that the $\alpha + \gamma / \gamma$ boundary should be lower. For the purposes of this investigation, the experimental ferrite boundary of Troiano and McGuire, with which Hillert agrees, has been used. Using the binary (0 - 2) form of equation 4 with the appropriate activity expressions

$$\frac{\Delta G_0}{RT} = \ln \frac{1 - X_2}{1 - X_2} + \frac{\varepsilon_{22} X_2^2}{2}$$
(15)

and the adjusted values of ΔG_0 , the $\alpha + \gamma / \gamma$ boundary has been calculated. This, along with Hillert's calculated and Troiano and McGuire's experimental boundaries, are shown in Figure 6. Hillert's calculation, while similar to the one presented here, is based on a regular solution model and uses an interaction constant in the austenite of -1200 cal/mole.^{*} This value was chosen to give good agreement between the calculated and experimental boundaries at low temperatures. The interaction constant for ferrite was taken to be zero. As in this investigation only the high temperature region is of interest, it was decided to use the Wagner formalism and the experimentally determined ε_{22} of -1, resulting in the $\alpha + \gamma / \gamma$ boundary shown in Figure 6.

Using this new phase diagram, $\Delta G_2 - RT \ln \frac{\gamma_2}{\gamma_2^0}$ was calculated at $10^{\circ}C$ intervals. (As the Henry's Law coefficient of Mn in ferrite is not known, both coefficients have been included in the ΔG_2 term). This is shown in Figure 6. Although there is an indication of an S-shaped curve as obtained by Hillert (1967), a linear least square fit has been made for the points between $700^{\circ}C$ and $830^{\circ}C$, giving the line

^{* -1200} cal/mole would correspond to a ε_{22} of approximately +1.2 at 1000 K although the comparison is not completely rigorous because of the different solution models used.

$$\Delta G_2 - RT \ln \frac{\gamma_2^{20}}{\gamma_2^{0}} = 6.118 T^0 K - 7808$$
(16)

The scatter in the calculated values of $\Delta G_2 - RT \ln \frac{\gamma_1^0}{\gamma_1^0}$ is due to the

rounding off of the concentrations calculated from equation 15.

As isotherms have been calculated only between $700^{\circ}C$ and $770^{\circ}C$, it is felt that equation 16 gives the least biased result in this region.

Thus, all of the critical information is available for the calculation of the ternary phase diagram.

(e) Calculation

The complete expressions used in the calculation of the ternary isotherms are the following (equations 4, 5 and 6 with the substitution of the activity expressions from equations 8, 9 and 11):

$$\frac{\Delta G_0}{RT} = \ln \frac{1 - X_1 - X_2}{1 - X_1 - X_2} + \varepsilon_{12}(X_1X_2 - X_1X_2) + \frac{\varepsilon_{11}X_1^2}{2} + \frac{\varepsilon_{22}X_2^2}{2}$$
(17)

$$\frac{\Delta G_1}{RT} = \ln \frac{x_1}{x_1} + \ln \frac{y_1^0}{y_1^0} - \varepsilon_{12}(x_2 - x_2) - \varepsilon_{11}x_1$$
(18)

$$\frac{\Delta G_2 - RT \ln \frac{Y_2^0}{Y_2^0}}{RT} = \ln \frac{X_2}{X_2} - \varepsilon_{12} (X_1 - X_1) - \varepsilon_{22} X_2$$
(19)

The method used in the solution of these equations was a graphical trial and error procedure. Hone's results indicated that the α / α + γ boundary should be nearly linear. Thus, as a first trial, linearity of this boundary was assumed and the corresponding values of X_1 and X_2 were substituted into equations 18 and 19. Various values of X1 were substituted into equation 18 and values of X_2 calculated. These points, which nearly form a straight line, were plotted (Figure 8). Similarly, values of X_2 were substituted into equation 19, X1 calculated and these values plotted on the same graph. The point of intersection of these two lines represents the solution of the simultaneous equations 18 and 19. The four concentrations were substituted into equation 17 and a value of ΔG_0 calculated and compared with the values from Figure 4. If the agreement was not satisfactory (± 0.5 cal), a new value of X_1 was chosen (X_2 held constant) and the process repeated until the four concentrations satisfied equation 17. (Changing the value of X_1 by a small amount makes a negligible change in the X_1 vs X_2 line from equation 19. Thus, there is only one line in Figure 7 representing all the values of X1.

The results of this calculation at 730⁰C and at 762⁰C are shown in Figures 9 and 10, respectively. The end-points of the calculated tielines are list in Table 2.

It should be noted that the calculated $\alpha / \alpha + \gamma$ phase field is concave away from the iron corner of the diagram. While the degree of curvature is small, it is nevertheless uniquely determined by the simultaneous solution of the three equations.

III EXPERIMENTAL DETERMINATION OF TIE-LINES

The calculated diagrams (Figures 9 and 10) are reasonable insofar as the phase boundaries have the same sign of curvature as those of Wells (1948) (Figure 2b) and the distribution of tie-lines is relatively uniform as would be expected from the diluteness of the solutions and the small interaction parameters. However, in the light of Purdy's contradictory results (1964), it would be more satisfactory to have additional experimental evidence.

The experimental determination of tie-lines in most ternary systems of interest in physical metallurgy is difficult. In these systems, the diffusion of the substitutional element, Mn, in austenite at the temperatures of interest is so slow that it is impracticable to allow sufficient time for a previously homogenized sample to reach complete thermodynamic equilibrium by conventional isothermal heat treatment. Although the electron beam microanalyser makes possible the measurement of relatively steep manganese concentration gradients, the extrapolation of the profiles to the phase interface usually results in significant error. Also, the Cameca microprobe at McMaster cannot analyse for carbon and thus this instrument cannot be used for the complete determination of tie-lines using local equilibrium concentrations at moving interfaces.

In this investigation, a new technique has been developed which produces an equilibrium dispersion of austenite in ferrite with diffusion distances such that equilibrium is reached in relatively short times.

(a) Preparation of Materials

The alloys used in this investigation were prepared from electrolytic iron and manganese (99.9%) melted in a non-consumable tungsten electrode arc furnace under an argon atmosphere. The analysis of the iron melting stock is given in Table 3. The buttons (usually about 100 grams) were turned and melted at least four times. They were cold rolled to about 5 mm thickness, followed by homogenization in an argon atmosphere at 1050°C for one week. The alloy was then rolled to its final thickness of about Samples (approximately 8 mm by 20 mm) were sheared from the sheet 1 mm. and a small hole was drilled in one end so that they could be suspended in a gas carburizing furnace. The samples were carburized in flowing CO-CO2 gas mixtures at 1000°C in an apparatus constructed by Brigham and Kirkaldy (1963) patterned after that described by Darken and Gurry (1945). The samples were carburized for times such that $\frac{D_{11}t}{L^2} > 3$, (L is the half thickness of the sample) sufficient to ensure homogenization of the carbon (Darken and Gurry, 1953) and then dropped out of the hot zone so that they quickly cooled to room temperature.

(b) Analysis of Material

In the early stages of the investigation carbon analysis of small samples was carried out using a micro-carbon determinator constructed by Purdy (1962) following the technique of Frazer and Holzmann (1960). Bulk carbon determinations on larger samples were carried out using a standard Leco apparatus (Orsat type). Later in the investigation carbon analysis of small samples was done on the Leco instrument using a gas chromatograph (thermal conductivity cell) to analyse the CO₂ produced.

Manganese analysis was carred out using a standard wet chemical method. The sample was dissolved in a nitric-sulphuric acid mixture, oxidized to permanganate and titrated with arseneous oxide.

(c) Tie-Line Experiments

The diffusion coefficient of manganese in annealed austenite has been measured by Wells and Mehl (1941). Their results indicate a diffusivity of approximately 10⁻¹⁵ at 730°C. However, Kurdjumov (1955) has shown that the diffusivity of substitutional elements in up-quenched ternary austenites may be greatly enhanced, apparently due to the presence of an extensive defect structure. He also indicates that at temperatures below 1000°C these defects are not easily annealed out. Krauss (1963) has observed high densities of tangled dislocations in up-quenched Fe-Ni martensites and this would appear to substantiate Kurdjumov's hypothesis.

The diffusion coefficient of Mn in ferritic Fe-Mn or Fe-Mn-C alloys has not been measured. However, the diffusion coefficient of manganese in austenite is approximately twice the self diffusion coefficient of iron in austenite. Therefore, one would expect manganese to diffuse in ferrite at a rate similar to that of iron self-diffusion in ferrite, or approximately 100 times faster in ferrite than in austenite at the same temperature.

(Fridberg, Torndahl and Hillert, 1969). P. N. Smith (1970) has observed this magnitude of difference between the diffusion of manganese in austenite and the high temperature delta ferrite. This is a commonly observed result for diffusion of both substitutional and interstitial elements in iron and is considered to be due to the more open BCC structure of the ferrite (Hume-Rothery, 1966).

Since the self-diffusion of carbon in both austenite and ferrite is rapid (Wells, Batz and Mehl, 1950, Borsov et al, 1970) relative to that of manganese, carbon can rapidly readjust to the manganese gradient in an equilibrating sample and therefore will not impede the approach to equilibrium.

In the light of the above information, it was decided to produce a sample having a structure consisting of a dispersion of austenite in a ferrite matrix, thus relying on the relatively rapid diffusion of manganese through the ferrite for equilibration, and to attempt to enhance the manganese diffusion in austenite by the reverse martensite transformation. Hickely and Woodhead (1954), during their study of the formation of ferrite, found that this type of structure is indeed produced by the reheating of martensitic alloys into the proeutectoid region.

Towards this end, samples of Fe-C-Mn alloys were prepared having a carbon content low enough to ensure a relatively high volume fraction of ferrite in the two phase $(\alpha + \gamma)$ region. The samples were encapsulated in silica and austenitized at $1200^{\circ}C$ (± $10^{\circ}C$) in a standard horizontal Kanthal furnace for 18 hours to ensure a homogeneous starting material. The capsules were quenched by breaking under water to produce a martensitic structure. They were then re-encapsulated and inserted in a preheated Kanthal furnace constructed by Dorward (1967) at the desired

temperature to produce the reverse martensite transformation. The temperature was periodically checked with a standardized Pt-Pt 10%Rh thermocouple and was regulated to $\pm 1^{\circ}$ C. After 3 days, the capsules were removed from the furnace and rapidly cooled by dropping unbroken into water. Metallographic examination indicated that this cooling rate was sufficient to produce a martensitic structure in the former austenite regions, now higher in manganese and thus having greater hardenability than the original homogeneous sample.

The samples were removed from the capsules and reduced in area approximately 10% by hammering. It was hoped that this working would enhance the rate of diffusion of manganese in the ferrite matrix by introducing a defect structure. The samples were again encapsulated and quickly reheated to the transformation temperature. This procedure was repeated 3 times giving a total time at temperature of approximately 10^6 sec. After the final isothermal treatment the capsules were broken under water. An example of the resultant structure is shown in Figure 11. It consists of a relatively uniform dispersion of martensite (austenite at temperature) in a matrix of ferrite. The size of the austenite precipitates varied; in high manganese samples (3.55A%Mn, 0.50A%C) the dispersion was in most areas too fine to be accurately analysed using the electron microprobe. In the other samples the austenite precipitates were, on the average, between 5 and 10 μ in diameter.

A complete study of the process by which the equilibrium mixture of austenite and ferrite is formed has not been carried out. However, metallographic examination of the specimens after each period of isothermal

anneal indicates that the austenite first forms as relatively long, closely spaced platelike precipitates, and after further working and annealing these tend to break up into larger, more uniaxed precipitates. This may be a process similar to the spheroidization of pearlite. Even after one three-day anneal these platelike precipitates show considerable manganese partition and are thus well on the way towards equilibrium. As these precipitates evolve into the more uniaxed final structure the manganese diffuses mainly within the high transport medium ferrite.

The samples were analysed for manganese using the Cameca microprobe, detecting the manganese K_{α} radiation. A preliminary scan is shown in Figure 12. The variation in peak height is due to the beam falling on the edge of a precipitate. Careful point counting across the sample did not indicate any manganese gradient in either phase. There is therefore good assurance that the phases are in thermodynamic equilibrium.

Both phases were quantitatively analysed for manganese using an accelerating voltage of 20 KV and a beam current measured at the sample of 150 nano-amps. Ten ten-second counts were taken on a large number of spots on the sample, care being taken to ensure that the beam was falling only on one phase (Due to the fine dispersion of phases this at times was difficult.). Three iron-manganese alloys were used as standards, and the background radiation was measured on a sample of Ferrovac E. Figure 13 shows a typical calibration curve from these standards. The samples had been lightly etched with 2% nital but this has been shown to have no effect on the microprobe analysis (Aaranson, and Domian, 1966).

A number of photomicrographs were taken of various areas of the

specimens, and using a standard grid technique (Rostoker and Dvorak, 1965, Hilliard and Cahn, 1961), the volume fraction of the phases was determined. The samples were analysed for bulk manganese and carbon after the microprobe and metallographic examination.

Knowing the bulk carbon and the volume fraction of the phases at temperature (a correction of 4% was made to allow for the volume expansion of the austenite to martensite transformation, Reed-Hill, 1964) and approximating the carbon in the ferrite by using the assumption of a linear $\alpha / \alpha + \gamma$ boundary, the carbon content of the austenite was calculated. These data, with the manganese analysis, resulted in the complete determination of a tie-line.

In the case of the 3.55 A% Mn alloy, the dispersion of austenite was too fine to allow the volume fraction to be determined with any degree of accuracy by metallographic means. For this alloy the tie-line was established by determining the intersection of a line drawn through the known ferrite composition and the bulk composition of the sample with a constant manganese line corresponding to the Mn composition of the austenite as determined by the microprobe.

For the 1.88 A% and 1.50 A% Mn alloys at 730^oC and 762^oC, respectively, an indication of the precision of the final tie-line determination is given by the relative position of the bulk composition to the tie-line. As shown in Figures 9 and 10 the internal consistency is excellent.

IV RESULTS AND DISCUSSION

The experimentally determined tie-lines are shown in Figures 9 and 10 (dashed lines) and listed in Table 4 along with the bulk composition of the alloys used.

The tie-line for the 3.55A%Mn alloy is the least reliable because of the difficulty in determining the volume fraction of phases present. In addition, for this experiment the microprobe analysis had to be confined to areas of the specimen where the precipitates were large enough so that the microprobe beam of about 2 micron diameter fell only on one phase. Thus, the carbon content of the austenite has been determined by drawing the tie-line through the known points given by the ferrite composition (manganese concentration measured by the microprobe) and the bulk sample composition until it intersected the manganese isoconcentration line determined from the microprobe results.

The agreement between the phase boundaries for the experimental and calculated diagrams is excellent, while the slope of the tie-lines show a slight disagreement. However, this discrepency is not sufficient to suggest that there is any significant error in the independently calculated diagram. This is the first experimental test of Hone's (1969) method of phase diagram calculation based on the extraction of necessary thermodynamic data from the binary diagrams.

Additional tie-lines have been calculated for temperatures needed in the kinetic calculations following in Part 2 of this thesis. All of these calculated tie-lines are included in Table 2.

PART 2

INTRODUCTION

During the past fifty or more years the study of the austenite decomposition reactions in steels has been undertaken by many investigators. In their pioneering work, Bain and Davenport (1930) presented the results of their systematic investigation of the isothermal decomposition product of austenite in the form of TTT curves and undoubtedly inspired many later investigators. Here one simple diagram contained quantitative information relating to the nucleation and growth of the various resulting phases.

The determination of the diffusion coefficients of carbon and other alloying elements during the next two decades encouraged the development of theoretical models for these transformations which could be checked against experiments.

Perhaps the least complicated of the austenite decomposition reactions is the proeutectoid ferrite transformation: it involves only one precipitating phase in contrast to the pearlite reaction which involves the simultaneous precipitation of two phases. This is also the first transformation which occurs on cooling in all of the common grades of plain carbon and low alloy steels, and it therefore in many cases determines the position of the nose of the C curve. This transformation then plays a major role in determining the hardenability of particular steels.

Hardenability is defined as the property which determines the depth of hardness in a quenched steel. That is, it refers to the relative ease of hardening, not the degree of hardness. In a steel with a high hardenability, the high temperature transformations are suppressed or occur slowly and the steel may be easily quenched and therefore hardened to greater depth. Manganese is known as a very effective hardenability agent and so the character of transformations in the ternary system Fe-C-Mn has considerable technological interest.

In this part of the thesis the various morphologies of proeutectoid ferrite will not be dealt with in detail, but most of the attention will be given to the growth of grain boundary allotriomorphs in Fe-C-Mn alloys. A short discussion of the previous experimental and theoretical work will be followed by a detailed consideration of the diffusion controlled grain boundary transformation in Fe-C-Mn alloys. The implications of this theoretical treatment will be discussed and the agreement or disagreement of the published data for this transformation dealt with. New experimental results will be presented and a new technique for the interpretation of microprobe analysis of steep concentration gradients is developed.

V PROEUTECTOID FERRITE TRANSFORMATION

(a) Nucleation and Morphology

When iron carbon alloys are cooled below the $\alpha + \gamma / \gamma$ phase boundary, the precipitating ferrite may form with one of several distinct morphologies, depending on the degree of supersaturation (i.e., undercooling). Aaronson, (1962) in his extensive review, discusses these various morphologies in detail, following the classification of Dubé (1948) and Dubé, Aaronson and Mehl (1958). Figure 14, taken from Aaronson (1962), shows that at relatively low undercooling, grain boundary precipitates are usually found. At higher undercooling, Widmanstätten plates appear. These Widmanstätten ferrite plates are related approximately by the Kurdjumov and Sachs (1939) relation to the parent austenite; that is,

(111), 11 (110), 5 [110], 11 [111],

so that there is a chance of partial lattice matching, and a semi-coherent interface structure.

C. S. Smith (1953) has postulated that the ferrite nucleates at a boundary between two austenite grains, and has a definite orientation relationship to one of them, resulting in at least a partially coherent interface with that grain. Since in general there will be no particular orientation relationship between the two austenite grains, the ferrite nucleus will have a non-coherent and thus mobile interface with the austenite grain adjacent to the one in which it nucleates. Hillert (1962) has presented convincing
evidence that this is indeed the usual condition of nucleation and growth. Shewmon (1965) has proposed, on the other hand, that the coherent interface is the more mobile, and therefore the precipitate growth will be into the grain in which the ferrite has nucleated. Townsend and Kirkaldy (1968) adopted Smith's hypothesis and, in light of their observations on the growth of Widmanstätten plates and some observations of Ryder, Pitsch and Mehl (1967), proposed that the orientation relation between the austenite and the nucleating ferrite interface is the K-S relationship. Widmanstatten plates grow when the orientation of the ferrite at the boundary is changed due to the curvature of the grain boundary and the coherent austenite-ferrite interface attempts to maintain the K-S relationship. This provides a protuberance at the bend of the boundary which acts as a perturbation. Using the methods of Mullins and Sekerka (1963) and Sekerka (1967) they show that this perturbation controls the resulting spacing of the plates, while diffusion of carbon governs the growth rate. In the temperature range studied by Townsend and Kirkaldy all Widmanstätten plates were found to grow from a grain boundary nucleus.

Zener (1949) presented solutions to the diffusion equations for the growth of precipitates from a supersaturated matrix in binary alloys applicable to the growth of ferrite from austenite in Fe-C alloys. It has been experimentally verified that this transformation is carbon diffusion controlled by Hickley and Woodhead (1954), Mazanec and Cadek (1958), Popov and Mikalev (1959), Purdy and Kirkaldy (1963), and Kinsman and Aaronson (1967).

(b) Effect of Alloying Elements

While it is generally accepted that the interface is in a condition of local equilibrium during proeutectoid transformation in Fe-C alloys, this general acceptance is not the case for the transformation in Fe-C-X alloys (X represents any substitutional element).

Bowman (1946) reported, on the basis of analysis using X-raydetermined lattice parameter measurements, that no partition of molybdenum was detected during the formation of proeutectoid ferrite in a number of Fe-C-Mo alloys transformed at 650° C and 750° C. Aaronson (1962), using electron probe microanalysis, found a similar result for chromium in a 0.17 % C, 2.92 % Cr steel isothermally transformed at temperatures between 500° C and 800° C. In a preliminary announcement, Aaronson, Clark and Doman (1963) reported that partitioning of manganese in a 0.11 to 0.17 % C, 3.1 % Mn steel was detected at transformation temperatures above 650° C, but not below. In a 0.11 to 0.17 % C, 3.3 % Ni steel, partitioning was found above 750° C. No partitioning was found in a 0.11 to 0.17 % C and one of 1.8 % Si, 2.9 % Cr, 1 % Co or 0.4 % Mo steel at any temperature investigated.

Purdy, Weichert and Kirkaldy (1964) published the results of an investigation on the growth of proeutectoid ferrite in Fe-C-Mn alloys. Using up-quenched diffusion couples produced by electroplating an iron nucleus onto a martensitic Fe-C-Mn substrate, they observed that manganese partitioned to austenite at low supersaturations where the growth rates were extremely slow. At higher supersaturations the precipitationing ferrite had the same composition as the original austenite, and the growth rate was many times faster. In all cases a parabolic growth rate was observed. Unfortunately the electroplated iron nucleus acted as a sink for manganese, and, in the case of the low supersaturated alloys (0.210 % C, 1.52 % Mn above 740° C; 0.335 % C, 1.52 % Mn and 0.282 % C, 3.16 % Mn at temperatures of from 725 to 745° C) where the growth rates are very low, this led to diffusion of manganese back through the precipitating ferrite and thus to higher growth rates than would be predicted for grain boundary precipitates.

Aaronson and Domian (1966) published the results of an exhaustive experimental study on the partitioning of alloying elements between austenite and ferrite or bainite. They concluded, on the basis of electron microprobe examination, that of the elements studied only the so-called austenite stabilizers (Mn, Ni and Pt) partitioned, and then only at relatively low supersaturation, the exact amount of supersaturation depending on the alloy composition. At lower temperatures no partitioning was observed. Ternary Fe-C-X alloys (X one of Si, Co, Mo, Cr or Cu) did not exhibit partitioning at any temperature studied. Partitioning of aluminum to ferrite was detected after relatively long transformation times, but not after short times. In a more recent paper, Kinsman and Aaronson (1967) have shown rather conclusively that grain boundary ferrite precipitates growing from supersaturated austenite in Fe, 0.5 A% C; Fe, 0.5 A% C, 1 A% Mn and Fe, 0.5 A% C, 1 A% Mo alloys exhibit parabolic growth kinetics. A more detailed discussion and interpretation of some of these results will be presented later.

(c) Theoretical Interpretations

Hultgren (1951), after studying the isothermal decomposition of austenite in alloyed steels, proposed that two types of proeutectoid ferrite could form. He noted that at relatively low supersaturation the kinetics of the transformation were slow while at higher supersaturation they were much faster, and these data could, in many cases, be represented by two C curves on the TTT diagram rather than by one. He proposed, therefore, that at low supersaturation the interface would be in local equilibrium and the transformation require the equilibrium redistribution of the slow diffusing substitutional alloying element. The ferrite produced under these conditions of local equilibrium he termed orthoferrite. At lower temperatures the slow diffusing alloying element could not redistribute and thus the transformation would proceed under carbon diffusion control and the precipitating ferrite have the same alloy content as the original austenite. He called this non-equilibrium product paraferrite.

Hillert (1952) and Rudberg (1952) discussed in more detail the position of the paraequilibrium phase boundaries in ternary alloy systems. Hillert has shown qualitatively that paraequilibrium boundaries can be calculated from a knowledge of the free energy surfaces. A true paraequilibrium tie-line must satisfy the criterion that the chemical potential of the high mobility component, carbon, must be the same on both sides of the ferriteaustenite interface. The only lines that can satisfy this are those radiating from the carbon corner of the diagram such that the ratio of the concentration of the two substitutional components is held constant. Rudberg has called these lines carbon "component rays". A tangent plane can be constructed at the point of contact of a component ray with each free energy surface. Since the tangent line lies in each tangent plane and the chemical potential of carbon is given by the intersection of the tangent plane with the carbon axes, the carbon activity is the same in both phases at the interface. However, the chemical potentials of the substitutional elements are not equal across the interface. As Hillert has shown, the paraequilibrium boundaries must lie within the thermodynamically stable two phase field. Unfortunately, Hillert (1969) has only proposed this as a possible mode of transformation at high transformation rates, and does not specify the degree of supersaturation required to produce such rates. Nor does he discuss in detail the calculation of these boundaries.

Detailed consideration of the paraequilibrium diagram, and the resultant prediction of transformation rates in Fe-C-Mn alloys will be considered in Sections VII and X of this thesis.

More recently, Aaronson, Domian and Pound (1966), in a paper accompanying their previously mentioned experimental results, have calculated for Fe-C-X alloys what they term no-partition Ae3 curves below which partition is impossible at a growing interface. The conditions required for this calculation are similar to the proposal of Hultgren; that is, that the activity of carbon as well as the concentration of manganese are the same on either side of the moving interface. In this calculation they have used Zener's (1955) two-parameter treatment of the effect of alloying elements on the postulated magnetic and non-magnetic components of the standard free energy at transformation, combined with a statistical thermodynamic treatment of Fe-C alloys (Aaronson, Domian and Pound, 1966).

The outcome of this theory is the prediction of a no-partition Ae3 line for constant alloy sections of the ternary diagram below which the proeutectoid transformation may occur without the redistribution of alloying elements, and above which partition is required. If the equilibrium Ae3 for the alloy lies sufficiently above the no-partition line, proeutectoid ferrite precipitating in this area may exhibit partitioning. Since it is impossible to correctly represent the equilibrium Ae3 surface (with proper tie-lines) of a ternary alloy in a section of the diagram at constant alloying element, this comparison of "equilibrium Ae3" and "no-partition Ae3" is somewhat ambiguous. It appears to be a consequence of this theory that alloys transformed above the no-partition Ae3 line should have the interface concentration lying at the ends of the tie-line passing through the bulk composition of the sample.

For the no-partition case to apply, the carbon composition of the precipitating ferrite must be higher than the equilibrium concentration, corresponding to Hillert's paraequilibrium boundary lying within the true two-phase field.

While Aaronson's no-partition theory and Hultgren's postulated paraequilibrium appear very similar in concept, Aaronson maintains that they are not alike. He does so primarily on the basis of the experimental result that the Fe-C-Cr TTT curve exhibits a double C and yet no partitioning of chromium has been observed under these conditions as Hultgren's orthoferrite hypothesis would predict. However Aaronson's theory does not predict the experimentally observed results in Fe-C-Cr alloys either. Hillert (1969) has stated that the no-partition calculations of Aaronson are essentially

the same as his paraequilibrium condition. It should be noted however that Aaronson does not appear to insist that his no-partition tie-line be a carbon component ray as does Hillert. While the physical magnitude of the difference between Hillert's paraequilibrium concept and Aaronson's nopartition calculation may be small, the difference in theoretical conception is important.

A number of investigators have considered the conditions at the interface during diffusion-controlled phase transformations in Fe-C-X alloys and have concluded that under certain conditions a precipitating phase may have substantially the same substitutional alloy composition as the original austenite and still maintain complete chemical equilibrium at the interface. Hillert proposed such a model in 1953 but unfortunately his description which was applied to growth of pearlite was not widely circulated. Kirkaldy (1958) published solutions to the diffusion equations for transformations in ternary alloys assuming local equilibrium and showed how these would predict the relative effect of silicon and manganese on the hardenability effect of these elements in steel. These solutions will be discussed in detail in a later section of this thesis. Popov and Mikhalev (1959), in their discussion of the kinetics of ferrite formation during decarburization of alloy steels, predicted that a pile up of manganese could occur at the ferrite-austenite interface if the interface were in local equilibrium. Darken (1961), in considering the reduction of the growth rate of proeutectoid cementite precipitation by a small amount of silicon, pointed out that local equilibrium at the interface could account for the observed results. As silicon is insoluble in cementite, it may pile up ahead of the growing

precipitate, thereby lowering the activity of carbon in this region. While the growth of the cementite is carbon diffusion controlled, the lowering of the activity of carbon (due to the large positive ternary interaction), and thus the driving force for the reaction, decreases the growth rate (Figure 15).

Purdy, Weichert and Kirkaldy (1964) extended Kirkaldy's (1958) solution of the diffusion equations for the Fe-C-Mn system to show that at low supersaturation these equations predict manganese partition and low growth rates due to manganese diffusion control, while at higher supersaturations the manganese would not partition and the transformation would proceed by carbon diffusion control. In both cases the interface could remain in local equilibrium. These diffusion solutions are discussed in detail in the theoretical section of the thesis.

In a review paper, Hillert (1969) has discussed this local equilibrium model and shown how the effect of the ternary interaction may be illustrated by the use of isoactivity lines on the phase diagram. He has also discussed qualitatively the effect of velocity on the interface concentrations. He concluded that at sufficiently high growth rates the interface concentrations will deviate from local equilibrium and that the paraequilibrium model may be applicable.

(d) Diffusion Data

The diffusion coefficient of carbon in austenite has been determined by Wells, Batz and Mehl (1950). Their data, along with that of Speich and Cohen (1960) on the growth of bainite, have been analysed by Kaufman, Radcliffe and Cohen (1962) who presented the following expressions for the diffusion of carbon in austenite:

$$D_{11}^{Y} = D_{0}(x) \exp[-Q(x)/RT] cm^{2}/sec$$
 (20)

where

$$D_0(x) = 0.5 \exp [-30x] \text{ cm}^2/\text{sec}$$
 (21)

$$Q(x) = 38,300 - 1.9 \times 10^5 x + 5.5 \times 10^5 x^2 \text{ cal/mole}$$
 (22)

where x is the mole fraction of carbon. Although the above expressions have been used in all calculations, it is worth noting here that the value of D_{11} at temperatures of interest here is approximately 10^{-8} cm²/sec.

The data of Wells et al (1950) indicate that the manganese content of the alloys used in the experiments would not alter the value of D_{11}^{γ} appreciably.

The diffusion coefficient of manganese in Fe-C-Mn austenites has been measured by Wells and Mehl (1941). They presented the following expression for the diffusion coefficient in the temperature range 1000° C to 1450° C:

$$D_{22}^{\gamma} = [(0.486 + 0.011 C_2)exp \left[\frac{66,000}{RT} \right] [1 + 2.53 C_1] cm^2/sec$$

where C_1 and C_2 are the weight percent carbon and manganese, respectively. This expression gives values in the order of 10^{-15} cm²/sec at 730°C.

The diffusion coefficient of manganese in ferrite is not available, but, as mentioned in Part I, it is expected to be at least an order of magnitude faster than that in austenite at the same temperature.

The off-diagonal term (D_{12}) for the diffusion of carbon on a manganese gradient in austenite only appears as a ratio of D_{12}/D_{11} . This has been calculated using the thermodynamic expression given by Brown and Kirkaldy (1964):

$$\frac{D_{12}}{D_{11}} = \frac{\varepsilon_{12} x_1}{1 + \varepsilon_{11} x_1}$$
(23)

where ε_{ij} are the Wagner interaction parameters and x_1 the mole fraction of carbon. They have demonstrated that this expression adequately represents the available experimental data.

VI LOCAL EQUILIBRIUM MODEL

(a) Diffusion Analysis

Diffusion in multicomponent systems is described by Onsager's (1945) extension of Fick's first law (1855), namely that the flux of each of the components is a linear function of all concentration gradients,

$$J_{i} = -\sum_{k=0}^{n} D_{ik}^{*} \nabla C_{k} \quad (i = 0, 1...n)$$
(24)

If the concentrations are expressed in units such that

$$\Sigma C_{\star} = constant$$

then equation 24 reduces to

$$D_{i} = -\sum_{k=1}^{n} D_{ik} \nabla C_{k}$$
 (i = 1, n) (25)

involving n independent concentration gradients.

Combining equation 25 with the continuity equation

div
$$J_i + \frac{\partial C_i}{\partial t} = 0$$
 (26)

the generalized diffusion equation (Fick's second law) is obtained.

$$\frac{\partial C_i}{\partial t} = \sum_{k=1}^{n} \nabla_* (D_{ik} \nabla C_k) \quad (i = 1, n)$$
(27)

If the diffusion coefficients are not functions of concentration, then equation 27 reduces to

$$\frac{\partial C_i}{\partial t} = \sum_{k=1}^{n} D_{ik} \nabla^2 C_k \quad (i = 1, n)$$
(28)

Kirkaldy (1958), following the method of Zener (1949) for binaries, has presented solutions of equation 28 applicable to the planar growth of grain boundary nucleated ferrite and cementite in supersaturated ternary austenite assuming that local equilibrium is maintained throughout the diffusion zone.

These solutions have the parametric form:

$$C_{i} = C_{i} (\lambda)$$
(29)

where

$$\lambda = x / \sqrt{t}$$
(30)

For constant coefficients ($D_{ik} = const$), and the following boundary conditions at infinity and at the interface (α) in λ -space

$$C_{i} (\lambda = \infty) = C_{i0}$$

$$C_{i} (\lambda = \alpha_{+}) = C_{i1} (i = 1, 2)$$

$$C_{i} (\lambda = \alpha_{-}) = C_{i1}$$
(31)

these solutions are

$$C_{i} = a_{i0} + \sum_{k=1}^{n} a_{ik} \operatorname{erfc} (\lambda/2 \sqrt{u_{k}}) \quad (i = 1, 2)$$
 (32)

The coefficients a_{ik} and u_k remain to be determined in terms of the diffusion coefficients and boundary conditions. The boundary conditions

at α_+ indicate that

$$\Delta_{i} = \sum_{k=1}^{n} d_{ik}$$

where $\Delta_i = C_{i1} - C_{i0}$

and
$$d_{ik} = a_{ik} \operatorname{erfc} \left[\alpha / 2 u_{k} \right]$$

The d_{ik} are given by

$$d_{11} = \begin{bmatrix} D_{12}\Delta_2 + [(D_{11} - D_{22}) + D] \frac{\Delta_1}{2} \end{bmatrix} / D$$
$$d_{21} = \begin{bmatrix} D_{21}\Delta_1 + [(D_{11} - D_{22}) - D] \frac{\Delta_2}{2} \end{bmatrix} / D$$
$$d_{12} = \Delta_1 - d_{11}$$

 $d_{22} = \Delta_2 - d_{21}$

where

$$D = \sqrt{(D_{11} - D_{22})^2 + 4 D_{12} D_{21}}$$

$$\mu_1 = (D_{11} + D_{22} + D) / 2$$

and

$$\mu_2 = (D_{11} + D_{22} - D) / 2$$

The interfacial mass balances are

$$(C_{i1} - C_{i1}) V = -J_i(\alpha)$$

(33)

(34)

where J_i are given by equation 25 and the velocity of precipitate growth is

$$V = \alpha/2 \sqrt{t}$$
(35)

Thus the parameter α , the position of the interface in λ space, can be used as a measure of the transformation rate.

In ternary systems α , often called the growth rate constant, must be determined by the simultaneous solution of the two flux balances derived by substituting V from equation 35 and $J_i(\alpha)$ from equation 25 into equation 34, resulting in the following equations:

$$(C_{i1} - C_{i1}) \frac{\alpha}{2\sqrt{t}} = \sum_{k=1}^{2} D_{ik} \frac{\partial C_k}{\partial x} \quad (i = 1, 2)$$
(36)

These equations involve only two independent functions, α and one of the concentrations, say C_{11} , as the other three concentrations (C_{11}, C_{21}, C_{21}) are fixed by the particular equilibrium tie-line in the two-phase region corresponding to the interfacial concentrations. Thus the interfacial tie-line provides the degree of freedom necessary for the simultaneous solution of the two equations to predict a unique growth rate. As these functions are separable in the above equations, a graphical solution is possible. These solutions predict two types of transformations, as discussed qualitatively in the following paragraphs.

As has been mentioned in Section V (d), D_{11} , the diffusion coefficient of carbon in austenite, is many orders of magnitude greater than D_{22} , the diffusion coefficient of manganese in austenite. In addition, the experimentally observed lack of partition of the substitutional element at high supersaturation requires that the precipitating ferrite have substantially the same alloy content as the original austenite.

Figure 16a shows a schematic isotherm for the Fe-C-Mn system. A sample with composition A rapidly cooled to the isotherm temperature would be relatively highly supersaturated. For this alloy, the "zero partition" tie-line is represented by line B _B. Any tie-line above this will not satisfy a manganese mass balance and would require the precipitating ferrite to have a greater manganese content than the original austenite. All other possible tie-lines thus lie below B -B. As $D_{11} >> D_{22}$, the carbon will duffuse many times farther ahead of the interface than the manganese. Any tie-line below B -B will require manganese partition; the lower the tie-line, the greater the partition. It is therefore obvious that the only tie-line which can simultaneously satisfy the diffusion equations for both carbon and manganese is one very close to B -B. This will result in diffusion profiles as shown in Figure 16a. The very small depletion of manganese in the ferrite (not experimentally detectable) would be balanced by the manganese "spike" at the interface. The steep manganese gradient will of course satisfy the equations for the rapid transformation rate, although the transformation is carbon diffusion controlled. This same analysis, if ternary thermodynamic interactions are ignored, applies to any alloy along line B -A, almost up to C. It. may be seen that this same argument may be made for any alloy lying within the dashed triangle in Figure 16a. If the ternary interaction is considered, this, in Fe-C-Mn alloys, will lower the driving force for the reaction even further, as there is a negative interaction between carbon and manganese.

Thus the carbon concentration curve is drawn as shown in Figure 16a, the sum of two modified error functions. The exact solution to the two mass balance equations confirms this qualitative argument.

Remembering that $D_{11} >> D_{22}$, and adopting the argument of Kirkaldy and Purdy (1962) that D_{21} , the diffusion of manganese on a carbon gradient, is negligible because in any unconstrained system the high mobility carbon can relax to the manganese gradient long before the manganese can readjust to the carbon gradient, the value of the d_{ik} in the previous equations becomes the following:

 $d_{11} = \frac{D_{12}}{D_{11}} \Delta_2 + \Delta_1$ $d_{12} = -\frac{D_{12}}{D_{11}} \Delta_2$ $d_{22} = \Delta_2$ $d_{21} = 0$

Also, $\mu_1 = D_{11}$

and $\mu_2 = D_{22}$

In this region of high supersaturation $C_{11} = 0$, $C_{20} = C_{21}$, and an approximate expression for the growth parameter β_1 (related to α by $\beta_1 = \alpha/2\sqrt{u_1} = \alpha/2\sqrt{D_{11}}$) may be obtained by substituting the expression for C_1 from equation 32 into equation 34 and performing the differentiation (values of d_{ik} and u_k from above). This results in the following expression:

$$\beta_{1} = \frac{\Delta_{1}}{\sqrt{\pi} c_{11}} \left(1 + \frac{D_{12}}{D_{11}} - \frac{\Delta_{2}}{\Delta_{1}}\right) \frac{e^{-\beta_{1}^{2}}}{erfc\beta_{1}}$$
(37)

This expression, originally presented by Purdy, Weichert and Kirkaldy (1964), contains only carbon diffusion coefficients and thus it is only necessary to know that the manganese coefficients are small. Also, this is the same expression as derived from the Dube (1948, 1958) Zener (1949) analysis for transformations in binary alloys with the addition of the ternary thermodynamic interaction. Thus the "effective" carbon concentration for the transformation is given by $\overline{C_{11}}$, such that

$$\overline{C_{11}} = C_{11} + \frac{D_{12}}{D_{11}} (C_{21} - C_{20})$$
(38)

where the other concentrations are as shown in Figure 16a.

It is concluded from the above that the driving force for the carbon diffusion controlled transformation in Fe-C-Mn is reduced by a constitutional effect and a ternary thermodynamic effect.

If an alloy lies outside the dashed triangle in Figure 16b, then all solutions of the mass balances require some manganese partition. This will result in very low growth rates. For an alloy of composition D in this figure, the limiting tie-line is given by E - E where the carbon depletion of the ferrite is balanced by a very small increase in the austenite spread over a large distance with a small local increase at the interface due to the ternary thermodynamic interaction. All other tie-lines lie below E - E. The only condition which will simultaneously satisfy both mass balances is that ΔC_1 is small, and thus the limiting tie-line E -E obviously is close to the correct one. The qualitative argument then predicts manganese partition in these alloys and the growth of ferrite controlled by manganese diffusion. This same argument would hold for all alloys outside the area of zero partition.

In this region of low supersaturations $C_{11} \stackrel{\sim}{=} C_{10}, C_{11} \stackrel{\sim}{=} 0$, and the equivalent expression for the growth parameter $\beta_2 = \alpha/2\sqrt{u_2} \stackrel{\sim}{=} \alpha/2\sqrt{D_{22}}$ is

$$\beta_2 = \frac{1}{\sqrt{\pi}} \frac{\Delta_2}{(C_{21} - C_{21})} \frac{e^{-\beta_2^2}}{erfc\beta_2}$$
(39)

This analysis, originally presented by Purdy, Weichert and Kirkaldy (1964), considers only the initial stages of the transformation while the carbon diffusion fields do not impinge to any appreciable extent. When an alloy is in the low supersaturation area carbon diffuses far ahead of the interface and impingement occurs "early" in the transformation although the actual time required might be relatively long, and, since the volume fraction of ferrite formed during any experimentally realizable time is very small, the deviation in the growth rate from that predicted by equation 39 should be small.

However, in the case of highly supersaturated alloys, the time required for impingement may be in the order of minutes. When impingement occurs, the growth rate will decrease, and eventually the driving force for the transformation due to carbon diffusion will be zero. However the transformation is far from complete for the manganese must redistribute before final equilibrium can result. It is these later stages of the transformation which will be considered next.

(b) High Supersaturation-Carbon Impingement

When the carbon concentration profiles impinge at the centre of the grain, the driving force for the transformation due to carbon activity gradients begins to drop, and thus the transformation rate falls. There is no analytical solution for the diffusion equations under these conditions and some approximation, or iterative solution, must be used. Iterative solutions using computer techniques have been published by Tanzilli and Heckel (1968), but an approximate solution patterned after Zener's (1949) treatment (error function represented as triangles) is presented here as it gives qualitatively correct values for the time required for impingement to be almost complete.

The purpose of performing such a calculation is to determine the time required for the carbon to come to uniform activity throughout the specimen. If this time is relatively short, then one may safely assume that the interface concentrations cannot vary appreciably from that predicted by the analysis for the infinite case presented previously and these may then be used as an initial condition for the redistribution of manganese. Thus the assumption will be made that the interface concentrations have not changed and this may then be checked by calculating the time required for the carbon to reach nearly uniform activity.

For this analysis some starting position of the interface must be chosen. Mathematically the carbon fields always impinge, as an error function has a finite value (although very small) at all values of the argument. However, only after some appreciable impingement has occurred will the interface velocity fall appreciably below that predicted by the parabolic solution for infinite diffusion fields. For this calculation it has been assumed that the interface (for a planar grain) will move parabolically to a position (X'_{α}) such that

$$X_{\alpha} = \frac{L(\overline{c_{11}} - c_{10})}{(\overline{c_{11}} + c_{10})}$$

where $\overline{C_{11}}$ is the effective carbon concentration for the transformation given by equation 38 and L is the half width of the grain. This position is shown schematically in Figure 17. The position of the interface when the carbon has reached uniform activity is given by

$$\chi_{\alpha}^{f} = L(1 - \frac{C_{10}}{C_{11}})$$
(41)

In both cases the mass of carbon in the carbon spike at the interface due to the ternary interaction with the manganese has been neglected.

When $X_{\alpha} < X_{\alpha} < X_{\alpha}^{f}$, the carbon mass balance is given by

$$c_{10}X_{\alpha} = (L - X_{\alpha}) \left[\frac{\overline{c_{11}}}{2} + \frac{c_{L}}{2} - c_{10} \right]$$
 (42)

or

$$C_{L} = \frac{2 L C_{10} - \overline{C_{11}} (L - X_{\alpha})}{L - X_{\alpha}}$$
(43)

where C_L is the concentration of carbon at the centre of the grain. (At uniform a_c , $C_L = \overline{C_{11}}$.)

(40)

The interfacial mass balance for carbon is

$$\overline{C_{11}} \quad \frac{dX_{\alpha}}{dt} = \frac{D_{11} (\overline{C_{11}} - C_{L})}{L - X_{\alpha}}$$
(44)

If the value of C_L from equation 43 is substituted into equation 44 and the terms rearranged, it may be shown that

$$\frac{dX_{\alpha}}{dt} = V_{\alpha} = \frac{2D_{11}(X_{\alpha}^{f} - X_{\alpha})}{(L - X_{\alpha})^{2}}$$
(45)

This velocity expression may be integrated to find a time interface position expression

$$\int_{X_{\alpha}=X_{\alpha}}^{X_{\alpha}} \frac{(L-X_{\alpha})^{2}}{x_{\alpha}^{f}-x_{\alpha}} dX_{\alpha} = 2 D \int_{t=0}^{t} dt$$
(46)

In this integration time zero has been taken as the time when the interface has moved to position X_{α} . The total time may be obtained by calculating the time required for the interface to move parabolically to X_{α} and adding this to the time of impingement.

Integration of equation 46 and substituting in the limits results in the following expression:

$$t = -\frac{1}{D_{11}} \left[\kappa^2 \ln \frac{x_{\alpha}^{f} - x_{\alpha}}{x_{\alpha}^{f} - x_{\alpha}} \right] + \left[2\kappa + 2x_{\alpha}^{f} \right] \left[x_{\alpha}^{-} - x_{\alpha} \right] - \frac{1}{2} \left[x_{\alpha}^{2} - x_{\alpha}^{-2} \right] (47)$$

where

$$k = L \frac{c_{10}}{\overline{c_{11}}}$$

Figure 18 shows the result of this calculation for various grain half widths in a 1.5 A % Mn, 0.45 A % C alloy transformed at 728° C. The times shown have been calculated by adding the time required for parabolic growth of the precipitate to position X_{α} to the time calculated from equation 47 for the interface to reach a position of 0.99 X_{α}^{f} . It is obvious from this curve that for any reasonable grain size the carbon will reach virtually uniform activity in, at the most, a period of a few hours. In any real sample the time required would be less, due to the impingement of the carbon diffusion fields from all sides of the pre-cipitating ferrite.

(c) Manganese Diffusion Control

If it is accepted that the carbon will come to virtually uniform activity in a relatively short time, then the interface concentrations cannot have changed appreciably from those predicted by the solution to the diffusion equations for infinite diffusion fields. If this is so, then the conditions for the redistribution of manganese may be represented as shown in Figure 19.

As outlined in Part 1, the diffusion coefficient of manganese in ferrite is several orders of magnitude higher than that in austenite.

(48)

Therefore the assumption will be made that the manganese gradient in the ferrite is negligible and the manganese content of the ferrite is uniformly lowered (Figure 19). In addition, the mass of carbon in the carbon spike will be ignored because

$$(C_{11} - \overline{C_{11}}) \frac{a}{2} \ll (\overline{C_{11}} - C_{10})(L - X_{\alpha})$$

As the manganese diffuses out of the ferrite and into the austenite, the tie-line representing the interface will move down the phase diagram while the interface moves very slowly forward. Since it is assumed that the interface is in local equilibrium, specifying any one interface concentration automatically fixes all other concentrations. The logical concentration to choose is, therefore, C_{21} , the concentration of manganese in the ferrite, for, if the above assumption is correct, then this concentration change should be experimentally measurable. It is assumed that the high mobility carbon can readjust rapidly to the changing manganese concentrations.

Referring to Figure 19, a carbon mass balance (ignoring the carbon spike) will give

$$X_{\alpha}C_{10} = [L - X_{\alpha}] [\overline{C_{11}} - C_{10}]$$
(49)
$$X_{\alpha} = \left[\frac{\overline{C_{11}} - C_{10}}{\overline{C_{11}}} \right] L$$
(50)

or

where L is again the half width of a planar grain and $\boldsymbol{X}_{\!\boldsymbol{\alpha}}$ the position of

(53)

the interface.

If

$$F_{1}(c_{21}) = \frac{\overline{c_{11}} - c_{10}}{\overline{c_{11}}}$$
(51)

then

$$X_{\alpha} = F_1(c_{21})L$$
 (52)

Therefore

The manganese mass balance may be written

 $\frac{dX_{\alpha}}{dt} = L \frac{dF_1(c_{21})}{dt}$

$$\frac{a}{2} [C_{21} - C_{20}] = X_{\alpha} [C_{20} - C_{21}]$$
(54)

or

$$a = 2 X_{\alpha} \frac{[C_{20} - C_{21}]}{[C_{21} - C_{20}]}$$
(55)

Also a manganese interfacial mass balance may be written

$$\frac{D_{22}}{a}(C_{21} - C_{20}) = (C_{21} - C_{21})\frac{dX_{\alpha}}{dt}$$
(56)

where D_{22} is the diffusion coefficient of manganese in austenite.

If the expression for X_{α} from equation 52 is substituted into equation 55, and the resultant expression and equation 53 substituted

into equation 56, the following expression results:

$$\frac{D_{22}}{2L^2} \frac{[C_{21} - C_{20}]^2}{[C_{20} - C_{21}][C_{21} - C_{21}]} = F_1(C_{21}) \frac{dF_1(C_{21})}{dt}$$
(57)

If

$$\frac{\left[c_{21}^{2}-c_{20}^{2}\right]^{2}}{\left[c_{20}^{2}-c_{21}^{2}\right]\left[c_{21}^{2}-c_{21}^{2}\right]} = F_{2}(c_{21}^{2})$$
(58)

then

$$\frac{D_{22}}{2L^2} dt = \frac{F_1(c_{21})}{F_2(c_{21})} dF_1(c_{21})$$
(59)

This expression may be integrated from an initial value of $C_{21} = C_{20}$ to some lower value of C_{21}

$$\frac{t D_{22}}{2 L^2} = \phi = \int_{F_1}^{F_1} (\hat{c_{21}}) \frac{F_1(\hat{c_{21}})}{F_2(\hat{c_{21}})} dF_1(\hat{c_{21}})$$
(60)
$$F_1(\hat{c_{21}} = \hat{c_{20}})$$

If the tie-lines on the ternary diagram are known, then this expression may be graphically integrated.

VII PARAEQUILIBRIUM MODEL

After Hultgren's (1951) original postulation of paraequilibrium, Rudberg (1952) and Hillert (1952) developed the concept in a more detailed form. They pointed out that the paraequilibrium tie-lines in the two phase area must lie on "component rays" of the high mobility species, carbon. Hillert has shown that the paraequilibrium boundaries must lie within the stable two phase field.

This concept of paraequilibrium may be explained with the aid of Figure 20 which schematically represents the two free energy surfaces for ferrite and austenite at a temperature in the two phase region. The ternary isotherm is drawn below these inverted free energy surfaces. Plane abde contains a line (ab) tangent to both ternary surfaces and the projection of this line on the isotherm is the carbon component ray (de). Line ab is also contained in the two planes of which one is tangent to the ferrite free energy surface at h and the other is tangent to the austenite free energy surface at m. These planes are labelled on the diagram.

As the chemical potential or partial molar free energy of a component is given by the intersection of the tangent plane with the component axes, it may be seen that the thermodynamic conditions for true paraequilibrium are the following:

$$\overline{G_1}^{\alpha} = \overline{G_1}^{\gamma}$$

(61)

$$\overline{G_2}^{\gamma} - \overline{G_2}^{\alpha} = -(\overline{G_0}^{\gamma} - \overline{G_0}^{\alpha}) \frac{X_0}{X_2}$$
(62)

where X_0/X_2 is the ratio of the solvent to the immobile solute along the particular component ray. In Figure 20 these conditions define the paraequilibrium tie-line op. It may also be seen that the limiting paraequilibrium boundaries on the binary diagrams are, for Fe-C, the true binary equilibrium and For Fe-Mn, the T_o composition.

In Part 1 of this thesis the standard expressions for the partial molar free energy were presented and values for the parameters involved for the Fe-C-Mn system were determined. These same expressions and parameters may be used in the above equations to calculate the true paraequilibrium boundaries. Substituting in the expressions for the partial molar free energy in terms of the standard free energy of transformation of the components (equations 4, 5 and 6, and the Wagner expansions for the activity coefficients, equations 8, 9 and 11) results in the following two equations:

a) from equation 61

$$\frac{\Delta G_1}{RT} = \ln \frac{x_1}{x_1} + \ln \frac{y_1^0}{y_1^0} - \varepsilon_{11} x_1 - \varepsilon_{12} (x_2 - x_2)$$
(63)

b) from equation 62

$$\frac{\Delta G_0}{RT} = -\frac{X_2}{X_0} \left[\frac{\Delta G_2}{RT} - \ln \frac{X_1}{X_2} + \varepsilon_{12} (X_1 - X_1) + \varepsilon_{22} X_2 \right] + \\ \ln \frac{X_0}{X_0} + \varepsilon_{12} (X_1 X_2) + \frac{\varepsilon_{11}}{2} X_1^2 + \frac{\varepsilon_{22}}{2} X_2^2 \right]$$

53

(64)

The third condition is of course that X_2/X_0 is a constant along the component ray.

While these equations appear formidable, their solution was straightforward. For a particular component ray, trial values of X_1 and X_2 were inserted in equation 63, and values of X_1 vs X_2 plotted on a ternary isotherm. The intersection of this line with the component ray defines the austenite concentrations. These values along with the trial X_1 and X_2 were substituted into equation 64 and the value of ΔG_0 calculated and then compared with that from Figure 4. If the agreement was not satisfactory (± 0.5 cal) then a new value of X_1 on the component ray was chosen and the process repeated. This "graphical iterative" method is very similar to that described in Part I for the calculation of the equilibrium tie-lines.

The paraequilibrium diagram calculated for a temperature of 730^oC in this manner is shown in Figure 21.

A section of the ternary diagram for a carbon component ray having $X_0/X_2 = 0.99/0.01$ is shown in Figure 22 and the calculated end points for the paraequilibrium tie-lines are listed in Table 5.

It is important to realise that, for the paraequilibrium condition, sections of the ternary diagram along carbon component rays correctly represent the carbon driving force for the reaction, provided of course that the system chooses this method of transformation rather than the complete local equilibrium model presented earlier. The expression for the growth parameter $\beta = \alpha/2\sqrt{D_{11}}$ in this case is the following:

$$B = \frac{1}{\sqrt{\pi}} \left[\frac{C_{11} - C_{10}}{C_{11} - C_{11}} \right] \frac{e^{-\beta^2}}{erfc\beta}$$

(65)

where C_{11} is now the carbon concentration at the austenite end of the paraequilibrium tie-line, C_{11} the corresponding ferrite composition and C_{10} the original austenite carbon composition.

While this carbon driving force for the transformation is uniquely determined by this model, it may not readily be extended to later times when the transformation rate decreases. This point will be dealt with in the discussion.

VIII EXPERIMENTAL PROCEDURES

When this project was initiated, it was hoped to be able to improve upon, and add to, the kinetic results obtained by Purdy, Weichert and Kirkaldy (1964). In their experiments the electroplated iron nucleus acted as a sink for manganese and thus, in the case of low supersaturated alloys, the back diffusion of manganese gave high growth rates. Although Weichert (1963) solved the diffusion equations for these boundary conditions, the result of the experiments was not directly applicable to grain boundary precipitation.

In investigating the parabolic growth of ferrite at high supersaturations in up-quenched martensitic samples, the same experimenters were troubled with precipitation of ferrite ahead of the interface. This caused the growth rates to decrease due to the impingement of the carbon diffusion fields and experimental measurements had to be confined to short times.

If experiments using more conventional austenitized and down-quenched samples are carried out, other complications arise. In the area of low supersaturation, the time required at temperature before nucleation occurs may be very long, and thus the accurate measurement of growth rates is difficult. In addition, there is the classic problem of correctly measuring the thickness of precipitated layers when the angle of intersection of the precipitate with the surface is unknown.

Samples austenitized and quenched into the region of high super-

saturation nucleate readily. However, since the time at temperature before carbon diffusion fields impinge is small, the error in measuring the true time of growth may be significant. There remains the problem of measuring the true thickness of the precipitates.

To overcome some of these difficulties, preliminary experiments were carried out which relied on the free surface of the sample to act as a nucleus for proeutectoid ferrite precipitation in much the same manner as Picklesimer et al (1960) who observed preferential nucleation of pearlite on the surface of Fe-C-Mn alloys. A considerable number of experiments were carried out in which samples* were austenitized by resistance heating while in a vacuum furnace preheated to the isothermal transformation temperature. The sample was then cooled to the furnace temperature with a stream of argon. A thermocouple had been spot welded to the sample so that the sample temperature could be monitored continuously. After holding at the transformation temperature for times up to one half hour, the samples were dropped from the hot zone and quenched in either mercury or silicon oil. Ferrite was found to nucleate on the surface and grow rapidly into the specimen. Unfortunately it was not realised for some time that the growth of ferrite was being controlled not by carbon diffusion but by the evaporation of manganese from the surface and the internal oxidation of the manganese to MnO. The oxygen potential in any vacuum furnace is sufficient to oxidize the manganese, and indeed a careful examination of the specimens revealed a very fine distribution of precipitates which are undoubtedly MnO. Later calculations showed that even

* The preparation and analysis of alloys is described in Part 1, III, (a).

during carburization the oxygen potential of the CO-CO₂ mixture is sufficient to internally oxidize manganese. This undoubtedly accounts for the very fine MnO particles invariably found in the specimens.

For these reasons it was decided to focus attention not so much on the kinetics of the precipitation but rather on the redistribution of manganese. Calculations quickly showed that in the case of high supersaturation the manganese "spike" would be far too narrow to detect with the electron probe microanalyser at any times obtainable before the impingement of the carbon diffusion fields. Thus the local equilibrium diffusion model was extended to long times as presented in Section VI. This theory is based on the premise that the initial concentration conditions for the redistribution of manganese in highly supersaturated samples are the same as predicted by the solution to the diffusion equations for the parabolic growth conditions.

To this end, alloys were prepared having 0.45 A% C and 1.5 A% Mn (alloy A) and encapsulated in small silica vacuoles, back-filled with about onethird atmosphere of argon. These were austenitized for 19 hours at 1200^oC and then rapidly placed in a furnace preheated to 728^oC. This rapid transfer was accomplished by placing two Kanthal tube furnaces end to end and sliding the capsule from one hot zone to the other. At the end of the transformation time (two days to two months) the capsules were rapidly withdrawn from the furnace and quenched by breaking the capsule under water. From the time the capsule left the hot zone of the furnace until it was broken under water was less than three seconds. During the isothermal transformation the furnace temperature was periodically monitored with a

standardized Pt-Pt 10% Rh thermocouple and was controlled to $\pm 1^{\circ}$ C of the desired temperature.

Another series of experiments using the same technique were carried out on a 1.11 A% C, 2.09 A% Mn alloy (alloy B) at 728⁰C. At this temperature, this alloy lies just outside of the area of zero partition as predicted by the local equilibrium diffusion analysis and should therefore show manganese partitioning.

Preliminary experiments showed that the distributions of manganese which were being investigated were, in all cases, confined to a very narrow region at the grain boundary. It became obvious that normal microprobe techniques would not be adequate to resolve with any certainty the concentration distributions involved and special techniques had to be developed.

(a) Electron Probe Microanalysis Techniques

While the electron probe microanalyser has greatly increased the experimentalist's ability to determine the composition of small particles and the distribution of diffusing alloying elements, its ultimate spatial resolution is limited by the dispersion of the electron beam in the sample resulting in the emission of X-rays from a finite volume element. Thus, if concentration gradients extend over only a few microns, or if a sudden concentration change such as at a phase boundary is analysed, the effect of the finite volume element being analysed is to "smear" the true concentration profile. If this smearing effect of the spot size can be mathematically eliminated, a significant improvement in resolution should result.

(i) Theory

When the electron beam is traversed across a specimen, the observed X-ray intensity distribution is the mathematical convolution of the true concentration profile with what may be called the probe function. This convolution may be expressed mathematically in the following equation:

$$f(x) = \int_{-\infty}^{+\infty} g(x') h(x-x') dx'$$
 (66)

where f(x) = observed distribution

g(x) = probe function

h(x) = true concentration distribution

The "probe function" is a rather nebulous concept physically although it is well defined mathematically. It may be thought of as the spatial intensity distribution of the emitted characteristic X-ray line being investigated, suitably normalized such that it is concentration independent.

If all concentration profiles to be measured are uniform in the direction of the X-ray take-off to the spectrometer and the sample moved only at right angles to this direction, then the three dimensional probe function may be represented as, and used in, only two dimensions.

The probe function may be determined by passing the beam over a known concentration distribution and deconvoluting the resultant curve with this known distribution. As the probe function will be dependent on the material being analysed, it is important that it be determined on materials similar in composition to that of the samples to be analysed.

It should be possible to carry out the deconvolution by fitting a mathematical function to the observed profile and using the convolution theorem of Fourier analysis. Thus the probe function may be obtained and then used in a similar manner to analyse experimental results. However, in practice this turns out to be more difficult than it would first appear.

(ii) Experimental Technique

To determine the probe function accurately, it is necessary to point count across a known concentration function at points less than 1 micron apart. This, of course, results in overlapping spots. To achieve this, the sample traverse motor on the Cameca microprobe was controlled by an electronic timer wired into the apparatus in such a way that the timer, and thus the traverse motor, were started at the same time as the scalar print out. The motor would then run for the pre-set time which must be less than the duration of the print out cycle as the X-rays are not being counted during this time. It was found that using the slowest geared motor supplied for the Cameca microprobe (1/30 rpm output) and setting the timer for 2 seconds gave a sample motion of 1/3 micron. Once the initial mechanical slack is taken up, no backlash is introduced as the motor starts and stops under load, provided that the operator does not touch the sample traverse controls. This step scan procedure is fully automatic once started.

The known concentration distribution used was a step function in manganese concentration made by clamping the polished surfaces of a sample of high purity iron to a Fe, 3.51 wt.% Mn alloy. This was mounted with

the interface perpendicular to the surface and polished using exactly the same procedure as used for the samples to be analysed. The circles in Figure 23 show the result of a step scan across this concentration step.

It was found in practice that the deconvolution procedure using Fourier analysis was impossible to apply. This technique required the fitting of an analytical function to the observed microprobe result. Due to the statistical error in the measurements, this is a difficult procedure and considerable bias may enter the calculation. In addition, the Fourier procedure, while straightforward in theory, proved mathematically complicated.

A convolution may also be performed mathematically by representing the functions by their ordinates at small intervals (the same interval for both functions), and multiplying these ordinates together as one would the coefficients of polynomials. This operation for high order polynomials may be carried out using a standard computer polynomial multiplication sub-routine. However, the reverse procedure of deconvolution is not possible by this means; i.e., using a polynomial division sub-routine. In any polynomial division, the first terms are the most important and, if the answer is to be even approximately correct, the ends of the curves where they become tangent to the uniform concentration must be very accurately known. This portion of the concentration curves determined by the microprobe is the least known; thus a polynomial division is impossible.

If it is assumed that the spot function is gaussian in shape then the observed apparent concentration curve when the spot is passed over a concentration step should be an error function. The particular gaussian
may be determined from an error function by drawing a tangent at the midpoint of the curve (point of inflection) and measuring the distance "d" as shown in Figure 23. The gaussian is then the following:

$$g(x) = \frac{1}{d} \exp - \frac{\pi}{4} \left[\frac{x}{d} \right]^2$$
 (67)

This gaussian may then be normalized such that the sum of its ordinates at the interval decided upon (0.2μ) is unity.

To show that the beam function may be represented as a gaussian, the particular normalized curve determined from the probe result in Figure 23 (d = 0.9) has been convoluted at 0.2 μ intervals with the step function.(The step function actually is represented mathematically as having a finite slope at the interface since only one ordinate is acceptable at each location on the distance axis.) The result of this convolution is drawn on Figure 23. To determine d, it is not necessary to convert the microprobe X-ray counts into concentrations.

As mentioned previously, it is impossible to deconvolute an experimental probe result using the polynomial division sub-routine. However, in the present investigation a model has been proposed which, it is hoped, will adequately describe the distribution of manganese at long times. Thus the "forward" calculation has been performed. The probe function (assumed gaussian, although d measured for each analysis) was convoluted with the manganese concentration profile predicted by the model to give a theoretical microprobe trace. This may then be compared with the experimentally obtained microprobe result.

IX EXPERIMENTAL RESULTS AND COMPARISON WITH THEORY

(a) High Supersaturation, Long Times

Figure 24 is a micrograph typical of all samples of alloy A (0.45 A% C, 1.5 A% Mn) transformed at 728°C for 2 days to 2 months. (Table 6 contains the transformation times.) These samples consist of a relatively blocky ferrite-martensite (former austenite) mixture. Figure 25 is a preliminary microprobe trace across an area of the sample transformed for about 2 months. This trace is similar to that obtained for all samples, except that, as the more detailed results will show, the size of the peaks due to the local increase of manganese at the grain boundary is not as great in samples transformed for shorter times.

Figures 26 to 32 contain the results of detailed electron probe microanalysis of these specimens. In all cases the austenite away from the interface was used as a probe standard, the background being measured on a sample of Ferrovac E. The use of the sample itself as a standard was necessitated by a slight drift in the beam current of the Cameca microprobe. If the sample had not been used as a standard, an apparent uniform difference in concentration between the observed and predicted curves would have resulted.

The experimental points on Figures 26 to 32 were determined by detecting the manganese K_{α} radiation and counting for 10 seconds, using the step scan procedure described in Section VIII, (a). The size of

the circles which represent the point counts in these figures has no physical significance. The 10-second counts were correctd for background and the manganese concentration calculated assuming linearity of the concentration X-ray intensity relationship. This has been shown to be valid in Figure 13.

All of these specimens, with the exception of the one transformed for 2 days, showed a noticeable increase of manganese at all ferriteaustenite interfaces. In many cases the measured peak height was not as great as those presented in the figures, but, in these cases, the increase was spread over a somewhat greater distance. This is undoubtedly due to the grain boundary intersecting the surface at an oblique angle. The increase in manganese at the ferrite-austenite interfaces in the sample transformed for 2 days was so small that at many interfaces it was not detectable from the random scatter of the point count^S. Figure 32 shows the results of two step scans across the same interface in this sample.

The integral from equation 60

$$\phi = \int_{F_1}^{F_1} \frac{(c_{21})}{(c_{21})} \frac{F_1}{F_2} \frac{(c_{21})}{(c_{21})} dF_1 (c_{21})$$
(68)

was evaluated for a variation in C_{21} from the initial value $C_{21} = C_{20}$ (1.50 A% Mn) to 1.30 A% Mn at intervals of $\Delta C_{21} = 0.01$ A% Mn. Rather than calculate the 20 tie-lines involved in this integration, certain approximations were used. The limiting tie-lines for $C_{21} = 1.5$ A% and $C_{21} = 1.3$ A% Mn were calculated (and are included in Table 2) and it was assumed that the distribution coefficient for manganese varied linearly over this range from 0.3876 to 0.3846 (Table 2).

The expression

$$c_{21} = \frac{c_{21}}{0.3651 + 1.5 c_{21}}$$
 (69)

correctly represents the limiting tie-lines and was used in the following calculations. The value of C_{11} was calculated from C_{21} assuming the $\alpha + \gamma / \gamma$ phase boundary was linear using the following equation:

$$C_{11} = -0.592 C_{21} + 0.0391$$
 (70)

 $\overline{C_{11}}$ was calculated using equation 38, the value of D_{12}/D_{11} from equation 23 evaluated at C_{11} . Thus all of the concentrations necessary for the calculation of $F_1(C_{21})$ and $F_2(C_{21})$ are known and the integral may be numerically evaluated. Figure 33 shows the result of this integration where ϕ is plotted as a function of C_{21} .

The experimental results were compared with the model by measuring the average difference in manganese concentration between the ferrite and the austenite away from the interface. This difference fixed the value of ϕ , and, using the data of Wells and Mehl (1950) for D₂₂, the time of the experiment for t, a value of L was calculated using equation 60,

i.e.,

$$\phi = \frac{t D_{22}}{2 L^2}$$

In the model, L represents the half width of a planar grain, a somewhat idealized concept. An estimation of this distance was made from direct observation of the sample while it was being analysed in the microprobe. The calculated and estimated values are compared in Table 6, which as well contains all of the parameters used in calculating the theoretical distribution.

The width of the base of the manganese spike, a, was calculated from equation 55 and its height is given by equation 69. This predicted profile was then convoluted at 0.2 μ intervals with the gaussian microprobe distribution function as described in Section VIII, (a). These curves, shown in Figures 26 to 32, have been positioned laterally with respect to the experimental curves by a visual best fit. It may be seen that the agreement between the predicted or theoretical microprobe curves, and the experimental results in the region of the grain boundary is, in most cases, excellent.

In the development of the model for these late times it has been assumed that the manganese gradients in the ferrite are very small. Based on Figures 26 to 29 it appears that this is a good assumption for experiments of long duration (20 days and two months). However, Figures 30 and 31 (6 days) show that a low gradient of manganese does exist in the ferrite near the interface at shorter times. The difference in manganese content of the ferrite and austenite in the samples transformed for 2 days (Figure 32) is so small that no gradient in the ferrite could be detected, although it undoubtedly exists.

The model used in the calculation does not require that the interface concentrations throughout a sample be uniform. Various interface concentrations

(but all tie-line values) may co-exist in the sample depending on the value of L in equation 60. From the experimental results it appears that this effect is greater early in the transformation. The more uniform ferrite composition (from grain to grain) observed in the 2 month sample is probably due to the redistribution of carbon from one grain to another to eliminate any long range carbon activity gradients, resulting in the same tie-line satisfying all ferrite-austenite interfaces.

(b) Low Supersaturation

To test the local equilibrium model for the regime of low supersaturation, several experiments have been carried out with alloy B (1.11 A% C, 2.09 A% Mn) transformed at 728^oC. According to the phase diagram this alloy should lie just outside the area of zero partition at this temperature and the solution to the diffusion equations requires the redistribution of manganese.

Figures 34, 35 and 36 show typical grain boundary precipitates formed after holding for times of 1, 5 and 37 days respectively. It will be noted that the precipitating ferrite does not form a continuous layer at the austenite grain boundaries. In many areas the ferrite develops as a line of equiaxed precipitates. These small precipitates appear to grow together at later times forming a more continuous layer of ferrite at the grain boundary.

Attempts to determine the growth rate of the ferrite from these samples proved fruitless, primarily due to the morphology of the precipitates. Many of the more equiaxed precipitates are obviously rejecting manganese in many directions and thus grow faster than predicted by the model for the uniform growth of planar grain boundary precipitates. Nucleation of new precipitates at later times will also tend to make the growth rate measurements difficult.

Figure 37 shows a typical microprobe result for a rather thick precipitate (average was about 1.8 μ) in the sample transformed for 15 days. The local equilibrium model would indicate that $C_{11} \approx 3.9$ A% Mn and $C_{21} \approx 1.5$ A% Mn resulting in $\beta = 0.97$. As this precipitate was 3 microns thick it was necessary to use a diffusion coefficient for manganese of 5 X 10⁻¹⁴ cm²/sec to fit the observed results. The data of Wells and Mehl (1941), extrapolated to this temperature, would predict a value of 4 X 10⁻¹⁵ cm²/sec. Nevertheless, the convoluted curve (d = 1 μ) agrees very well with the experimentally observed result. Appreciable deviations of the angle of intersection of this precipitate with the surface could account for its width, but, if this were so, the buildup of manganese ahead of the interface would appear less.

On the basis of the microprobe results (such as Figure 37) most of the precipitates in this sample appear to be growing only into one austenite grain.

In the sample transformed for 37 days, many of the precipitates analysed showed a buildup of manganese at both interfaces with the austenite as shown in Figure 38. This is probably due to the re-crystallization of the ferrite leading to non-coherent interfaces with both austenite grains. To fit these curves a value of $D_{22} = 1.7 \times 10^{-15} \text{ cm}^2/\text{sec}$ has been used.

The interface concentrations are the same as given above for the 5 day sample. However, if the precipitate did not nucleate until relatively late in the experiment it is possible that a higher value of D_{22} would be equally acceptable as only the product D_{22} t appears in the solution of the diffusion equations.

Microprobe analysis of the sample transformed for only one day was inconclusive. While the ferrite was of lower composition than the austenite, the small width of these precipitates (usually less than 1μ) and the morphology made accurate interpretation of these results impossible. A typical trace across a lenticular-shaped precipitate which appeared less than 2 μ thick is shown in Figure 39. It may be seen that to draw conclusions from this sample other than that the manganese is partitioning is impossible.

X DISCUSSION

The excellent agreement between the predicted and measured manganese concentration profiles presented in the previous section indicate that after long transformation times for alloys which are in an area of high supersaturation, and at all times for alloys in an area of low supersaturation, the solution to the diffusion equations assuming local equilibrium correctly describes the transformation.

However as discussed previously, other investigators have proposed that during the early stages of the transformation in highly supersaturated alloys where parabolic kinetics are observed the interface may not be in complete local equilibrium. Hillert's theoretically sound concept of paraequilibrium has been developed in detail in Section VII. Aaronson's no-partition calculation has not been discussed in detail. Although similar in concept to paraequilibrium, it is not based on as thermodynamically viable arguments.

The literature contains only two detailed investigations of the growth kinetics of proeutectoid ferrite in Fe-C-Mn alloys and the interpretation of the results of these investigations will be considered in light of the two theoretical interpretations.

Purdy, Weichert and Kirkaldy (1964) reported excellent agreement between their theoretically predicted and experimentally measured parabolic growth parameters. However, if the parabolic growth rate constants for the alloy (0.97 A% C, 1.53 A% Mn) are recalculated at the temperatures

of interest (700 to 740° C) using concentrations given by tie-lines calculated as described in Part I and equation 37 (D₁₁ evaluated at $\overline{C_{11}}$, Wagner, 1952) the agreement is not as good (as shown in Figure 40). However, as the true temperature of these experiments is in doubt and may have been higher than reported (Section I) this discrepancy is not significant. A calculation based on the paraequilibrium model would predict appreciably higher transformation rates. The only factor which could cause the experimental results to be artificially low would be the precipitation of ferrite ahead of the interface resulting in the impingement of the carbon diffusion fields. Although this was observed after the longer times of transformation employed it was not observed during the earlier stages and thus cannot be considered to be the cause of the low results. One concludes therefore that for this alloy in the temperature range of 725°C to 740°C the interface is in a state of complete local equilibrium.

Kinsman and Aaronson (1967) have published excellent growth rate data for a 0.5 A% C, 1.5 A% Mn alloy transformed at temperatures of from 620° C to 800° C. These experiments were carried out in a thermionic emission electron microscope by measuring the growth of particular grain boundary precipitates intersecting the surface of the specimens. The samples were austenitized at 1300° C for 15 minutes while in the vacuum system and, as discussed in Section VIII, evaporation from the surface and internal oxidation resulting in a loss of manganese from the alloy may occur under these conditions. Kinsman and Aaronson state that in samples sectioned after transformation they did not observe any preferential growth of ferrite at the surface, implying that the evaporation of manganese was not a problem in their experiments. The results of the measured parabolic growth rate constants from these experiments are shown in Figure 41. Included is the predicted parabolic growth rate constant given by Kinsman and Aaronson based on the carbon diffusion control no-partition calculation of Aaronson, Domian and Pound (1966). Also shown is the parabolic growth rate constant calculated from the local equilibrium model. It will be noted that at the higher temperatures the local equilibrium curve approaches the experimental results but deviates considerably at lower temperatures.

Using the paraequilibrium interface concentrations of carbon calculated in Section VII and equation 65, (the value of D₁₁ corresponding to C₁₁, Wagner, 1952) the parabolic growth rate constant for this alloy has been calculated and is also shown on Figure 41. It is obvious that this model fits the experimental results far better than either the complete local equilibrium condition or Aaronson's no-partition calculation.

Thus while the local equilibrium model fits the results of Purdy, Weichert and Kirkaldy, the paraequilibrium model obviously provides the best description of Kinsman and Aaronson's results. As both the alloy used by Purdy et al and the 1.11 A% C, 2.09 A% Mn alloy used in the present investigation fall within the "two phase" paraequilibrium area (Figure 21), it is clear that an appropriate composition is not a sufficient condition for predicting the occurence of a paraequilibrium transformation.

Hillert (1953, 1969) has proposed that the interface velocity is the critical factor in determining the mode of transformation. He argues that at very high interface velocities the slow diffusing alloying element will be unable to readjust to the local equilibrium concentration and the transformation will be correctly described by the paraequilibrium conditions. The factor determining the interface velocity is of course the degree of supersaturation. At lower supersaturations and thus lower interface velocity the alloying element can "pile" up at the interface and complete local equilibrium be approached, while the precipitating ferrite has substantially the same alloy content as the original austenite. This is of course the area of high supersaturation as defined by the local equilibrium model. At even less supersaturation the transformation is controlled by the long range diffusion of the alloying element corresponding to the area of low supersaturation. Thus, on a schematic ternary Fe-C-Mn diagram. Figure 42, it would appear that there are three areas to be defined. The division between the local equilibrium low and high supersaturation areas is uniquely defined by the solution to the diffusion equations. Unfortunately it does appear to be impossible at this time to divide the area at high supersaturation into unique local equilibrium and paraequilibrium areas.

It is informative to consider qualitatively the difference in the hardenability effects of other alloying elements on the basis of the theoretical models. For this discussion only the effect of manganese and nickel will be considered. It is known (Grossman, 1952) that nickel has less than half the hardenability effect of manganese.

The ternary isotherms for Fe-C-Mn and Fe-C-Ni in the proeutectoid region are undoubtedly very similar for the limiting binary diagrams for Fe-Mn and Fe-Ni are almost identical. The paraequilibrium diagrams for Fe-C-Ni will also be similar to that presented for Fe-C-Mn. However, the Wagner interaction parameter for manganese is -4.2 while for nickel

it is +4.6. (Brown and Kirkaldy, 1964). While the effect of this parameter on the ternary isotherms and paraequilibrium diagram will not be great, it will have a significant effect on the transformation rate predicted by the local equilibrium model.

Figure 43 is a representation of the Fe-C-Mn and Fe-C-Ni diagrams at the temperature of interest. These have been drawn identical to each other although they may be somewhat different. Nevertheless, the local equilibrium model predicts that an alloy of composition A quenched from the austenite will transform with the interface compositions given by the tie-line shown. The effect of the ternary interaction parameter on the transformation rate may be illustrated with the use of carbon isoactivity lines for the austenite phase extended into the two phase region until it intersects with the immobile solute isocomposition line for the alloy. This intersection is the effective carbon concentration for the transformation, $\overline{C_{11}}$. The isoactivity lines on the ternary diagrams have been drawn with the correct sign of the slope determined by the interaction parameter. It may be seen that the effect of the ternary interaction in Fe-C-Mn alloys, as has been pointed out previously, is to change the effective carbon concentration for the transformation to a value below what it would be due to the constitutional effect alone, viz.,

 $\overline{c_{11}} < c_{11}$

However, the effect of the positive interaction parameter in Fe-C-Ni alloys is to increase the effective carbon concentration for the transformation: $\frac{\overline{C_{11}} > C_{11}}{C_{11}} > C_{11}$

If it is assumed that the phase diagrams are identical, then the transformation rate is dependent only on the carbon diffusion coefficient D_{11} , $\overline{C_{11}}$ and C_{10} , the carbon content of the original austenite. The effect of the alloy content on D_{11} is not great and if the alloys have the same solute composition the only factor which varies is $\overline{C_{11}}$. Thus the ternary thermodynamic effect of increasing $\overline{C_{11}}$ is relatively large and one would expect Fe-C-Ni alloys to transform significantly faster than Fe-C-Mn alloys. The predicted diffusion profiles are shown in Figure 43. The local equilibrium model does, therefore, qualitatively predict the relative effects of manganese and nickel on the proeutectoid reaction, and by inference on the hardenability. By comparison, the paraequilibrium model does not predict such an effect as the paraequilibrium diagrams for the two systems will be very similar leading to similar growth rates.

Of course, the argument is incomplete as the hardenability of an alloy depends not only on the proeutectoid transformation rate but also on the pearlite transformation rate and the nucleation rates. Bolze (1970), in his recent thesis, has laid the framework for the analysis of a ternary pearlite transformation.

XI CONCLUSIONS

- 1. The phase boundaries and a number of tie-lines in the ferrite plus austenite region of the Fe-C-Mn phase diagram have been calculated. Many of the necessary thermodynamic data for this calculation have been extracted from the limiting binary diagrams. The calculated tielines show that the $\alpha + \gamma / \gamma$ boundary is concave toward the iron rich corner while the $\alpha / \alpha + \gamma$ boundary is concave away from this corner.
- 2. Experimentally determined tie-lines at 730°C and 762°C are in good agreement with the calculated diagram. This is the first test of Hone, Subramanian and Purdy's (1969) method of ternary isotherm calculation.
- 3. Approximate solutions to the diffusion equations assuming a local equilibrium interface have been extended to very late stages of the proeutectoid transformation in highly supersaturated Fe-C-Mn alloys. Manganese concentration increases at the ferrite-austenite interface detected with the electron probe microanalyser are in satisfactory agreement with the predictions based on this local equilibrium model at long times.
- 4. Electron probe microanalysis of Fe-C-Mn alloys transformed in the area of low supersaturation show that the manganese distribution is close to that predicted by the local equilibrium model and that diffusion

of manganese is the rate controlling process.

- 5. Hillert's (1953) concept of paraequilibrium has been examined and the thermodynamic conditions which uniquely define the paraequilibrium tie-lines have been established in general. A number of such tie-lines for the Fe-C-Mn system have been calculated. It has been shown that the parabolic growth rate constants calculated from these paraequilibrium tie-lines agree with the growth rates experimentally observed for a very highly supersaturated Fe-C-Mn alloy by Kinsman and Aaronson (1967).
- 6. A qualitative argument has been put forward based on the local equilibrium model which would explain the significant difference in hardenability between manganese and nickel. It appears that the paraequilibrium concept would not predict an appreciable difference in hardenability between these elements.
- A convolution technique has been developed which significantly improves the interpretation of the results of electron probe microanalysis of strongly localized concentration changes.

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TABLE 1

Activity Data for the Fe-C	C-Mn S	System
----------------------------	--------	--------

Parameter	Value	Reference
٤	8.9	Smith (1946)
ε ^γ ₂₂	-1	Roy and Hultgren (1965)
ε ^γ 12	-4.2	Smith (1948)
٤	0	Smith (1946)
ε ^α 22	0	. 1
ε ^α 12	-4.2	2
γ ^{0^Υ}	8.0	Smith (1946)
γ ^{0^α}	56.7	Smith (1946)
r2 ^{or}	1.52	Roy and Hultgren (1965)
γ ₂ ^{o^α}		3

Standard State -- Pure components

 $1 - \varepsilon_{22}^{\alpha}$ should be small, set equal to 0.

2 - $\varepsilon_{12}^{\alpha}$ unknown, expected to be nearly equal to $\varepsilon_{12}^{\gamma}$.

3 - $\gamma_2^{0^{\alpha}}$ unknown, included in calculated ΔG_2 values.

Calculated Tie-Lines*						
т ^о с	xη	x ^a ₂	x٫Ÿ	x²	k _ا	k ₂
762	0.0 0.00015 0.00036 0.00057 0.0008	0.0236 0.0177 0.0118 0.0059 0.0	0.0 0.0058 0.0125 0.0183 0.0232	0.0504 0.0384 0.0260 0.0131 0.0	0.026 0.029 0.031 0.035	0.468 0.461 0.454 0.450
760	0.0 0.00024 0.00042 0.00080	0.0231 0.0153 0.010 0.0	0.0 0.0089 0.0144 0.0240	0.492 0.0337 0.0223 0.0	0.027 0.029 0.033	0.454 0.448
730	0.0 0.00020 0.00035 0.00043 0.00055 0.00067 0.00096	0.264 0.0198 0.0153 0.0132 0.010 0.0066 0.0	0.0 0.0097 0.0157 0.0185 0.0224 0.0265 0.0338	0.0652 0.0498 0.0391 0.0339 0.0259 0.0172 0.0	0.021 0.022 0.023 0.025 0.025 0.025 0.028	0.405 0.398 0.391 0.389 0.386 0.384
728	0.0 0.00036 0.00044 0.00097	0.0266 0.015 0.013 0.0	0.0 0.0162 0.0191 0.0344	0.0662 0.0387 0.0338 0.0	0.022 0.023 0.282	0.3876 0.3846
700	0.0 0.00041 0.00044 0.00062 0.00112	0.0290 0.0153 0.0145 0.010 0.0	0.0 0.0225 0.0236 0.0304 0.0436	0.0806 0.0456 0.0433 0.0303 0.0	0.018 0.019 0.020 0.026	0.360 0.329 0.335 0.330

TABLE 2

Terminal points from the binary diagrams are also included.

*

TABLE 3

Analysis of Melting Stock

Si	Mn	S	Р
0.02 0.01		0.01	0.01

TABLE 4

Experimental Tie-Lines

тос	Ferrite		Alloy Co	omposition	Austenite	
	C A%	Mn A%	C A%	Mn A%	C A%	Mn A%
730	0.06	1.06	0.97	1.88	2.10	2.94
730	0.02	2.00	0.50	3.55	1.00	5.05
. 762	0.04	1.05	0.46	1.50	1.38	2.45

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т ^о с	xη	x ₂ ^a	xĩ	x²
800	0.00035	0.01	0.0090	0,0099
760	0.00056	0.01	0.0178	0.0098
730	0.00074	0.01	0.0270	0.0097
730	0.0005	0.02	0.195	0.0196
730	0.00028	0.03	0.0117	0.0296
730	0.00006	0.04	0.0027	0.0399
700	0.00084	0.01	0.0358	0.0096
670	0.0010	0.01	0.0490	0.0095

TABL	E	5
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Calculated Paraequilibrium Tie-Lines

TABLE 6

Data Required to Calculate Predicted Manganese Concentration Curves

Figure	26	27	28	29	30	31	32
Time (sec)	5.37X10 ⁶	5.37X10 ⁶	1.78X10 ⁶	1.78X10 ⁶	5.12X10 ⁵	5.12X10 ⁵	1.6X10 ⁵
C21	1.30	1.30	1.39	1.44	1.44	1.41	1.47
c ₂₁	3,38	3,38	3.60	3.72	3.72	3.66	3.80
F1(C21)	0.7472	0.7472	0.7260	0.7129	0.7129	0.7209	0.7044
φ	1.863X10 ⁻³	1.863X10 ⁻³	5.49X10 ⁻⁴	1.62X10-4	1.62X10 ⁻⁴	3.66x10 ⁻⁴	4.03X10 ⁻⁵
L(µ)	24.6	24.6	26	48	25.7	17.1	30
a	3.9	3.9	2	1.9	1.0	1.0	0.6
L(µ)*	35	45	50	60	70	80	50
d(µ)	1	1	0.9	0.9	0.9	0.9	0.9

* Estimated from sample.



Figure 1. Portion of the Fe-Fe₃C constitution diagram.



Figure 2. (a) Fe-C-Mn isotherms determined by Purdy Weichert and Kirkaldy (1964). (b) Fe-C-Mn isotherm at 750⁰C. (after Aaronson)



Figure 3. Activity coefficient of Fe-Mn alloys, after Roy and Hultgren (1965).



Figure 4. Standard free energy change for the transformation Fe (BCC) to Fe (FCC).



Figure 5. Calculated standard free energy change for the hypothetical transformation BCC graphite to FCC graphite.







Figure 7. Standard free energy change for the hypothetical transformation BCC Mn to FCC Mn.



Figure 8. Graphical method of solution of equations 17, 18and 19, curves 1, 2, 3 and 4 are from equation 18 and the values of X_1 and X_2 shown. Curve 5, from equation 19, does not change a significant amount with small changes in X_1 . X_1 and X_2 values in the table are from the intersection of the curves.



Figure 9. Isotherm of the Fe-C-Mn system at 730° C.



Figure 10. Isotherm of the Fe-C-Mn system at 762°C.



Figure 11. Typical photomicrograph of the ferrite-martensite mixture in the equilibriated Fe-C-Mn alloys. (500X)




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Figure 14. Temperature-composition regions in which the various morphologies are dominant at late reaction times in specimens with ASTM grain size Nos. 0-1. GBA = grain boundary allotriomorphs, W = Widmanstatten sideplates and/or intragranular plates, and M = massive ferrite. (Aaronson, 1962).



Figure 15. Concentration profile in vicinity of advancing cementite interface. (Darken, 1961).





Fig 16 (b)

Figure 16 (a), (b). Schematic penetration curves in λ space for ferrite growth in Fe-C-Mn austenites. The mass balances are represented by equal shaded areas on either side of the interface ($\lambda = \alpha$). (after Purdy, Weichert & Kirkaldy)



Figure 17. Carbon concentration profile for the calculation of impingement time.

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Figure 19. Approximate concentration profiles for manganese diffusion control at long times in highly supersaturated alloys.



Figure 20. Schematic free energy surfaces for ferrite and austenite illustrating the paraequilibrium conditions.



Figure 21. Calculated paraequilibrium diagram for Fe-C-Mn alloys at 730°C. Also shown is the true equilibrium diagram and one equilibrium tie line.



Figure 22. Section of the paraequilibrium surface at a ratio of $X_2/X_0 = .01/.99$.



Figure 23. Electron probe microanalysis of a manganese concentration step. Predicted line is assuming a gaussian probe function with $d = 0.9 \mu$.



Figure 24. Micrograph typical of samples of alloy A (0.45 A% C, 1.50 A% Mn) transformed at 728°C for 2 days to 2 months. (130X)



Figure 25. A typical microprobe scan across a sample of alloy A transformed for 5.37X10⁶ sec (2 months) at 728°C.



Figure 26. Detailed microprobe analysis of alloy A transformed for 5.37X10⁶ sec (2 months) at 728^oC. These are the same two grain boundaries as shown on the left of Figure 25.







Figure 28. Microprobe analysis of alloy A transformed for 1.78X10⁶ sec (20 days) at 728^oC.







Figure 30. Microprobe analysis of alloy A transformed for 5.12X10⁵ sec(6 days) at 728^oC.







Figure 32. Microprobe analysis of alloy A transformed for 1.6X10⁵ sec (2 days at 728⁰C.







Figure 34. Typical micrograph of alloy B transformed for 8.6X10⁴ sec (1 day) at 728°C. (500X)



Figure 35. Typical micrograph of alloy B transformed for 4.32X10⁵ sec (5 days) at 728°C. (500X)



Figure 36. Typical micrograph of alloy B transformed for 3.15X10⁶ sec (37 days) at 728°C. (500X)







Figure 38. Microprobe analysis of alloy B transformed for 3X10⁶ sec (37 days) at 728^oC.







Figure 40. Calculated parabolic rate constant for a 0.97 A% C, 1.53 A% Mn alloy. Experimental points of Purdy, Weichert and Kirkaldy (1964).



Figure 41. Comparison of Kinsman and Aaronson's experimental results with the various predicted parabolic growth rate curves.

126







Figure 43. Representation of the difference between the effect of manganese and nickel on the proeutectoid ferrite trans-formation assuming local equilibrium (high supersaturation).